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A Holistic Approach to Understanding the Desorption of Phosphorus in Soils

Daniel Menezes-Blackburn,^{*,†} Hao Zhang,^{*,†} Marc Stutter,[‡] Courtney D. Giles,[‡] Tegan Darch,[§] Timothy S. George,[‡] Charles Shand,[‡] David Lumsdon,[‡] Martin Blackwell,[§] Catherine Wearing,[‡] Patricia Cooper,[‡] Renate Wendler,[‡] Lawrie Brown,[‡] and Philip M. Haygarth[†]

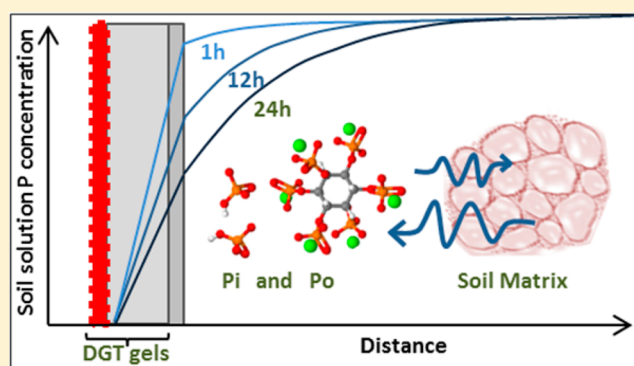
[†]Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, U.K.

[‡]The James Hutton Institute, Aberdeen AB15 8QH Scotland, U.K.

[§]Rothamsted Research, North Wyke, Okehampton, Devon EX20 2SB, U.K.

Supporting Information

ABSTRACT: The mobility and resupply of inorganic phosphorus (P) from the solid phase were studied in 32 soils from the UK. The combined use of diffusive gradients in thin films (DGT), diffusive equilibration in thin films (DET) and the “DGT-induced fluxes in sediments” model (DIFS) were adapted to explore the basic principles of solid-to-solution P desorption kinetics in previously unattainable detail. On average across soil types, the response time (T_c) was 3.6 h, the desorption rate constant (k_{-1}) was 0.0046 h^{-1} , and the desorption rate was $4.71 \text{ nmol l}^{-1} \text{ s}^{-1}$. While the relative DGT-induced inorganic P flux responses in the first hour is mainly a function of soil water retention and % C_{org} at longer times it is a function of the P resupply from the soil solid phase. Desorption rates and resupply from solid phase were fundamentally influenced by P status as reflected by their high correlation with P concentration in FeO strips, Olsen, NaOH–EDTA and water extracts. Soil pH and particle size distribution showed no significant correlation with the evaluated mobility and resupply parameters. The DGT and DET techniques, along with the DIFS model, were considered accurate and practical tools for studying parameters related to soil P desorption kinetics.



INTRODUCTION

Modern agriculture is dependent on phosphorus (P) fertilizer applications to maintain their productivity. The application of P fertilizer in soil is an inefficient practice since, in general, just a small fraction of the applied P is taken up by plants and represents an inadequate use of finite mineral resources.¹ Phosphorus is perhaps, among all the essential plants macronutrients, the one with most limited bioavailability in soils.² To ensure optimal plant growth, P fertilizers are applied to agricultural soils in excess of plant requirements to overcome soil P fixation processes and maintain soil solution P at sufficient levels for plant growth.³ The use of P in excess of crop requirements and the inefficient acquisition of soil P by plants have led to an accumulation of a largely unavailable pool of soil P as well as the eutrophication of receiving water courses.

Phosphorus from freshly added P fertilizer adsorbs to soil particles, displacing other anions with lower affinity to the surface of the soil solid phase.³ Precipitation with metals and their oxy/hydroxides also plays an important role in the short term (hours to days) fixation of soil P.⁴ The reduced mobility of P in soils is one of the main factors that influences its limited availability.⁵ Differences in soil mobility and P fixing capacity are generally

assumed to be a function of soil type and the associated surface properties of their minerals. Phosphorus mobility in soils has been commonly studied by quantifying P in different extracts as a way of assessing its lability (availability). Lability is defined as the likelihood of P undergoing a change of state; in this study it is generally referred to as the process of P desorption from the surface of soil particles induced by the depletion of solution concentration (e.g., due to the P uptake by plants). The P desorbed to soil solution is therefore assumed to be readily plant-available. In this study we explore the use of diffusive gradient in thin films (DGT) and diffusive equilibrium in thin films (DET) as tools to assess intrinsic P mobility properties of different agricultural soils. The similarities of this system to a plant root and its usefulness as “plant proxy” to study bioavailability was reviewed by Degryse et al. (2009).⁶ Better knowledge of these mobility properties will allow better understanding and management of the administration of appropriate amounts of P for

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agricultural production, while minimizing environmental losses and optimizing P inputs.

It is well established that plant P uptake is limited by its diffusion and resupply from solid phase in soils.⁵ The combined use of DGT and DIFS offer a unique opportunity to assess the basic principles of P movement through soil in previously unattainable detail.^{7,8} Although the sorption/desorption of P has been studied on many model clays and soils, there is still limited knowledge of the P geochemical response to perturbations in natural conditions (e.g., mineral and organic fertilizer application, tillage systems, crop type, irrigation, etc.), including how soil properties may drive the variations in its response to these perturbations.

The specific aims of this study were (a) to evaluate the use of DGT and DET techniques, and the DIFS model, as tools to estimate the variability of P distribution coefficients, (de)sorption rate constants, depletion distance, and other parameters reflecting P resupply from soil solid phase across a range of 32 UK soils; and (b) to contrast the data obtained by DGT, DET, and DIFS to standard soil P tests, physical properties, % organic C, oxalate extractable Fe, Al, and pH in order to evaluate their relative contribution to P mobility in agricultural soils. More broadly, the work aimed to develop and apply this new approach of resolving and understanding soil phosphorus exchange and release kinetics.

Theory. The DGT device contains a binding layer (P sink) and a diffusive layer that modulates the diffusion of P from soil solution. The time-averaged P concentration (P_{DGT}) in the soil solution at the outer surface of the DGT device is calculated from the P mass accumulated on the DGT binding layer using Fick's law of diffusion. The theory behind the calculation of DGT parameters can be found in Zhang et al. (1995).¹⁵ Using P_{DGT} , a soil effective concentration (P_E) can be calculated, accounting for both the solution concentration and the adsorbed concentration that can be mobilized by depleting soil solution P. The P_E is calculated from P_{DGT} using the R_{diff} ratio, which is estimated using a numerical model of the DGT-soil system (DIFS model) by setting input parameters emulating diffusion supply only. The theory behind the P_E calculation has been previously discussed by Zhang et al. (2001; 2004).^{9,10} In this study we are also interested in solving the DIFS model using empirically measured input parameters in order to estimate the variability of response time of the system, (de)sorption rate constants, P depletion distance and other parameters reflecting P resupply from solid to solution phase across a range of different soils.

MATERIAL AND METHODS

Soil Samples and Characterization. Samples used in this study were collected from 32 representative UK soils and characterized by Stutter et al. (2015).¹¹ These had been previously collected across UK sites comprising mostly arable, grassland and several moorland topsoils in a study of soil P speciation and cycling according to soil organic C, land use and assumed P fertilizer inputs. As part of this earlier study, characterization included soil pH, oxalate extractable Al and Fe, P saturation index (Psat) soil organic carbon, microbial biomass P, total P and inorganic P in Olsen, NaOH, citric acid and water extracts. This detailed characterization was used here to draw interrelations between DGT-based parameters and the physicochemical background properties studied by Stutter et al. (2015).¹¹ Please refer to the original paper for the methodological details of the mentioned parameters.

Gel Preparation and Assembly of DGT and DET Devices. DGT cylindrical devices designed for soil deployment (DGT Research Ltd., Lancaster-UK) consisted of a binding and a diffusive gel layer tightly packed into a plastic support comprised of a backing plate and a front plate with an exposure window ($A = 2.54 \text{ cm}^2$). Diffusive gels (0.78 mm) were placed on top of a binding layer (gel containing ferrihydrite) and a 0.13 mm thick poly(ether sulfone) filter ($0.45 \mu\text{m}$) was placed on top of the diffusive gel for physical protection. The filter layer has been shown to behave as an extension of the diffusive layer.¹² The DET devices contained only the diffusive gel (0.78 mm) and the membrane filter tightly packed into a plastic support with similar dimensions to the ones used for the DGTs.

The diffusive gels containing acrylamide cross-linker (DGT Research Ltd., Lancaster-UK) were prepared and cast according to published procedures.¹² To prepare the ferrihydrite gel for the binding layer, diffusive gels (0.78 mm) were incubated for 2 h in a 0.1 mM FeCl_3 aqueous solution to allow uniform distribution of Fe inside and outside of the gels.¹³ Each gel was then placed in a freshly prepared 0.05 M 2-(N-Morpholino)ethanesulfonic acid (MES) pH 6.7 buffer for 30 min to allow the ferrihydrite to precipitate. The gels were then washed 3 times every 2 h with reagent grade water and stored at 4 °C in 0.01 M NaNO_3 solution.

DGT Deployment. Soil samples (150 g air-dried) were adjusted to approximately 50% water holding capacity (WHC) with ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$) 3 days before DGT and DET deployment. 24 h before deployment, the soil slurry was prepared by mixing and continuously adding ultrapure water until maximum retention (MR) was reached. A visual assessment of soil malleability and the glistening of water on the soil surface was used to determine MR. This subjective criteria of setting maximum water retention (or near maximum) in the slurry was verified in several pretests. In the cases where too much water was added, liquefying the sample or leaving a film of water on the surface of the slurry, more soil was added to the mixture, and the whole procedure was repeated to those cases using the correct moisture content. These criteria were used for 30 of the 32 used soils; however, they were not suitable for Dartmoor and Tentsmuir soils. Dartmoor is a highly organic (44% organic C), low density (0.38 g cm^{-3}), and very high porosity (0.87 v/v) leading to high water retention during the slurry preparation. Because soil glistening and plasticity were not obvious criteria for this soil, the optimum slurry retention was determined by pressing the organic matrix to check its saturation. Tentsmuir, on the other hand, is a sandy soil and optimum slurry retention was determined as the maximum moisture before a free film of water could be formed on the surface of the mixture. For each soil, three independent slurry preparations were made, and for each slurry preparation 2 independent DGT and DET deployments were performed.

In all cases, the soil pores are assumed to be filled with water and no air was trapped in the soil slurry, the final moisture concentration was used to determine the particle concentration (ratio between dry weight and soil solution), porosity (% of volume occupied by water) and tortuosity using the equation proposed by Boudreau (1996).⁷ Physical properties of the samples are displayed in Table 1. DGT devices were deployed after 24 h by gently pressing them against the soil slurry while ensuring complete surface contact. The air temperature was accurately monitored every hour and averaged for use in further calculation of diffusive coefficients.

Table 1. Physical Properties from Dry Soils and Slurries Prepared for Diffusive Gradient in Thin Films Analysis^a

soil	WHC		slurry retention		P _c	ρ _s	ρ _o	φ	θ ²	D _s
	g g ⁻¹	g g ⁻¹	% of WHC	g cm ⁻³						
Alness 1	0.64	0.45	70.74	2.20	1.21	1.09	0.55	2.19	2.50	
Alness 2	1.00	0.66	66.31	1.51	0.97	0.83	0.64	1.89	2.77	
Alness 3	0.72	0.43	60.61	2.30	1.24	1.05	0.54	2.23	2.47	
Alness 4	0.65	0.64	98.74	1.56	0.99	0.88	0.63	1.91	2.74	
Balruddery	0.67	0.47	70.03	2.14	1.20	1.01	0.56	2.17	2.52	
Banadl	0.82	0.61	74.74	1.63	1.02	0.88	0.62	1.94	2.71	
Benzie	0.62	0.37	59.15	2.71	1.35	1.13	0.50	2.39	2.36	
Bicton	0.53	0.39	73.09	2.58	1.32	1.13	0.51	2.34	2.39	
Bronydd high P	0.87	0.66	76.52	1.51	0.97	0.94	0.64	1.89	2.77	
Bronydd low P	0.97	0.69	71.81	1.44	0.94	0.86	0.65	1.86	2.80	
Canol	0.95	0.74	77.16	1.36	0.90	0.83	0.67	1.82	2.84	
Dartmoor	1.15	2.48	215.15	0.40	0.35	0.38	0.87	1.28	3.51	
De Bathe	0.58	0.38	64.87	2.64	1.33	1.23	0.51	2.36	2.38	
Dunsdon impr.	0.77	0.60	78.47	1.66	1.03	0.97	0.62	1.96	2.70	
Dunsdon unimpr.	0.78	0.64	81.69	1.57	0.99	0.97	0.63	1.91	2.74	
Friockheim 1	0.64	0.40	61.54	2.52	1.30	1.09	0.52	2.32	2.41	
Friockheim 2	0.64	0.39	60.64	2.57	1.32	1.09	0.51	2.34	2.39	
Haddington 1	0.68	0.40	58.38	2.52	1.30	1.05	0.52	2.32	2.41	
Haddington 2	0.69	0.40	57.44	2.52	1.30	1.05	0.52	2.32	2.41	
Haddington 3	0.67	0.39	57.81	2.57	1.32	0.97	0.51	2.34	2.39	
Haddington 4	0.63	0.37	58.16	2.74	1.36	1.13	0.50	2.40	2.35	
King's sedge	1.24	0.98	79.65	1.02	0.74	1.01	0.73	1.64	3.03	
Rothamsted	0.51	0.36	71.23	2.74	1.36	1.35	0.50	2.40	2.35	
Rowden	0.84	0.70	83.80	1.42	0.93	0.94	0.65	1.85	2.81	
Southlake north	1.03	0.95	92.24	1.05	0.76	0.94	0.72	1.66	3.01	
Southlake south	0.88	0.97	110.80	1.03	0.75	0.83	0.72	1.65	3.02	
Tayport	0.51	0.36	69.49	2.81	1.38	0.83	0.49	2.43	2.33	
Tentsmuir	0.84	0.47	55.91	2.13	1.19	1.23	0.56	2.17	2.52	
Vealand impr.	1.03	0.63	61.38	1.58	1.00	0.88	0.63	1.92	2.73	
Vealand unimpr.	0.88	0.79	89.73	1.27	0.86	0.91	0.68	1.77	2.88	
Woburn 1	0.48	0.45	93.55	2.21	1.21	1.35	0.55	2.20	2.50	
Woburn 2	0.51	0.29	55.97	3.49	1.52	1.35	0.44	2.66	2.18	

^aWHC, water holding capacity; P_c, particle concentrations: soil dry weight divided by the soil solution volume; ρ_s, bulk density of the soil slurry; ρ_o, bulk density of the dry soil; φ, soil porosity; θ², diffusive tortuosity according to Boudreau, (1996); D, diffusive coefficient in soils at 20 °C.

After 24 h of deployment the DGT and DET devices were removed and rinsed with ultrapure water to remove any adhering soil particles. The ferrihydrite gels from the DGTs and the diffusive gels from the DETs were retrieved and eluted with 2 mL of 0.25 M H₂SO₄ solution overnight before analysis. Three nondeployed DGT and DET “blanks” were prepared concurrently with each deployment and treated identically to the devices deployed on the soil samples. The soil slurry was centrifuged at 5000 rpm for 15 min in 50 mL tubes in order to separate the pore water from solid matrix. The concentration of the molybdate-reactive P (inorganic P) in the DGT and DET eluents as well as in the pore water extract (P_{pw}) was measured colorimetrically as described by Murphy and Riley (1962).¹⁴ The reaction volumes proportionally reduced to a final 240 μL in order to be developed in 96 wells microplates and were read on a Multiskan spectrophotometer (Thermo Fisher Scientific Inc., UK). Total phosphorus was measured by inductively coupled plasma mass spectrometry (XSERIES 2 ICP-MS, Thermo Fisher Scientific Inc., Hemel Hempstead, UK) and the molybdate-unreactive P in DGT and DET extracts was estimated as the difference between the total P and the molybdate-reactive P (P_i); this solution molybdate unreactive P is hereby termed P_o.

Calculation of P_{DGT}, P_E, K_d, R_{diff}, X_{sol} and X_{ads}. The concentration of solution P at the surface of the DGT device was calculated using eq 1 according to Zhang and Davison (1995).¹²

$$P_{DGT} = \frac{M\Delta g}{DA t} \quad (1)$$

where *M* is the accumulated P mass in the DGT binding layer, *A* is the surface area of the DGT sampling window, *t* is the deployment time, Δ*g* is the total thickness of the diffusive gel layer and the filter membrane, and *D* is the diffusion coefficient of P in the diffusive gel. The DGT is a passive sampler and, therefore, results from eq 1 reflect a time-averaged concentration in the soil solution immediately adjacent to the outer surface of the DGT device.

P_{DGT} was converted to an effective concentration using eq 2 to represent the effectively available P from both soil solution and the solid-phase labile pool.¹⁰

$$P_E = \frac{P_{DGT}}{R_{diff}} \quad (2)$$

R_{diff} is the hypothetical ratio of the P_{DGT} to the concentration in soil solution if no resupply from the solid phase occurred (only pore water P diffusion). R_{diff} was calculated using the DIFS

dynamic numerical model of the DGT-soil system.⁸ Input parameters of particle concentration (P_c ; ratio between dry weight and volume of soil solution), soil porosity (ϕ), and the diffusion coefficient of P in the soil (D_s) were calculated according to Harper et al. (2000).⁷ To simulate “diffusion only” conditions the system response time, T_c , was set to 1×10^{10} s and K_d was set as $0 \text{ cm}^3 \text{ g}^{-1}$. While R represents the empirical relative contribution of the system to dynamically maintain the solution concentration adjacent to the DGT device, R_{diff} is the minimal possible R value in the absence of solid phase resupply (diffusion only). The difference of R and R_{diff} , $R - R_{\text{diff}}$, was used as an estimation of expected dynamic contribution from desorption during the DGT deployment, relative to the original soil solution concentration.

The R ratio was calculated as the mean P concentration measured by DGT relative to the solution P concentration measured using DET (eq 3). Assuming that P_{Olsen} provides an estimate of the labile solid phase pool, the distribution coefficient between the solid and solution phases (K_d) was calculated as $P_{\text{Olsen}}/P_{\text{DGT}}$. The value of T_c derived using DIFS corresponds to the time needed to bring the interfacial concentration of P, P_i , from 0 to 63% of its pseudo steady state value.⁷ Assuming that the desorption rate constants are much lower than the sorption rate constant ($k_1 \gg k_{-1}$), the sorption rate constant can be estimated as in eq 4 and the desorption rate constant can be calculated as in eq 5.^{7,15} The estimated desorption rates can therefore be calculated as in eq 6. The desorption rate constant is independent of DGT deployment time.

$$R = \frac{P_{\text{DGT}}}{P_{\text{DET}}} \quad (3)$$

$$k_1 = \frac{1}{T_c} \quad (4)$$

$$k_{-1} = \frac{k_1}{K_d P_c} \quad (5)$$

$$\text{Dspt rate} = P_{\text{Olsen}} P_c k_{-1} \quad (6)$$

The distance from the DGT device to which the soil solution (x_{sol}) or the adsorbed labile P (x_{ads}) are depleted after 24 h were also estimated by DIFS model.⁸ The limit to depletion was arbitrarily set on reduction of at least 5% of solution concentration (x_{sol}) or the 5% of K_d (x_{ads}) based on the resolution of the outcome data from the DIFS model, as a standard limit that could be used to compare all the studied soils. Similarly, the dependency of the output R values on time was used to calculate the maximum R (R_{max}) and the time at which R_{max} was reached ($T_{R_{\text{max}}}$).

The output parameters from the DIFS model (R_{diff} , R_{max} , x_{ads} , x_{sol} , T_c and $T_{R_{\text{max}}}$) reflect both the model assumptions and the variation of all empirically determined input data used to run this model, including the DGT and DET measurements at 24h.

Statistical Methods. Pearson's correlation was used between independent variables and the significance of correlations was judged using standard t test (significant at $p \leq 0.05$ and very significant at $p \leq 0.01$). Where necessary, according to results of Andersen–Darling test for normality, data were ln transformed prior to correlation analyses. Nonlinear regression functions (exponential or logarithmic) were fitted to the selected plots in order to draw patterns of general interrelations between parameters. All statistical calculations were performed in Microsoft Excel.

RESULTS

Phosphorus Availability Indices. The soils used in this study correspond to a wide range of P status as reflected in the parameters displayed in Table 2. Olsen P averaged 49.1 mg kg^{-1} and ranged from 5.6 (Tentsmuir site) to $184.4 \text{ (Haddington1)} \text{ mg kg}^{-1}$. Olsen P is related to a regulatory P index for crop nutrition used in the UK,¹⁶ which ranges from 0 (insufficient P supply) to 7 (excessive availability). In the current study, half of the soils analyzed belong to indexes 3 and 4 (26 to 70 mg L^{-1}), corresponding to “high” and “very high” available P. The phosphorus effective concentration (P_E) is calculated using the measured P_{DGT} and calculated R_{diff} . It accounts for both soil solution P and easily desorbable P. In our soils, P_E averaged $2.32 \pm 2.41 \text{ mg L}^{-1}$. The organic soil Dartmoor had a moderate P_{Olsen} , but a very high iron oxide strip P (P_{FeO}), P_{DGT} and P_E compared to the other soils in this study. Tentsmuir, the sandy soil, showed a similar pattern, but to a lesser degree, with very low P_{Olsen} (5.6 mg kg^{-1}), average P_{FeO} (11.4 mg kg^{-1}), and a high P_{DGT} (0.35 mg L^{-1}) and P_E (5.21 mg L^{-1}). Other mineral soils with average physical properties and high P_{Olsen} , (e.g., Vealand improved, Bicton and Frickheim 1 and 2) contrastingly had low P_{DGT} and P_E . In these cases, as for Tentsmuir and Dartmoor soils, P_{FeO} appears to be better explaining P_{DGT} and P_E variation than P_{Olsen} .

Comparing with other common soil P parameters, P_{DGT} was better correlated with P_{FeO} strips and several other P indexes (P_{water} , $P_{\text{NaOH/EDTA}}$, and P_{sat}) than with P_{Olsen} (Table 3). Similarly, P_{DET} was better correlated with P_{FeO} and P_{water} than with other parameters. K_d was poorly correlated with every tested parameter (Table 3). Differences between P_{DGT} and P concentration in soil extracts (e.g., P_{water} and P_{Olsen}) certainly reflect the fact that DGT method includes dissimilarities in soil P diffusion and kinetics of P resupply from solid phase, while P extraction methods just consider equilibrium P at constant solid to solution ratio. The phosphorus effective concentration (P_E) was better correlated with most P concentrations in soil extracts than P_{DGT} (Table 3), indicating that this parameter may be a better representation of P availability than P_{DGT} alone.

Organic P, P_o , was estimated in the DGT and DET extracts as the difference between the total accumulated mass of P and the mass of molybdate-reactive P (P_i). The P_o fraction that accumulated in the DGT binding layer averaged $38.9 \pm 12.4\%$, slightly less than the $43.7 \pm 15.9\%$ accumulated in the DET diffusive gel. P_o eluted from the DET gel represents molecules capable of diffusing from soil solution through the filter membrane and the polyacrylamide gel. The proportion of P_o in the DGT binding layer is based only on the accumulated mass, since the speciation of the numerous P_o forms and their diffusive coefficients in the diffusive layer are unknown.

Phosphorus Mobility and Resupply from Solid Phase Evaluated by the DIFS Model. The ratio of P_{DGT} to P_{DET} (R) ranged from 0.08 to 0.36 and corresponded to the contribution of both P_i diffusion through soil pores and the replenishment of pore water P_i due to its desorption from solid phase (Table 4). The dependency of the P_{DET} on P_{DGT} followed a log linear pattern (Figure 1B), tending to proportionally reduce increases in R ratios at greater P_{DGT} values. The contribution of diffusion (R_{diff}) to the accumulated mass was estimated using the DIFS model by setting K_d as 0 and T_c as 1×10^{10} . R_{diff} ranged from 0.05 to 0.12 (Table 4) and was dependent on the amount of water added during the slurry preparation and the resulting porosity, tortuosity and diffusive coefficients in soil (Table 1).

Table 2. Phosphorus Concentrations in P_{Olsen} , P_{FeO} , P_{water} , Soil Pore Water (P_{pw}), P_{DGT} , P_{DET} , and Calculated Effective P Concentration (P_{E}) in Relation to the Following

soil	P_{Olsen}^a	P_{FeO}^a	P_{water}^a	P_{pw}^b	P_{DGT}^c			P_{DET}			P_{E}
	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg L ⁻¹	Pi (mg L ⁻¹)	Pi (%)	Po (%)	Pi (mg L ⁻¹)	Pi (%)	Po (%)	mg L ⁻¹
Alness 1	51.3	34.5	2.7	0.80	0.14 ± 0.02	54.6	45.4	0.93 ± 0.06	59.5	40.5	2.11
Alness 2	27.7	5.7	1.5	0.65	0.07 ± 0.03	50.9	49.1	0.66 ± 0.13	46.3	53.7	0.84
Alness 3	48.8	30.9	2.7	0.44	0.10 ± 0.02	65.0	35.0	0.86 ± 0.07	68.2	31.8	1.57
Alness 4	46.1	41.1	6.0	1.24	0.31 ± 0.02	61.1	38.9	1.16 ± 0.29	60.4	39.6	4.01
Balruddery	60.0	40.3	1.7	0.46	0.07 ± 0.02	50.0	50.0	0.70 ± 0.05	49.9	50.1	1.03
Banadl	72.7	38.2	7.6	1.51	0.15 ± 0.02	52.5	47.5	0.75 ± 0.03	47.2	52.8	2.00
Benzie	65.7	39.0	3.8	0.65	0.13 ± 0.01	66.3	33.7	0.81 ± 0.02	64.4	35.6	2.22
Bicton	80.7	49.2	9.1	1.79	0.30 ± 0.08	65.7	34.3	1.18 ± 0.15	79.1	20.9	5.03
Bronydd high P	28.9	17.0	2.6	0.72	0.09 ± 0.01	55.4	44.6	0.57 ± 0.10	32.9	67.1	1.15
Bronydd low P	9.2	8.0	1.6	0.63	0.06 ± 0.02	43.0	57.0	0.58 ± 0.03	31.3	68.7	0.77
Canol	25.1	17.5	2.4	0.70	0.10 ± 0.03	63.9	36.1	0.72 ± 0.17	41.0	59.0	1.15
Dartmoor	28.4	108.9	31.5	1.89	0.50 ± 0.20	70.7	29.3	2.29 ± 0.35	88.8	11.2	4.28
De Bathe	46.7	21.0	1.9	0.86	0.09 ± 0.03	62.3	37.7	0.63 ± 0.20	56.9	43.1	1.49
Dunsdon impr.	24.0	11.2	1.7	0.70	0.09 ± 0.02	62.3	37.7	0.54 ± 0.11	30.3	69.7	1.21
Dunsdon unimpr.	12.4	8.9	1.0	0.19	0.09 ± 0.02	66.0	34.0	0.50 ± 0.06	42.3	57.7	1.10
Friockheim 1	72.1	47.4	3.5	0.46	0.11 ± 0.01	53.8	46.2	1.20 ± 0.43	70.5	29.5	1.74
Friockheim 2	79.5	57.9	2.5	0.36	0.10 ± 0.01	51.3	48.7	0.89 ± 0.02	70.3	29.7	1.72
Haddington 1	184.4	139.0	12.2	1.85	0.84 ± 0.06	82.6	17.4	2.35 ± 0.20	77.2	22.8	13.72
Haddington 2	50.7	31.9	4.1	1.85	0.09 ± 0.02	60.8	39.2	0.76 ± 0.01	61.1	38.9	1.55
Haddington 3	87.2	51.9	4.0	0.94	0.12 ± 0.01	58.2	41.8	0.73 ± 0.14	51.9	48.1	2.04
Haddington 4	42.3	23.9	3.2	1.80	0.09 ± 0.02	66.6	33.4	0.47 ± 0.05	47.3	52.7	1.53
King's sedge	26.5	6.3	1.0	0.25	0.08 ± 0.01	65.3	34.7	0.76 ± 0.01	42.9	57.1	0.82
Rothamsted	38.2	18.2	1.2	0.35	0.08 ± 0.01	86.9	13.1	0.70 ± 0.11	63.6	36.4	1.42
Rowden	43.0	34.3	1.8	0.57	0.13 ± 0.01	93.3	6.7	0.84 ± 0.06	60.1	39.9	1.58
Southlake north	15.9	26.9	2.5	0.37	0.12 ± 0.02	43.8	56.2	0.94 ± 0.19	40.1	59.9	1.36
Southlake south	19.3	32.8	3.0	0.68	0.11 ± 0.03	44.4	55.6	0.92 ± 0.08	55.6	44.4	1.19
Tayport	84.5	57.6	6.3	1.31	0.21 ± 0.02	55.4	44.6	1.35 ± 0.01	67.6	32.4	3.77
Tentsmuir	5.6	11.4	4.2	1.46	0.35 ± 0.00	77.2	22.8	1.56 ± 0.01	80.8	19.2	5.21
Vealand impr.	86.8	26.9	3.5	1.10	0.08 ± 0.01	39.7	60.3	0.46 ± 0.08	29.6	70.4	1.09
Vealand unimpr.	18.7	21.8	4.5	0.43	0.10 ± 0.01	53.3	46.7	0.60 ± 0.15	42.2	57.8	1.23
Woburn 1	25.4	8.3	0.5	0.08	0.07 ± 0.01	69.6	30.4	0.91 ± 0.22	76.5	23.5	1.14
Woburn 2	63.1	45.9	6.4	0.43	0.16 ± 0.04	64.2	35.8	1.05 ± 0.01	64.6	35.4	3.15

^aPi in different extractants, data published in Stutter et al. (2015). ^bP concentration in soil pore water extracted by two cycles centrifugation of the slurry in which DGTs were deployed. ^c% values refer to difference of total P mass accumulated in the gel and does not account for differences in diffusive coefficients.

The difference between R and R_{diff} is a quantitative measurement of the ability of each soil to resupply P_i to the pore water in response to DGT-induced depletion. The T_c and desorption rate showed a tighter fit to $R-R_{\text{diff}}$ (Figure 1E and 1F) than to the R ratio likely due to the variability of soil wetting parameters and their influence on the R_{diff} values.

The maximum distance of pore water depletion (X_{sol}) averaged 0.42 ± 0.10 cm and for the desorbable P_i concentration the maximum distance of depletion (X_{ads}) averaged 0.36 ± 0.07 cm. The distance of depletion represents the maximum distance where roots can influence soil P concentrations.

The P_i concentration at the surface of the DGT is time dependent and the R values peak at R_{max} at T_{Rmax} seconds after the deployment begins (Figure 1A). By analyzing the shape of R -time dependency, two patterns emerge. The most common pattern is the case in which the R values peak (R_{max}) at T_{Rmax} (between 20 and 50 min) and decrease to equilibrium near constant value after 10 h (Figure 1A). Alternatively, some soils do not display this peak and do not reach a constant R until after 24 h (e.g., Tentsmuir and Dartmoor; Figure 1A). R_{max} appears to be a function of porosity (and therefore C_{org} concentration), with the exception of the outliers Tentsmuir and Haddington 1.

The difference $R_{\text{max}}-R$ is a direct negative proportion of $R-R_{\text{diff}}$ in other words, with increasing resupply capacity of the soil ($R-R_{\text{diff}}$) the R curve in time will become less peak-shaped (low $R_{\text{max}}-R$; Figure 1D). While the relative P_i flux response in the first hour is mainly influenced by soil wetting properties, at longer time it tends to be a function of the resupply capacity ($R-R_{\text{diff}}$) of the soil solid phase (Figure 1D and F). This behavior as well as the shape of the time series curves of the R ratio reflects both the DIFS model assumptions^{7,8} and the variability of input parameters, specific for the used soil samples. The system response time (T_c) is very sensitive to variations in the input values for R in the DIFS model. Therefore, absolute values must be interpreted with caution due to the effects of possible accumulated errors. T_c values showed a log-normal distribution and were found to be log-linear with respect to $R-R_{\text{diff}}$ exponentially decaying with increasing $R-R_{\text{diff}}$ values (Figure 1E). T_c values averaged 3.63 h (considering the log transformations), and ranged from 0.038 s in Tentsmuir to 88h in King's sedge soils.

In the (de)sorption rate constant analysis, Tentsmuir was a clear outlier with low T_c and very high k_1 and k_{-1} values, and was therefore excluded from the trend line analysis of Figures 1

Table 3. Pearson Correlation Coefficient of Experimental Soil Parameters, DGT, DET, and DIFS Calculated Parameters^a

	P _{pw}	P _{DGT}	P _{DET}	P _E	K _d	R	R _{diff}	R-R _{diff}	R _{max}	T _{Rmax}	Ln T _c	k ₁	k ₋₁	Dspt rate ^b
surface area	0.10	0.05	-0.11	0.19	0.39	0.05	-0.49	0.16	-0.35	0.41	-0.28	0.41	-0.22	0.42
clay	0.18	0.13	-0.02	0.28	0.38	0.11	-0.57	0.24	-0.40	0.45	-0.35	0.46	-0.16	0.48
C _{Org}	0.14	0.26	0.40	0.00	-0.24	0.06	0.83	-0.14	0.70	-0.07	0.23	-0.13	0.71	-0.09
P _{Olsen}	0.40	0.57	0.43	0.69	0.27	0.51	-0.48	0.61	-0.19	0.72	-0.64	0.78	0.10	0.76
P _{FeO}	0.53	0.83	0.82	0.78	0.07	0.61	-0.02	0.60	0.21	0.69	-0.60	0.71	0.63	0.71
P _{ox}	0.33	0.57	0.41	0.68	0.20	0.47	-0.30	0.53	0.02	0.82	-0.47	0.77	0.04	0.77
P _{sat}	0.42	0.60	0.50	0.73	0.20	0.52	-0.58	0.64	-0.30	0.67	-0.65	0.73	0.09	0.71
P _{NaOH/EDTA}	0.40	0.65	0.50	0.76	0.24	0.52	-0.38	0.60	-0.05	0.84	-0.55	0.81	0.13	0.81
P _{tot-fusion}	0.39	0.57	0.39	0.59	0.02	0.49	0.03	0.46	0.30	0.76	-0.43	0.70	0.28	0.73
P _{water}	0.61	0.69	0.77	0.51	-0.23	0.53	0.39	0.42	0.43	0.29	-0.42	0.35	0.93	0.37
P _{pw}	1.00	0.62	0.50	0.57	-0.51	0.70	-0.03	0.69	0.11	0.38	-0.67	0.56	0.64	0.59

^aGray shade intensity is used as a visual aid that indicates how high r values are, ranging from white at 0.00 to maximum shade at 1.00 or -1.00. r values over 0.35 are significant (p ≤ 0.05) and over 0.45 are very significant (p ≤ 0.01) using Student's t test. All parameters listed in the columns are original from this study, whereas surface area, clay, C_{Org}, P_{Olsen}, P_{FeO}, P_{ox}, P_{sat}, P_{NaOH/EDTA}, P_{tot-fusion}, and P_{water} were determined by Stutter et al. (2015)³. ^bDspt rate—desorption rate in mg of P per liter of soil solution per second.

Table 4. DIFS Derived Parameters Reflecting P Depletion from Soil Pore Water by DGTs, Soil P Diffusion and Kinetics of P Resupply from Soil Solid Matrix

soil	X _{sol}	X _{ads}	K _d	R	R _{diff}	R-R _{diff}	R _{max}	T _{Rmax}	T _c	k ₁	k ₋₁	Dspt rate ^a
	cm	cm	cm ³ g ⁻¹					10 ³ s	s	s ⁻¹	s ⁻¹	mg L ⁻¹ s ⁻¹
Alness 1	0.54	0.50	64.45	0.15	0.07	0.08	0.27	1.66	1.39 × 10 ⁴	7.21 × 10 ⁻⁵	5.08 × 10 ⁻⁷	5.74 × 10 ⁻⁵
Alness 2	0.57	0.45	42.51	0.10	0.08	0.02	0.32	1.33	9.98 × 10 ⁴	1.00 × 10 ⁻⁵	1.56 × 10 ⁻⁷	6.53 × 10 ⁻⁶
Alness 3	0.45	0.31	111.98	0.12	0.06	0.05	0.31	1.33	4.42 × 10 ⁴	2.26 × 10 ⁻⁵	8.76 × 10 ⁻⁸	9.85 × 10 ⁻⁶
Alness 4	0.33	0.33	37.32	0.27	0.08	0.19	0.33	2.37	3.72 × 10 ³	2.69 × 10 ⁻⁴	4.63 × 10 ⁻⁶	3.32 × 10 ⁻⁴
Balruddery	0.48	0.37	129.89	0.10	0.07	0.03	0.29	1.33	5.54 × 10 ⁴	1.80 × 10 ⁻⁵	6.48 × 10 ⁻⁸	8.33 × 10 ⁻⁶
Banadl	0.44	0.44	48.24	0.20	0.08	0.13	0.31	1.91	8.35 × 10 ³	1.20 × 10 ⁻⁴	1.52 × 10 ⁻⁶	1.80 × 10 ⁻⁴
Benvie	0.42	0.37	100.39	0.16	0.06	0.10	0.26	1.66	8.96 × 10 ³	1.12 × 10 ⁻⁴	4.10 × 10 ⁻⁷	7.30 × 10 ⁻⁵
Bicton	0.47	0.47	45.01	0.26	0.06	0.20	0.29	2.94	2.30 × 10 ³	4.35 × 10 ⁻⁴	3.74 × 10 ⁻⁶	7.80 × 10 ⁻⁴
Bronydd high P	0.35	0.32	40.34	0.16	0.08	0.08	0.33	1.43	2.06 × 10 ⁴	4.86 × 10 ⁻⁵	8.00 × 10 ⁻⁷	3.48 × 10 ⁻⁵
Bronydd low P	0.55	0.44	14.55	0.11	0.08	0.03	0.32	1.33	7.97 × 10 ⁴	1.25 × 10 ⁻⁵	5.98 × 10 ⁻⁷	7.93 × 10 ⁻⁶
Canol	0.47	0.38	35.60	0.13	0.08	0.05	0.33	1.43	4.06 × 10 ⁴	2.46 × 10 ⁻⁵	5.09 × 10 ⁻⁷	1.74 × 10 ⁻⁵
Dartmoor	0.39	0.36	15.03	0.22	0.12	0.10	0.41	1.77	1.30 × 10 ⁴	7.68 × 10 ⁻⁵	1.27 × 10 ⁻⁵	1.45 × 10 ⁻⁴
De Bathe	0.28	0.27	54.15	0.14	0.06	0.08	0.28	1.43	1.57 × 10 ⁴	6.39 × 10 ⁻⁵	4.47 × 10 ⁻⁷	5.51 × 10 ⁻⁵
Dunsdon impr.	0.29	0.28	34.43	0.17	0.08	0.09	0.32	1.43	1.51 × 10 ⁴	6.63 × 10 ⁻⁵	1.16 × 10 ⁻⁶	4.62 × 10 ⁻⁵
Dunsdon unimpr.	0.30	0.29	65.80	0.17	0.08	0.09	0.32	1.54	1.61 × 10 ⁴	6.20 × 10 ⁻⁵	6.02 × 10 ⁻⁷	1.17 × 10 ⁻⁵
Friockheim 1	0.48	0.23	157.93	0.09	0.06	0.03	0.28	1.24	6.00 × 10 ⁴	1.67 × 10 ⁻⁵	4.18 × 10 ⁻⁸	7.61 × 10 ⁻⁶
Friockheim 2	0.35	0.42	221.17	0.12	0.06	0.06	0.27	1.33	2.46 × 10 ⁴	4.07 × 10 ⁻⁵	7.17 × 10 ⁻⁸	1.46 × 10 ⁻⁵
Haddington 1	0.29	0.32	99.50	0.36	0.06	0.30	0.37	20.9	9.98 × 10 ²	1.00 × 10 ⁻³	4.00 × 10 ⁻⁶	1.85 × 10 ⁻³
Haddington 2	0.33	0.29	27.37	0.12	0.06	0.06	0.28	1.24	2.06 × 10 ⁴	4.85 × 10 ⁻⁵	7.05 × 10 ⁻⁷	8.99 × 10 ⁻⁵
Haddington 3	0.41	0.38	92.60	0.17	0.06	0.11	0.26	1.77	8.36 × 10 ³	1.20 × 10 ⁻⁴	5.02 × 10 ⁻⁷	1.13 × 10 ⁻⁴
Haddington 4	0.35	0.35	23.53	0.19	0.06	0.13	0.26	1.77	5.71 × 10 ³	1.75 × 10 ⁻⁴	2.72 × 10 ⁻⁶	3.15 × 10 ⁻⁴
King's sedge	0.66	0.49	104.55	0.10	0.09	0.01	0.35	1.54	3.17 × 10 ⁵	3.15 × 10 ⁻⁶	2.97 × 10 ⁻⁸	8.00 × 10 ⁻⁷
Rothamsted	0.32	0.33	108.25	0.12	0.06	0.06	0.27	1.33	2.16 × 10 ⁴	4.64 × 10 ⁻⁵	1.56 × 10 ⁻⁷	1.64 × 10 ⁻⁵
Rowden	0.37	0.34	75.90	0.15	0.08	0.07	0.33	1.43	2.43 × 10 ⁴	4.12 × 10 ⁻⁵	3.82 × 10 ⁻⁷	2.34 × 10 ⁻⁵
Southlake north	0.52	0.43	42.65	0.13	0.09	0.04	0.35	1.54	5.37 × 10 ⁴	1.86 × 10 ⁻⁵	4.15 × 10 ⁻⁷	6.95 × 10 ⁻⁶
Southlake south	0.58	0.46	28.41	0.12	0.09	0.03	0.35	1.54	8.26 × 10 ⁴	1.21 × 10 ⁻⁵	4.14 × 10 ⁻⁷	8.22 × 10 ⁻⁶
Tayport	0.41	0.38	64.64	0.16	0.06	0.10	0.25	1.66	8.53 × 10 ³	1.17 × 10 ⁻⁴	6.45 × 10 ⁻⁷	1.53 × 10 ⁻⁴
Tentsmuir	0.39	0.38	3.84	0.22	0.07	0.16	0.64	1.77	3.87 × 10 ⁻²	2.58 × 10 ¹	3.15 × 10 ⁰	3.76 × 10 ¹
Vealand impr.	0.28	0.27	78.95	0.18	0.08	0.11	0.33	1.54	1.37 × 10 ⁴	7.32 × 10 ⁻⁵	5.86 × 10 ⁻⁷	8.05 × 10 ⁻⁵
Vealand unimpr.	0.32	0.31	43.30	0.18	0.09	0.09	0.34	1.54	1.83 × 10 ⁴	5.46 × 10 ⁻⁵	9.90 × 10 ⁻⁷	2.36 × 10 ⁻⁵
Woburn 1	0.55	0.26	302.73	0.08	0.07	0.02	0.29	1.24	1.10 × 10 ⁵	9.13 × 10 ⁻⁶	1.37 × 10 ⁻⁸	7.66 × 10 ⁻⁷
Woburn 2	0.38	0.38	147.97	0.15	0.05	0.10	0.23	1.66	7.85 × 10 ³	1.27 × 10 ⁻⁴	2.47 × 10 ⁻⁷	5.44 × 10 ⁻⁵

^aDspt rate—desorption rate in mg of P per liter of soil solution per second.

(C, D, E, and F). For the other soils, sorption rate constants (k₁) averaged 1.07 × 10⁻⁰⁴ s, whereas k₋₁ values averaged 1.29 × 10⁻⁰⁶ s, k₁ was, as expected, on average 83 fold greater than k₋₁. The estimated P₁ desorption rates during depletion by DGTs averaged 4.71 nmol L⁻¹ s⁻¹, and was found to exponentially

increase with increasing resupply capacity of the soils (calculated as R-R_{diff}; Figure 1F).

The maximum response (R_{max}) is highly correlated to C_{Org} and other parameters influenced by C_{Org}, which indicates that it affects the rate of desorption. C_{Org} was also strongly correlated

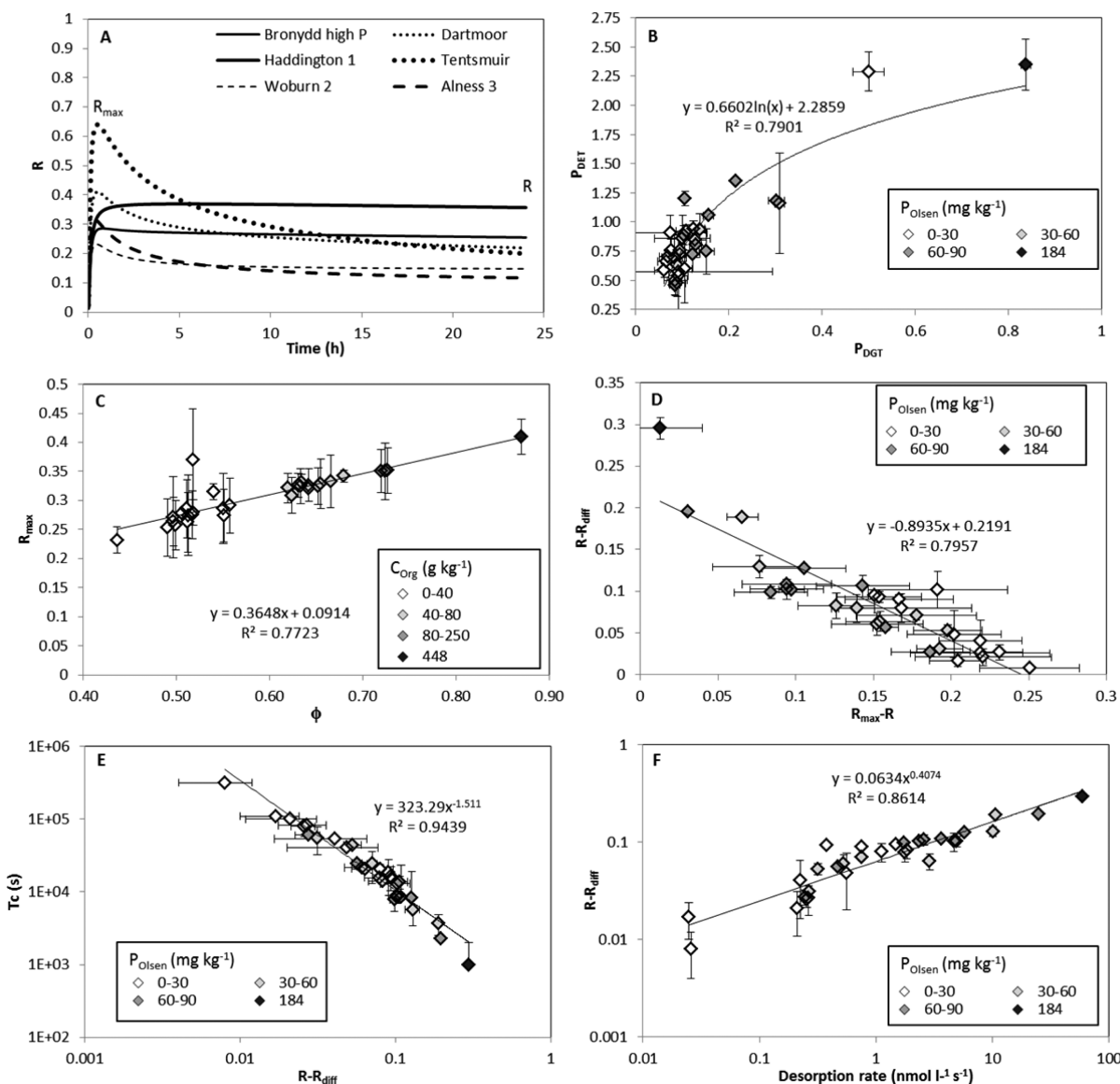


Figure 1. Patterns and interrelations in P_i resupply analysis using DIFS model: (A) Sample of different time dependency of R shaped curves; (B) R ratio as a function of P_{DGT} ; (C) Peak R (R_{max}) as a function of soil porosity ϕ ; (D) Size of the peak R ($R_{max}-R$) as a function of soil P_i resupply capacity ($R-R_{diff}$); (E) Equilibration time (T_c) as a function of soil P_i resupply capacity ($R-R_{diff}$); (F) Desorption rates as a function of soil P_i resupply capacity ($R-R_{diff}$). Error bars represent \pm one standard deviation.

with all wetting parameters (data not shown) and their related soil P mobility parameters R_{diff} and R_{Max} (Table 3). The effect of C_{Org} was clearly greater than the effect of surface area and particle size distribution, which were not strongly correlated with any P related soil property.

The $\ln T_c$, k_1 , and the desorption rate showed similar patterns, showing good correlations with P concentration in soil extracts (except for P_{water}). Desorption rate constant (k_{-1}) was highly correlated with P_{water} and moderately correlated with P_{FeO} , P_{pw} , P_{DGT} , P_{DET} , and R (Table 3). In general, all correlation coefficients for the P mobility and resupply parameters were improved when the sandy soil Tentsmuir was removed from the data set. The organic soil Dartmoor also behaved as an outlier in a few cases.

DISCUSSION

The DGT Methodological Approach: Advantages, Issues and Possible Improvements. The combined DGT

and DET techniques, and the DIFS model, have been previously applied to estimate the mobility and resupply parameters of soils for metal contaminants,¹⁰ but has not yet been used to study soil phosphorus. The data set here presented is therefore a unique opportunity to discuss the methodological issues involved, along with the behavior and drivers of the variation of the evaluated parameters.

The effective concentration (P_E) is a hypothetical concentration that represents the concentration of P in the soil pore water if resupply was only dependent on diffusion. Under the assumption of diffusion only, there would be no resupply of P from the solid phase. This approach is useful for representing, in the same parameter, both the equilibrium soil solution concentration and the easily desorbable/soluble P forms.^{9,10} The conversion of P_{DGT} to P_E using R_{diff} depends solely on the amount of water that is added to the slurry preparation (and the final porosity), which is set to a maximum for the soils used in this study. This maximum water retention in the slurry was shown to

be highly dependent on the organic matter content of the soils. The use of the DIFS model to estimate the soil specific R_{diff} is still useful, as illustrated by its strong variation and the higher correlation of most of the extractable P concentrations with P_E than with P_{DGT} (Table 3). Additionally to the R_{diff} , the wetting conditions and resulting porosity were clearly influencing the short-term (30–50 min) response in the fluxes into the DGT, reflected in the R_{max} parameter (Figure 1C). Soil structure is completely lost during slurry preparation and in undisturbed conditions, aggregate size has been demonstrated to influence both wetting properties and P desorption.¹⁷ The effect of moisture content and soil structure on θ^2 , D_s , R_{diff} , T_c , and K_{-1} needs to be further studied.

Differences between P concentrations in water extracts (1:4 w/v; P_{water}), and in soil pore water (P_{pw}) in the equilibrated slurry can be explained by the huge differences in solid: liquid ratio, extraction time and the amount of color interference during the P_i spectrophotometric determination. Methodologically, the DET preparation returned a much cleaner sample than pore water and water extracts and therefore a more accurate colorimetric determination of P_i . Additionally, the filter membrane and the polyacrylamide gel exert a size exclusion factor, which is likely to contribute to P_{DET} having a different pattern of values than those observed for P_{water} and P_{pw} . The same size exclusion factor is present for the DGT, since the same filter membrane and the diffusive gels are used. Therefore, we consider P_{DET} to be the most appropriate measurement of soil pore water concentration when it is compared to DGT measurements and these values have been used to calculate the ratio R shown in Table 4. Furthermore, P_{DGT} showed a higher correlation with P_{DET} than with P_{pw} which supports the previously stated (Table 3).

DGT and DET extracts maintain limited contamination from the soil matrix due to the size exclusion factor, and less interference is observed in color development by Murphy and Riley (1962)¹⁴ method, represented by smaller background levels in controls. Color development artifacts in wet chemistry P determination may be significantly large, especially for water based extracts (P_{water} and P_{pw}), where the concentrations are lower and therefore unsuitable for dilutions (Dr. Jane Hawkins, personal communication, December 3, 2014). For these extracts the total phosphorus measured by ICP-MS is a much more accurate parameter, but cannot be used in DGT calculations since organic P forms are abundantly present in soil extracts and in the eluates from the DGT ferrihydrite binding layer. Each one of the dozens of different organic P forms has its own unique diffusive coefficients in the DGT diffusive layer, needed to calculate their unique C_{DGT} and C_E . Enzyme hydrolysis and HPLC methods may be suitable for further studying the differential behavior of different organic P forms in soils using DGTs.

The use of DGT, DET, and the DIFS model are accurate and practical tools for the study of soil P mobility and resupply from solid phase. The theoretical basis of the DGT assay, which can be related to P uptake by plant roots, as well as the additional parameter estimates gained through the method (e.g., P_E , R , R_{diff} , R_{diff}) represent significant improvements to typical extract-based soil P tests (e.g., Olsen P). Namely we here propose the use of the R - R_{diff} value as the soil test parameter that best shows the P resupply from the soil solid phase.

More broadly, the holistic approach taken to resolve phosphorus mobility in soils brings a better understanding and new insights into P exchange and release kinetics of P from solid phase to solution. The further use of this method for soils treated in controlled experimental conditions (e.g., use of amendments,

fertilizers and high salinity irrigation waters) or in particular sample sets (e.g., chronosequence, slope and other field gradients) will allow the re-examination of old assumptions under a new light and with increased detail.

Further work is needed in order to fit the DIFS model using repeated experimental R values at increasing times of exposure, such as the studies performed by Ernstberger et al. (2002, 2005) for Cd, Cu, Ni, and Zn.^{18,19} This analysis will allow further verifying the accuracy of our estimation of K_d as the ratio of P_{Olsen} to P_{DET} .

Implications for Plant Phosphorus Bioavailability. The P availability for plants depends on its speciation in soil. The P sorption on the soil solid phase is represented by the solid/liquid P_i distribution coefficient (K_d). In this study K_d was calculated as the ratio between P_{Olsen} and P_{pw} , as the P_{Olsen} is currently the most used as the best accepted representation of labile adsorbed P in soils. Nevertheless there is not a consensus for the use of P_{Olsen} for estimating labile P even after decades of related research,²⁰ and many other extracts have been proposed as P bioavailability indicators in soils such as, Mehlich 1, Bray 1, Mehlich 3, water, ammonium acetate, and DTPA.²¹ Moreover, many P indices that employ a strong chemical extractant, were not introduced as a quantitative measure of P availability, but as availability indexes. For lack of better methods, these are often used as a quantitative measure of plant available P. In some cases the different extractants have been theoretically designed to work with the dominant soil matrix and pH of specific geographical regions (e.g., alkaline calcareous soils), others are unspecific respect to type of soil matrix. Some of these P bioavailability methods are currently being used and recommended to soils with conditions fundamentally different than the ones these methods were designed for. Ultimately, the greatest challenge for predicting the availability of soil P to plants will be the design of an easily implemented analytical tool, which best represents the P bioavailability regarding both the residual soil P and plant response to fertilization. In a critical P experiment (crop response to increasing P fertilizer doses) P_{DGT} was shown to be the best predictor of maize P uptake compared to P_{Olsen} , anion exchange membrane P, oxalate extractable P, Colwell, Bray-1, Mehlich-3 and $CaCl_2$ -P, but not as good at predicting rice P uptake.²²

The used two pool model (labile and nonlabile P) is an oversimplification, and many different adsorbed, precipitated and organic forms are more likely to occur. The separation of the labile pool into weak and strong binding sites has been proposed, nevertheless with the available data this is over parametrization.²³ The majority of the P associated with the soil solid phase is nonlabile during the 24 h of the DGT deployment.⁶ In this binary model approach, K_d should account for the easily desorbable and readily soluble forms of inorganic P, assuming that no significant contributions of organic P mineralization would take place in this short period. Although in our study we did not have an accurate estimation of this labile pool, the actual K_d can be estimated by regression of a time series of DGT measurements.²⁴ This analysis would help to elucidate the real resupply potential of the soils and which extractant reflects more accurately the absolute values of the labile P forms therein. The estimation of P_i K_d using time series DGT analysis should be further studied in future experiments.

The DGT method samples soil solution P and a small fraction of solid phase P desorbed into soil solution by the DGT device perturbing the equilibrium condition.^{12,22} Plants on the other hand, are active mobilizers of soil adsorbed P, using many different mechanisms to induce P desorption, like root exudation

of organic acids, siderophores, enzymes, surfactants, and microbial growth stimulants.^{2,25,26} It is expected that these exudates will change the balance between adsorbed and solution P, reducing K_d and increasing T_c , after the induced desorption of labile P has occurred. This effect should be dependent on the type (or combination of types) and dose of the exudate, as well as their indirect effect as microbial growth stimulants. Therefore, a realistic indicator of plant available P will depend both on the labile P concentration and the plant mechanisms involved in P mobilization, making the agronomical K_d a crop dependent parameter. Future work on how plant exudates interfere with solid phase resupply using DGT and DET analysis would give quantitative information on active P mobilization by specific mechanisms.

In general, DGT and DET parameters are expressed in soil solution concentration (e.g., mg/L) while other P concentration in soils extracts are usually expressed per kg of soil dry weight. The lack of a constant solid to liquid ratio adds inaccuracies in back-calculating P_{DGT} and P_E concentrations on a dry weight basis. When compared to adsorbed concentrations, the solution concentrations (as used from DGT related data) are expected to be more realistic to those experienced by the plant, but harder to compare between soils due to their different wetting properties. Moisture is set to a maximum during slurry preparation, therefore the DGT method naturally accounts for differences soil wetting properties, which in turn are shown here to have significant impact on short-term P mobility. This may be one of the factors why P_{DGT} have shown in some cases stronger correlation with plant P uptake compared with P_{Olsen} and other soil extracts.^{22,27}

Drivers of Phosphorus Lability. Except for the sandy Tentsmuir soil, resupply from solid phase was considered small compared to other elements such as Cd, Cu, Ni, and Zn.^{10,18} For other elements, T_c usually ranged from 0.01 to 1000 s¹⁰ while here the majority of T_c values were in the range of 1×10^4 to 1×10^5 s (20 samples, Table 4). Desorption rates are expected to be much slower than sorption rates and the P hysteretic behavior has been previously described by Okajima et al. (1983).²⁸ The majority of desorption rate constants were in the range of 1×10^{-6} to 1×10^{-7} (18 samples, Table 4) averaging 1.29×10^{-6} s⁻¹. In previous studies the average k_{-1} values were 2.9×10^{-6} s⁻¹ to 35 non calcareous soils²⁹ and 1.4×10^{-5} s⁻¹ to 12 calcareous soils.³⁰ Although different methodologies may affect the results of desorption studies, the average k_{-1} values were similar between our data and previous research^{29,30} indicating that DGT and DIFS based estimation are in the expected range of variation.

Although pH is expected to be positively correlated to P desorption,²⁹ for our soils pH was not correlated with P mobility parameters. No treatment was applied in our study to force pH shifts and observe its effect on P mobility parameters. The effect of natural pH values across different soils on P desorption, and the effect of pH changes within one specific soil (i.e., rhizosphere pH changes) are not necessarily the same. Similarly, particle size distribution was expected to significantly affect P desorption.³¹ Here, however, P resupply parameters were poorly correlated with particle size distribution. As our set of soil samples were very diverse in their intrinsic properties, the effects of pH and particle size distribution were probably overcome by other factors such as surface properties of clays and organic matter, and predominantly the fertilization history and the resulting P saturation of the soil exchange complex. Nevertheless, the use of median diameter (representative of particle size distribution) as a second response variable in multiple regression analysis was shown to

significantly increase the explained variance for P_{DET} , P_{DGT} , and P_E by 17%, 6.8%, and 4.1% respectively (data not shown). This may indicate that particle size distribution is a secondary driver of P mobility parameters.

The P resupply from solid phase ($R-R_{diff}$) and the desorption rates during DGT deployment were well correlated with P_E , P_{DGT} , and most of the P concentrations in different tests. This was considered hard evidence that P status is the main driver of P resupply from soil solid phase into solution, and hence P lability and bioavailability. In general, the soils with extreme P_{Olsen} were also extreme in P mobility and resupply parameters (Figures 1B, D, E, and F). Long-term P fertilization rates are directly proportional to the degree of soil saturation with P and the concomitant reduction P-retention capacity.³² Many European soils are excessively fertilized, accumulating soil P pools to environmentally unacceptable levels.^{33,34} This is certainly reflected in our soil sample set as 81.25% of the samples belong to P fertility indexes over three corresponding to “high” and “very high” P availability. The wide range of soil types and P concentration of our sample set, gives strong support to the case that soil P status (and the assumed related saturation of the soil interchange complexes) is the main driver of P resupply from soil solid phase into solution, and hence P lability. More data from a bigger sample set including other soils types and conditions are required to further verify these conclusions.

Environmental Implications. The high P status in soils and the resulting nutrient pollution of receiving water courses are a major environmental concern. Considering both freshwaters and oceans, current planetary conditions exceed all limits for P discharges.³⁵ There is an urgent need to reduce total P in soils into environmentally acceptable levels, while maintaining optimal crop growth conditions.³³ The chemical exchange of P between soil solid and solution phase is expected to be the main mechanism influencing the bioavailability of P to crops. The present work has provided new insight and an alternative approach for studying the dynamics and mobility of P in soil. High levels of available P were found using the DGT method among soils that represented a wide range of P indices. This unexpected result indicates that extract-based methods for estimating P availability may vastly overestimate fertilizer requirements and the risk of on-farm nutrient use and loss. The DGT method described herein could therefore be used to improve estimates of crop P requirements while minimizing the use of mineral fertilizers and the subsequent risks associated with surface water nutrient enrichment and eutrophication.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05395.

Additional information as noted in the text (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*(D.M.-B.) E-mail: d.blackburn@lancaster.ac.uk.

*(H.Z.) E-mail: h.zhang@lancaster.ac.uk.

Author Contributions

The manuscript was drafted by Daniel Menezes-Blackburn, who also performed the DGT, DET, and DIFS analysis under direct supervision of Hao Zhang and Philip M. Haygarth. Patricia Cooper, Renate Wendler, Marc Stutter, Charles Shand, David Lumsdon, Timothy S. George, and Martin Blackwell were

involved on the sample collection and characterization of P-related parameters. Courtney D. Giles, Tegan Darch, Catherine Wearing, and Lawrie Brown were involved in various laboratory analyses. All authors were involved in the conceptual planning, discussions and corrections of the manuscript.

Notes

The authors declare no competing financial interest.
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ABBREVIATIONS AND SYMBOLS

- P_i inorganic phosphorus
 P_o organic phosphorus measured as the difference between total and inorganic P
 DGT diffusive gradients in thin films using a ferrihydrite containing gel as a P binding layer
 DET diffusive equilibration in thin films (same DGT setup without the binding layer)
 DIFS 'DGT induced fluxes in soils and sediments' model
 P_{DET} (mg l⁻¹) pore water (dissolved) P concentration determined using DET
 P_{DGT} (mg l⁻¹) DGT measured time averaged soil solution P concentration at the surface of DGT device
 P_E effective P concentration – DGT estimated soil solution P + labile P concentration from the solid phase
 P_{Olsen} (mg kg⁻¹) phosphorus concentration (solid phase) measured using NaHCO₃ extraction
 D_0 (cm² s⁻¹) diffusion coefficient in diffusive layer of DGT device
 D_s (cm² s⁻¹) diffusion coefficient in soil
 k_{-1} (s⁻¹) desorption rate constant
 k_1 (s⁻¹) sorption rate constant
 K_d (cm³ g⁻¹) equilibrium distribution coefficient between solid phase and soil solution
 P_c (g cm⁻³) particle concentration–mass of particles in unit volume of soil solution
 R ratio of P_{DGT} to P_{DET}
 R_{diff} ratio of P_{DGT} to P_E in the case where there is no P resupply from the solid phase, estimated using DIFS for diffusion only case
 T_c (s) response time of (de)sorption process
 X_{sol} (cm) estimated distance to which DGT device depletes at least 5% of pore water P concentrations
 X_{ads} (cm) estimated distance to which DGT device depletes at least 5% of adsorbed P concentrations
 WHC water holding capacity of the soil
 MR maximum water retention in the soil prepared for DGT deployment
 ρ_s bulk density of the soil at MR
 ρ_o bulk density of the dry soil
 ϕ soil porosity
 θ^2 diffusive tortuosity

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