

The partitioning of P in soil determines the fluxes and deliveries of labile P in soil solution

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1 Abstract

Phosphorus (P) is an increasingly limited resource for food production, which necessitates studying soil factors controlling rates of P release to soil solution. Phosphorus use efficiency is among other, affected by the plants, the plant root induced displacement of P equilibrium in soil during uptake and the following rates of replenishment from geochemically active P stores in soil. Here, soil P partitioning and flux data collected from a 50 year field trial, based on application of differing P masses, was investigated using a diffusive gradients in thin films (DGT) technique and “DGT-induced fluxes in sediments” (DIFS) model. Partitioning of P in soil was accomplished by deploying DGT at increasing contact times (6 hours to 120 hours). DGT induced P fluxes increased with soil P, and they were highest the first hours after installation. A Langmuir adsorption approach to determine K_d concealed accumulated P labile stores, whereas K_d estimations from ammonium lactate (AL) extractions did not. The estimated fluxes in the latter situation stabilized after 24 hours deployment, and they were more clearly reflecting the long term P treatments. The two K_d approaches showed the importance of considering inherent P-stores for calculating fluxes and deliveries of labile P available for plants during P-uptake. The use of DGT and DIFS in combination enabled good estimations of fluxes. Such fluxes may be used to estimate, *In Situ*, critical soil solution P concentrations available for plants during growth, in different soil types.

2 Introduction

Access to mineral phosphorus (P) is a societal issue of great concern because it is a limited resource (Zapata, 2004). This is a natural consequence of the inevitable food production increase following global population growth. The fact that P is an essential and non-renewable element for all life, binding strongly in mineral soil, necessitates its precise application to field soils. Plant growth is primarily limited by insufficient N supply, but P-limitations also occur frequently (Aerts and Chapin, 2000). Over the years, P has been applied in excess to ensure sufficient supply to farm crops, particularly to high-intensity crops such as vegetables (Johnston et al., 2014; Pierzynski and Logan, 1993). However, erosion of such soils has resulted in increased eutrophication of low land waters (Krogstad and Lovstad, 1989; Schindler et al., 2008; Ulen et al., 2010). European countries which have committed to the EU water framework directive (EU, 2000), have implemented several means to meet the quality criteria for surface waters. Norway must reach its quality criteria by 2018. An increasing future challenge seems to be providing a sustainable and steady supply of P to feed an increasing world population (FAO, 2009; Lal, 2013), without compromising quality of low land aquatic systems.

The overapplication of P fertilizer to soil is problematic, but understandable due to the need for steady food supply. Hence, it is generally a need for research focusing on acquiring the large P stores accumulated in many agricultural soils (Stutter et al., 2012) and specifically on the geochemical fate of P in rhizosphere during growth. Plants take up P in a relative short time period, and for effective uptake to occur, plant roots explore enough root space to provide sufficient nutrient supply for germination. Fertilization of grass and grain crops is normally in balance, with the ratio between uptake and application averaging close to 1 (Johnston et al., 2014). Fertilization of vegetable crops, on the other hand, is normally unbalanced, and fertilization can be several times higher than the amount taken up by crops (Pierzynski and Logan, 1993). During the growth season, plants take up P from soil solution, where the P concentration in solution is controlled by rates of replenishment from larger P soil stores. This P partitioning in soil is dynamic, and geochemical factors controls P fluxes between soil solutions, from readily to slowly available to nearly unavailable P. Conceptual understanding of P partitioning

and kinetic responses to external factors are used as model parameters for P: predicting uptake (Wang et al., 2010), managing use and agricultural efficiency (Johnston et al., 2014). But most P assessments rely on the assumption of slow redistribution kinetics; hence, equilibrium extraction methods are used most often. Extractions are easily conducted on a large number of samples with reproducible and accurate enough results to estimate plant available stores of interest. However, the use of extraction methods, such as the ammonium lactate (Egner et al., 1960) and Olsen-P (Olsen et al., 1954) methods, conceals kinetic P release from solid to solution phases in soil as these methods primarily estimate potential plant available P stores during the growth season. Hence there is a need for a understanding the P kinetics better, *In Situ*, ideally without the use of extracting agents in unrealistic solid solution ratios.

For direct assessment of trace metal and (oxy)anion availability in water, sediment and soil, the diffusive gradient in thin films (DGT) technology (Davison and Zhang, 1994) is a better alternative than classic soil extraction protocols. The DGT technology have had more than 20 years of rapid development, and its application spans from in situ measurements to speciation and kinetic studies (among other uses) of various elements in the samples of interest (Zhang et al., 2014). The device can be placed directly in moist soil and the ions diffuse through a protective membrane, via a well-defined inert hydrogel before its being bound and accumulated to a resin. The hydrogel discriminate large dissolved molecules from diffusing through, and hence only free or labile elements are measured. The measured concentration after termination, is a time integrated concentration conditional to the ion diffusing properties and the geochemistry at the near surface of the DGT. This makes the DGT technology highly applicable for investigating in situ investigating impacts on the fate of labile forms of components in soils as affected by external factors such as soil texture, humidity, pH, time etc. Ernstberger et al. (2002), Lehto et al. (2006) and Menezes-Blackburn et al (2016), applied the DGT technique (Zhang and Davison, 2015) in combination with the DIFS model (Harper et al., 2000) in various trials to study the distribution and desorption kinetics of metals or P in different soils. The DIFS model can predict response time (T_c) and fluxes in wet soil, if the estimated ratio of DGT-accumulated P to the labile P in soil solution at start

(P_{DGT}/P_{C0} ; the R -value) in combination of a K_d value are provided. Additionally, the DIFS estimates dissolved P concentrations as a function of distance from the DGT surface with time. Menezes-Blackburn et al. (2016) conducted a study on factors controlling P kinetics in 32 UK soils, and found that the desorption rates and resupply was positively influenced by the P status. Likewise, Lehto et al. (2006)'s comparison of results from DIFS modeling with a classic Barber uptake model, showed the relevance of desorption kinetics for supplying reactive zinc (Zn); in most cases, DGT deployment emulated supply processes governing plant uptake. In our study, we compared the P fluxes in P exhausted soils with the same soil type receiving normal fertilizer treatments during the same period, from 1966 to 2014. As soon as DGT is deployed to moist soil, labile ions diffuse through the diffusive layer creating a depletion zone at the DGT surface. In soil, such a depletion zone develops with increasing contact time. The depletion gradient and spatial impact with distance from the DGT surface is affected by concentration of the geochemically active element, soil surface chemistry, but also the nature of the sink (Degryse et al., 2009b; Lehto et al., 2006; Zhang and Davison, 2015). The plant is a biogeochemically active organism maintaining homeostasis. A DGT cannot fully mimic a plant, but as suggested by Lehto et al. (2006), deploying a DGT in moist soil enables kinetic studies based on disruption of geochemical equilibrium better than traditional extraction methods. We hypothesize that i) long-term P-exhaustion in soils results in a lower P flux toward the DGT compared to soils receiving annual P applications, and ii) long term fertilization loading of slowly reacting P fractions in soils quickly replenishes reactive P-fractions, presumably bioavailable, when chemically labile P is removed by the DGT. To test these hypotheses, we collected soils from P-exhausted and P-fertilized field trials and exposed them to DGTs with increasing contact times.

3 Materials and Methods

3.1 Experimental site and soil sampling.

A long-term field trial at the Norwegian University of Life Sciences, Ås, Norway, has been conducted since 1966. Annual P additions have been applied at four different levels (P1-P4): P1=0 kg haa⁻¹; P2=16

kg haa⁻¹; P3=32 kg haa⁻¹ and P4=48 kg haa⁻¹ in a partly randomized block design on a uniform horizontal site. Treatment parallels of the two highest P-treatments are randomized within one great block and the two lowest P-treatments are randomized within another great block. Nitrogen has also applied since mid-1980 in the amount of 116 kg haa⁻¹ annually. Before the 1980s, N applications comprised less N, in accordance with older fertilizer norms. The whole trial area also contains different K-treatment levels, but we collected soils from plots where K-fertilizations were maintained at 10 kg haa⁻¹y⁻¹. Soil data for the whole field trial, is shown in table 1; we report results from our soil investigations, sampled from two parallel fields at four different P treatments. All N, P and K were applied as mineral fertilizers. Sampling occurred early June 2014, one week before wheat crop harvest. Plots are 3.6 m wide and 7.5 m long. To avoid edge effects, within each trial plot, samples were taken from a smaller rectangle (sampling plot) with a width of 2.4 m and length of 5.5 m. We used an auger to obtain subsamples of topsoil (0-20 cm depth) within the sampling plot, providing one thoroughly mixed sample of approximately 200-300 g raw mass. A total of eight samples were prepared for DGT exposure and other lab analyses.

3.2 Laboratory experiments.

The eight soil samples (approximately 200 g), 4 duplicated P treatments, were used for the DGT-exposure experiment, ammonium lactate extractions (P_{AL}) and determination of P-adsorption as described below. Other soil chemical characteristics of the collected soils were determined earlier and are shown in table 1.

3.3 DGT exposures

DGT disks loaded with Fe-oxide resins, provided by DGT-Research, were used (www.dgtresearch.com). Prior to the experiment each soil sample was homogenized by hand without drying or sieving. This procedure maintained the soil as close to field conditions as possible while providing benefits of stable temperature, humidity and reduced heterogeneity by executing the exposure

in laboratory. Soils were placed in new plastic boxes that were brought to near field capacity by repeated additions of distilled water. Boxes were covered by clean plastic film and equilibrated for 24 hours before installing the DGTs. Five DGTs were placed in each P-treated soil treatment and withdrawn after 6, 12, 24, 72 and 120 hours exposure time. Withdrawn DGTs were immediately rinsed in distilled water to stop soil contact. Hence, 20 DGT units were exposed (2 repeats, 4 P treatments and 5 exposure times). In addition, 3 DGTs were unexposed and used as DGT blanks.

Each Fe-oxide resin was removed and dissolved in 1.6 M ultra-pure HNO₃ and left > 24 hours before determining the P mass. P-determination was carried out directly in the extract solution using an ICP-OES analyzer (Perkin Elmer, Optima 5300 DV). Certified reference water was used (NIST, 2004) spiked with 2.5 mg L⁻¹ P. The limit of quantification (LOQ) was determined in the 1.6 M ultra-pure HNO₃ extracts of the DGT/Fe-oxide blanks. Internal standards were added to samples during analysis by ICP-OES.

The P mass (μg) in extract solutions measured in the laboratory were corrected for a default elution factor $f=0.8$ prior to use. The time-integrated concentration of P_{DGT} (μg l⁻¹) is calculated using equation 1:

$$P_{DGT} = \frac{M\Delta g}{D_0 t A} \quad (1)$$

where M is P mass (μg), Δg is the sum of P diffusion length through gels and membrane ($\Sigma\Delta g$), D_0 is the P diffusion coefficient in water (cm² s⁻¹), t is exposure time in seconds (s) and A is the effective exposure area (cm²).

If we argue that the capacity of the Fe-oxide is in the range of 15-20 μeq., that phosphate ions have higher selectivity for the resin compared to other competing ions, and that inorganic P-ions are dominated by PO₄³⁻, the maximum theoretical capacity is between 150 to 200 μg P. Since our DGT's

are exposed to soil with less control of competing ions, our conservative estimates limits the capacity to 10% of this.

3.4 Ammonium lactate extraction

In accordance with Egner et al., (1960), two g dried and sieved soil (< 2 mm) from each of the eight samples, were suspended in 40 mL 0.1 M ammonium lactate (AL) solution and shaken for 1.5 h. in 50 mL unused HDPE test tubes from VWR laboratories (vwr.com). The extracted P- concentrations were determined spectrophotometrically (Gilford, Stasar II) according to Murphy & Riley (1962), after filtration through a blue band filter. Experimental blanks were prepared using the same procedures as the samples. P_{AL} concentrations are presented in table 1.

3.5 P-adsorption experiment.

Two grams dried and sieved soil (< 2 mm) from each of the eight samples was extracted in 40 mL P- solutions in a 2.5 mM $CaCl_2$ matrix with 3 drops of toluene. P- solutions were mixed with soil subsamples equal to 0, 10, 20, 40, 80, 160 and 320 mg P/kg soil in 50 mL unused HDPE test tubes from VWR laboratories (vwr.com). Each suspension was shaken for 24 h. and centrifuged at 10 000 x g for 10 minutes before filtering the supernatant through 0.45 μ m micro pore filters. Experimental blanks were prepared. Total-P in extracts were determined spectrophotometrically (Gilford, Stasar II) according to Murphy & Riley (1962).

3.6 DIFS input parameters

The DIFS 2D model (Harper et al., 2000) was run in parameter estimation mode to calculate the development of response time (T_c), fluxes and concentrations of P in dissolved phase with distance from the DGT surface as induced by the DGT exposures. The input file provides some key soil chemical and soil physical parameters of the experimental soils and soil types investigated (Table 2).

P- concentrations after extracting the 8 soils with 2.5 mM CaCl₂ containing 0 mg P from the P-adsorption experiment were used as the equilibrium soil solution P-concentration C_0 (Table 2). These values were, in combination with the average P_{DGT} from 6-24 h. exposures (n=6), used to calculate the experimental R -values ($R=P_{DGT}/P_{C0}$) (Harper et al., 2000) for each P treatment (Table 2). Ideally C_0 -concentrations when used to calculate R , should discriminate inorganic P and labile P from inert complexed P in solution (Harper et al., 2000). Our determination of spectrophotometrically detectable P (Murphy and Riley, 1962) is a crude estimate of inorganic P in soil solution (Hylander et al., 1996), where an unknown fraction of labile P may be underestimated. However, we believe this is a better experimentally derived P_{C0} estimation compared to an ICP-MS determination of total P in pore water.

The distribution coefficient (K_d) was determined using two different approaches: first, fitting a Langmuir adsorption isotherm (K_{d-L}) and second, from P_{AL}/P_{C0} (K_{d-AL}) ratios obtained for each P treatment. The two different approaches provided different K_d -values. The K_{d-L} was outlined from the Langmuir isotherm by rearranging the general Langmuir equation as outlined in Essington (2004) (pages 339-342). The general Langmuir equation is expressed as:

$$q = \frac{bK_L c_{eq}}{(1+K_L c_{eq})} \quad (2)$$

where q is adsorbed P concentration, b is the adsorption maxima, K_L is a measure of the adsorption isotherm intensity and C_{eq} is the equilibrium concentration in solution. This equation can be rearranged to:

$$\frac{q}{c_{eq}} = bK_L - qK_L \quad (3)$$

In this case, because q/c_{eq} defines the distribution coefficient for P, between sorbed and solution phases, K_d can be expressed as:

$$K_d = bK_L - qK_L \quad (4)$$

Generally, in a plot of q/c_{eq} and (K_d), as y-variables and q as x-variables, a regression line can be fit to observations, characterized by a $-K_L$ slope intercepting the x-axis at b , the adsorption maxima (Table 3). K_d at $q=0$ is interpreted as K_d (here indicated as K_{d-L}) for different P-treated soils in the field at

sampling time, before the adsorption experiment occurs. Estimated K_{d-L} values from this Langmuir adsorption isotherm approach are shown in table 3, together with K_{d-AL} values obtained from the P_{AL} and P_{C0} concentration ratios ($K_{d-AL}=P_{AL}/P_{C0}$).

Relevant soil physical parameters for DIFS-modeling were obtained from soils of the same soil type 50 – 100 m away, and these values are shown in table 2. The particle concentration (P_c), porosity (Por_s , Φ) are measured parameters, whereas tortuosity (θ^2) is derived from porosity (Φ) as in Bourdreau (1996). The diffusion coefficient for P in soil D_s , is estimated from D_0 :

$$D_s = \frac{D_0}{\theta^2} \quad (5)$$

The porosity of the DGT-gel (Por_d , Φ), the sum diffusion layer thickness ($\Sigma \Delta g$) and the self-diffusion coefficient (D_0) for P, are obtained from www.dgtreserach.com. We earlier determined the P diffusion coefficient in the DGT diffusive gels (D_{DGT}) (Sogn et al., 2008), which was a little higher ($7.3\text{-}7.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), but we chose to use the tabulated D_0 -value for sake of easier comparison with other DIFS modeling outputs.

3.7 Statistical analysis and graph production

The DGTs are exposed to a small area and the DGT-accumulation of P between repeat experiments of equal treatment and exposure time vary due to some heterogeneity developed in the soil, but since the experiment was conducted with only one set of duplicates, standard deviations could not be calculated. In relevant figures, both parallels are shown.

Two observations were treated as missing values, as they were 3 to 9 times higher than expected compared to the repeat observations and observations either before or after during the time series. One removed data point was from at P2 after 120 h. (ca 3 x higher), and the other was at P3 at 6 h. (ca 9 x higher) exposure. Graphs were produced in SigmaPlot v 13.0 (Systat, 2014), whereas linear regression analysis were conducted using JMP v 11.0 (SAS-Institute, 2016).

4 Results

4.1 P soil adsorption

P soil adsorption flattened out (estimated by the adsorption maxima b , table 3) with increasing P-concentrations, and the curves can be described with Langmuir sorption isotherms. The key parameters are given in table 3. From the graphs in figure 1, the adsorption intensity (see K_L in table 3) increases inversely with P treatments in soil (from P1 to P4). The estimated K_{d-L} also increased inversely from 56 to 291 L kg⁻¹, corresponding to treatments P4 to P1, respectively (Table 3). The estimated adsorption maxima (b , table 3) do not vary in the same way. No treatment related trends are observed. The field trial is conducted on one soil type and this is more important for sorption maxima than P- treatments. The lowest adsorption maximum is estimated for soil P2, where the variation between repeat experiments at maximum P-addition was greatest. One of the repeat experiments was much lower than expected, and this value forced the estimated adsorption maxima down. The adsorption experiments indicated that different P treatments primarily affected adsorption intensity K_L (affinity for P-adsorption) and K_{d-L} more than adsorption maxima (b).

4.2 P accumulation in DGT with time

The soil samples were not dried or sieved and hence were incompletely homogenized. The variability in mass of P accumulated by the DGT reflects the physio-chemical heterogeneity in the non-homogenized soil, which in turn has affected the diffusion of P to the DGT surface. This effect is greatest when exposure time is short; the trend can be visually inspected in figure 2 a&b. When comparing P_{AL} with P_{DGT} , we observe the correlation between P_{AL} and P_{DGT} is positive irrespective of exposure time (6 to 120 h.), but the correlation is strongest when comparing P_{AL} with P_{DGT} after 120 h. exposure compared to 6 and 72h. exposure (figure 2a). In figure 3a, P_{DGT} development with time is displayed. Estimated equilibrium P_{DGT} concentrations are higher when exposed only at 6 hours because the relative replenishment of soil P is slower with time. Finally, soils containing the lowest P_{AL}

concentrations also provide the lowest P mass for DGT accumulation. *Visa versa*, the DGTs exposed to P4 soil accumulate the most P (figure 3a&b).

The graph in figure 2b indicates that in soil treatment P1, where the P_{AL} is lowest, the ratio of P accumulated after 6 h. to that accumulated after 120 h. is highest. The ratio is expressed based on the accumulated P mass ($\mu\text{g P}$) in the DGT. This ratio falls as P_{AL} increases. By increasing the exposure time from 6 h to 120 hours, the total accumulated P mass from soil P1 increases negligibly compared to soil where the P_{AL} is high (P2 to P4, figure 3b). In other words, the slowly available P- stores (120 h.) are small in treatment plot P1. P_{DGT} concentrations generally reduces with exposure time because the accumulated P mass is incompletely replenished from soil as exposure time (Equation 1) increases. The accumulated P mass increases with time, but not linearly (figure 3b). However, even at 120 h exposures, the DGT's accumulated less P than our conservative capacity limit for the Fe-oxide resin set at 15-20 μg (10% of theoretical maximum). Fluxes of P ($\text{mg s}^{-1} \text{cm}^{-2}$, figure 3 c&d) are generally lowest in soil from P1 and highest in soil from P4, and values reduce from 6 h. to the 120 h. exposures. K_{d-L} derived fluxes develop very little (from 6 to 120 h.) in soil P1 and P2 and reduce steadily, but less and less with time, in soils P3 and P4 (figure 3c). K_{d-AL} derived fluxes change very little beyond the 24 h. exposure time (figure 3d).

The kinetic limitations of the soil to maintain equilibrium P concentrations in soil solution during DGT exposure, can be used to describe dynamic partitioning of P in soil (figure 4). If the accumulated P mass after 120 hours is defined as the sum of quickly and slowly available P (100%), the P- exhausted test plot P1 contains relatively little slowly reacting P. In other words, the fraction of available P is quickly exhausted during a growing season in P1 soil compared to an analogue situation in P4 soil. The relative distribution of P from free and quickly reacting to more slowly reacting P shifts towards the slowly reacting P with higher annual P applications. This is displayed graphically in figure 4. The figure shows the relative amount of quickly reacting P (6 h.) dominating plot P1 in contrast to the relative distribution

of P fractions in plot P4, for instance. In figure 3b, the mass-ratio of P_6/P_{120} is highest at low P_{AL} . At higher P_{AL} concentrations (P4), only 10-20% of P is partitioned in quickly available P-fractions (6 h.), possibly in pore water. DGTs are individually exposed in the soils, and hence some heterogeneity is observed. For example, the odd drop in DGT-P for P1 after 12 h. exposure and P3 after 24 h. exposure, may be connected to heterogeneity (figure 4). In general, the principle of kinetically controlled differences in P-partitioning is easily observed and the trend from low-P soil to high-P soil is fairly consistent.

4.3 DIFS-modeling

The DIFS model was run in parameter estimation mode, and measured estimations of both the R - and the K_d values were provided as input parameters. These and other input parameters for DIFS modeling are displayed in table 2, where K_d values from both estimation approaches are provided (K_{d-L} and K_{d-AL}). R -values ($R=P_{DGT}/P_{C0}$) reduced with increasing contact time due to slower P-replenishment with time (not shown). There was also a drop in R from P1 to P2, possibly related to relative slower replenishment (P_{DGT}) with increasing P in soil in comparison to the equilibrium concentration of extractable P (C_0). As indicated above, high-P soils replenish P over much longer times compared to low-P soils due to the larger reservoir of DGT-reactive P (figure 4). In the P1 soil, nearly 60% of total DGT-reactive P (within 120 h.) is recovered by the DGT during the first 6 hours. Hence the P_{DGT}/P_{C0} ratio (R , table 3) is relatively higher in the P1 soil. The three other trial plots received a substantial amount of P in comparison; therefore, the concentration of P from different DGT-fractions are more evenly distributed, although there is a tendency for slow reacting P to dominate with increasing P amendments (figure 4).

The almost total exhaustion of DGT-reactive P in soil P1 and increasing DGT-reactive reservoirs with P treatment is confirmed by the DIFS calculation, illustrated in figure 5. First, it is evident that the DGT-induced P fluxes in soil P1 developed a noticeable concentration gradient already at 6 h., affecting

dissolved P concentration at approximately 1.0 cm distance from the DGT. After 120 hours, the P-flux affected dissolved P only < 0.5 cm deeper (1.5 cm distance). The combination of low C_0 - values and “high” R , makes soil P1 special in comparison to the remaining soils. Soils P2-P4 have the same R - values but increasing C_0 - and decreasing K_{d-L} values with P application (Table 2). From soil P2 to soil P3, the striking difference is the much steeper concentration gradient curves (less developed in P3, figure 5) and much lower response time (T_c , Table 2). The shape of the P-concentration curves are not very different when comparing soil P3 and P4, but due to larger difference in C_0 relative to the difference in K_{d-L} , estimated T_c is an order of magnitude lower for soil P4 (0.0014s) than soil P3 (0.01 s, Table 2).

In the model estimation where the K_{d-AL} was used as input parameter as an alternative to K_{d-L} and comparing 24 h. exposure times only, we observe in figure 6 that concentration curves estimated for the four soils are marginally different (K_{d-AL}). For soil P1 and P2 there is no difference in P-concentration curve development when comparing 24 h. data providing either K_{d-L} or K_{d-AL} . T_c values are also almost identical (Table 2). For soils P3 and P4, development of dissolved P (K_{d-AL}) looks very much like that of soils P1 and P2 (figure 6) as the decrease develops to approximately 1.5 cm distance. Hence, higher K_d -values resulting from the AL-extractions, forced P-fluxes to affect deeper soils (between 1.5 to 2.0 cm distance), even in situations where C_0 is higher, as in soils P3 and P4. Estimated T_c values are almost the same for P3 to P4 as for P2 and are much higher than when K_{d-L} was provided.

5 Discussion

5.1 Estimations of K_d and DIFS-model outputs

A strategy for predicting solid solution P partitioning is of great importance for understanding the impact of soil P fluxes with different P concentrations respond to labile soil P uptake. We conducted DIFS modeling in parameter estimation mode, meaning the parameter optimized by the model was T_c . The R and K_d were experimentally estimated, where the R -value comes from the ratio between P_{DGT}

(average from 6-24 h. exposure time) and P_{CO} . The choice of P_{CO} estimation might affect model outputs. However, here we see that methods for determining the distribution coefficient K_d for P in soil truly affect later geochemical dynamics interpretation. Different strategies for obtaining sensible distribution coefficients for metals in soil have been thoroughly reviewed by Degryse et al., (2009a). If for instance, the fraction of adsorbed metals are estimated by extracting soil in strong to very strong reacting agents (e.g., concentrated acids), other geochemical parameters controlling metal solubility, such as pH, might be ignored (Degryse et al., 2009a). Hence, such distribution coefficients will be of little biological relevance. Our results shows that choosing an adsorption approach (coined K_{d-L}), which affects soil P less than the equilibrium extraction approach (coined K_{d-AL}), changes the model output. Equilibrium extraction with ammonium lactate is not as strong an agent as concentrated acid, but it affects the geochemistry of soil P directly by exchange reactions (Egner et al., 1960; Otabbong et al., 2004), just as plants exert geochemical changes in the rhizosphere (Aerts and Chapin, 2000; Almås et al., 2014; Hinsinger, 2001; Schachtman et al., 1998). The DIFS model provides predictions of response time (T_c) and fluxes, and the combination of R and K_d impacts estimations of dissolved P concentrations as a function of distance from the DGT surface (figure 6). Although K_{D-L} was 4-6 times lower than K_{d-AL} (Table 2) in soils P1 and P2, the T_c was negligibly different, probably because the differences in K_d were not very large, even if R was reduced by approximately 1/10 from P1 to P2. When K_{d-L} lowered by 9-10 times (as in soils P3 and P4), the K_{d-L} approach provided a relatively larger fraction of quickly reactive P in soil solution, resulting in a substantial reduction in T_c . This means the soil P stores are interpreted as labile with little diminution at the DGT interface. This is observed as small T_{c-L} and higher fluxes in P3 and P4 soils (figure 6c). Because $R = P_{DGT}/P_{CO}$ is unchanged at 0.04, the use of K_{d-AL} for soils P3 and P4 resulted in high T_c values to compensate for the stronger partitioning of adsorbed P and slightly lower flux (figure 6d). Hence, the decrease at the device interface is stronger (figure 6). Letho et al. (2006) conducted a similar but theoretical study on the DGT and DIFS prediction on solution metal phases, among other model tests, as affected by K_d and T_c . The T_c and K_d were manipulated (simulation mode), and effect of changing T_c was strong only when K_d was high. In other words, when K_d was high, T_c shifts from low to high reduced the equilibrium solution concentration at the DGT interface stronger than when K_d was low. This agrees with our study, where high K_d and high T_c are

followed by a stronger decrease at the uptake surface. According to Menezes-Blackburn et al. (2016), T_c is very sensitive to variations in R ; therefore, absolute values should be handled pragmatically.

The interpretation of available P using an extracting agent, such as the ammonium lactate (P_{AL}), for the K_d estimation takes the “buffering-factor” into consideration better than through an adsorption isotherm approach. The latter conceals the fact that our soil was initially loaded with different amounts of various reacting soil P, which can buffer the soil solution P. This mechanism is also addressed by Degryse et al., (2009a). From figure 1, it can be seen that the P1 soil adsorbs P much faster and to a larger extent than the P2-P4 soils, but the estimated K_{d-L} (table 2) does not take into account that the supply of available P is the other way around. Soil P4 supplies total DGT with much more P than soil P3 to P1 (figure 3b). Moreover, we know that plants can extract its P from reservoirs other than what is immediately available in pore water (Hinsinger, 2001; Johnston et al., 2014). Therefore, comparing DIFS modeling provides a scenario, at least in the high loaded P soil, for the risk of ignoring the chain of geochemical reactions responding to a shift in the equilibrium P concentration in soil solution. In light of such knowledge, the use of an adsorption approach when estimating a K_{d-L} , may lead to an overestimation of soil solution P reservoir (figure 6). This difference is less visible as total soil P is low to very low.

5.2 Kinetically controlled partitioning of P in soil

The use of DGT in partitioning P between kinetically controlled fractions in soil enables an interpretation of available and slowly available P stores, without the pitfalls often associated with using sequential extractions, SE (Bermond, 1992; Young et al., 2005). The application of DGT reduces problems related to re-adsorption and dissolution of complexing ligands to a minimum, if at all. The method is non-destructive and the approach allows soil investigations without adding reactive agents in an unrealistic solid:solution ratio. The only required pretreatment is humidification to saturation, a frequent moisture soil status in boreal soils. Although the method does not provide insight into specific

binding surfaces, DGTs can be applied in a time series to provide valuable observations on fluxes (Zhang and Davison, 2015) and functional lability of P. In this investigation, we have shown how DGT-induced P fluxes relate to long-term applications of differing P amounts to soils. The kinetically controlled partitioning of labile P (figure 4), shows the dependence of a “soil factor”, which for modeling requires making decisions (figure 6). Whatever method used to quantify P kinetics, the obvious finding is that soils loaded with high P amounts, have stored up P in increasing amounts of slowly reacting fractions. Here, the slowly available P was made available to the DGT as a response to the initial uptake of quickly available P. During a growth season, with a near steady P uptake in plants during elongation, more and more P will be liberated from solid soil to soil solution. The DGT is only a passive sampler, and the total P mass available to the DGT must be available to plants as well. In other words, DGT recovery of labile P likely reflects rates of daily or weekly P uptake by plants. According to Hinsinger (2001) a grass plant would require from 1-5 μM P at the root surface. If we calculate the equilibrium P concentrations for within the first 24 hours, since P fluxes are highest the first 24 hours before leveling out (figure 3d), P_{DGT} range from 0.5-1.8 μM in P1 to 4.3-9.1 μM in P4. Hence soil P1 seems not to provide sufficient labile P. Although the concentration of labile P at a root- and a DGT surface is not in equilibrium as long as there is an offtake by these, the DIFS calculated fluxes indicates smaller changes after the first disruption (up to 24 h), and hence soils P2-P4 seems to provide solution concentrations in the range required for grasses. In addition to these factors, the rhizosphere does affect different plants’ ability to acquire its P (Hinsinger, 2001; Hinsinger et al., 2011). Plants can impose a larger concentration gradient (equal to modeled developments displayed in figures 5 and 6) by root exudate excretion, etc., imposing a higher net flux towards the roots (Almås et al., 2014; Dakora and Phillips, 2002; Schachtman et al., 1998). This effect will “mine” P from slower reacting fractions. Indications of such mechanisms can be indirectly measured by investigating the relative recovery of P by plants over P added through fertilizers (U_p/U_F*100) (Johnston et al., 2014). A so-called balanced fertilization would end up in a rate close to 100 (%), whereas higher (>100) or lower (<100) uptake than applied, would be unbalanced. In such a context combined information on P distribution between soil solution and solid soil (K_d) with P partitioning between quickly and slowly available soil stores will provide great value for assessing the potential for reducing mineral P use. P stores can be measured by

various extracting agents, but most fail in providing information on how P fluxes towards a sink depend on the current geochemistry of a soil in the field and root activity of a growing plant. Our trials have shown the DGT and DIFS models can be used to investigate the partitioning of P in soils and their impacts on fluxes of P in time and space in a soil investigated in near-field conditions.

The DGT-DIFS data presented here support our hypothesis in that P exhausted soils is quickly depleted and provided slower rates of P supply to the DGT. The DGT-results confirmed that the replenishment of P as a response to offtake, increased by P loads. Moreover, the input parameters in the DIFS model are based on assumptions and estimations requiring validation, and here we showed the impact on K_d and how it is determined on the model outputs. The use of DIFS for modelling the P dynamics in time and space can provide valuable knowledge, particularly if it is tested at different soil chemical and physical regimes, ideally in the presence of plants.

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7 References

- Aerts, R., Chapin, F.S., 2000. The mineral nutrition of wild plants revisited: A re-evaluation of processes and patterns. In: A.H. Fitter, D.G. Raffaelli (Eds.), *Advances in Ecological Research*. *Advances in Ecological Research*, pp. 1-67.
- Almås, Å.R., Afanou, A.K., Krogstad, T., 2014. Impact of Lignosulfonate on Solution Chemistry and Phospholipid Fatty Acid Composition in Soils. *Pedosphere* 24(3), 308-321.
- Bermond, A.P., 1992. Thermodynamics applied to the study of the limits of sequential extraction procedures used for the speciation of trace-elements in sediments and soils. *Environ. Technol.* 13(12), 1175-1179.
- Boudreau, B.P., 1996. The diffusive tortuosity of fine-grained unlithified sediments. *Geochim. Cosmochim. Acta* 60(16), 3139-3142.
- Dakora, F.D., Phillips, D.A., 2002. Root exudates as mediators of mineral acquisition in low-nutrient environments. *Plant Soil* 245(1), 35-47.
- Davison, W., Zhang, H., 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature* 367, 546-548.
- Degryse, F., Smolders, E., Parker, D.R., 2009a. Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications - a review. *Eur. J. Soil Sci.* 60(4), 590-612.
- Degryse, F., Smolders, E., Zhang, H., Davison, W., 2009b. Predicting availability of mineral elements to plants with the DGT technique: a review of experimental data and interpretation by modelling. *Environmental Chemistry* 6(3), 198-218.
- Egner, H., Riehm, H., Domingo, W.R., 1960. Untersuchungen über die chemische Boden-analyse als Grundlage für den Beurteilung des Nährstoffzustandes der Böden. II. Chemische Extraktionsmethoden zur Phosphor und Kaliumbestimmung. *Kungl. Lantbrukshögskolans annaler* 26.

- Ernstberger, H., Davison, W., Zhang, H., Tye, A., Young, S., 2002. Measurement and dynamic modeling of trace metal mobilization in soils using DGT and DIFS. *Environmental Science & Technology* 36(3), 349-354.
- Essington, M.E., 2004. *Soil and water chemistry: an integrative approach*. 1 ed. CRC Press LLC, Boca Raton, Florida.
- EU, 2000. The EU Water Framework Directive - integrated river basin management for Europe. In: E. Union (Ed.). OJ L 327, Brussels.
- FAO, 2009. *Global agriculture owars 2050, How to feed the world 2050*. High level expert forum. FAO, Rome.
- Harper, M.P., Davison, W., Tych, W., 2000. DIFS - a modelling and simulation tool for DGT induced trace metal remobilisation in sediments and soils. *Environ.Modell.& Softw.* 15(1), 55-66.
- Hinsinger, P., 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. *Plant Soil* 237(2), 173-195.
- Hinsinger, P., Brauman, A., Devau, N., Gerard, F., Jourdan, C., Laclau, J.P., Le Cadre, E., Jaillard, B., Plassard, C., 2011. Acquisition of phosphorus and other poorly mobile nutrients by roots. Where do plant nutrition models fail? *Plant Soil* 348(1-2), 29-61.
- Hylander, L.D., Svensson, H.I., Siman, G., 1996. Different methods for determination of plant available soil phosphorus. *Communications in Soil Science and Plant Analysis* 27(5-8), 1501-1512.
- Johnston, A.E., Poulton, P.R., Fixen, P.E., Curtin, D., 2014. *Phosphorus: Its Efficient Use in Agriculture*. In: D.L. Spark (Ed.), *Advances in Agronomy*, Vol 123. *Advances in Agronomy*. Elsevier Academic Press Inc, San Diego, pp. 177-228.
- Krogstad, T., Lovstad, O., 1989. Erosion, phosphorus and phytoplankton response in rivers of South-Eastern Norway. *Hydrobiologia* 183(1), 33-41.
- Lal, R., 2013. Food security in a changing climate. *Ecohydrology & Hydrobiology* 13, 8.

Lehto, N.J., Davison, W., Zhang, H., Tych, W., 2006. Theoretical comparison of how soil processes affect uptake of metals by diffusive gradients in thinfilms and plants. *Journal of Environmental Quality* 35(5), 1903-1913.

Menezes-Blackburn, D., Zhang, H., Stutter, M., Giles, C.D., Darch, T., George, T.S., Shand, C., Lumsdon, D., Blackwell, M., Wearing, C., Cooper, P., Wendler, R., Brown, L., Haygarth, P.M., 2016. A Holistic Approach to Understanding the Desorption of Phosphorus in Soils. *Environmental Science & Technology* 50(7), 3371-3381.

Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta* 26, 31-36.

NIST, 2004. National Institute of Standards & Technology, Certificate of Analysis. Standard Reference Material 1643e. Trace Elements in Waters, Gaithersburg, MD 20899, USA.

Olsen, S., Cole, C., Watanbe, F., Dean, L., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. United states department of agriculture, pp. 403-429.

Otabbong, E., Leinweber, P., Schlichting, A., Meissner, R., Shenker, M., Litaor, I., Sapek, A., Robinson, S., Nidermeier, A., Hacin, H., Otabbong, J., 2004. Comparison of ammonium lactate, sodium bicarbonate and double calcium lactate methods for extraction of phosphorus from wetland peat soils. *Acta Agric. Scand. Sect. B-Soil Plant Sci.* 54(1), 9-13.

Pierzynski, G.M., Logan, T.J., 1993. Crop, soil, and management effects on phosphorus soil test levels. *J. Prod. Agric.* 6(4), 513-520.

SAS-Institute, 2016. JMP, Statistical Discovery Software, v 13.0.0. SAS Institute, Inc., Cary, NC, USA.

Schachtman, D.P., Reid, R.J., Ayling, S.M., 1998. Phosphorus uptake by plants: From soil to cell. *Plant Physiol.* 116(2), 447-453.

Schindler, D.W., Hecky, R.E., Findlay, D.L., Stainton, M.P., Parker, B.R., Paterson, M.J., Beaty, K.G., Lyng, M., Kasian, S.E.M., 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: Results of a 37-year whole-ecosystem experiment. *Proc. Natl. Acad. Sci. U. S. A.* 105(32), 11254-11258.

- Sogn, T.A., Eich-Greatorex, S., Royset, O., Ogaard, A.F., Almås, Å.R., 2008. Use of diffusive gradients in thin films to predict potentially bioavailable selenium in soil. *Communications in Soil Science and Plant Analysis* 39(3-4), 587-602.
- Stutter, M.I., Shand, C.A., George, T.S., Blackwell, M.S.A., Bol, R., MacKay, R.L., Richardson, A.E., Condon, L.M., Turner, B.L., Haygarth, P.M., 2012. Recovering Phosphorus from Soil: A Root Solution? *Environmental Science & Technology* 46(4), 1977-1978.
- Systat, 2014. SigmaPlot, Systat Software Inc, v 13.0. Systat Software Inc, San Jose, CA , USA.
- Ulen, B., Aronsson, H., Bechmann, M., Krogstad, T., Oygarden, L., Stenberg, M., 2010. Soil tillage methods to control phosphorus loss and potential side-effects: a Scandinavian review. *Soil Use Manage.* 26(2), 94-107.
- Wang, Y.P., Law, R.M., Pak, B., 2010. A global model of carbon, nitrogen and phosphorus cycles for the terrestrial biosphere. *Biogeosciences* 7(7), 2261-2282.
- Young, S.D., Zhang, H., Tye, A.M., Maxted, A., Thums, C., Thornton, I., 2005. Characterizing the availability of metals in contaminated soils. I. The solid phase: sequential extraction and isotopic dilution. *Soil Use Manage.* 21, 450-458.
- Zapata, F.R., R.N., 2004. Use of phosphate rocks for sustainable agriculture. *Fertilizers and plant nutrition bulletin* 13. FAO: Food and agricultural organization of the united nations, Rome.
- Zhang, C.S., Ding, S.M., Xu, D., Tang, Y., Wong, M.H., 2014. Bioavailability assessment of phosphorus and metals in soils and sediments: a review of diffusive gradients in thin films (DGT). *Environ. Monit. Assess.* 186(11), 7367-7378.
- Zhang, H., Davison, W., 2015. Use of diffusive gradients in thin-films for studies of chemical speciation and bioavailability. *Environmental Chemistry* 12(2), 85-101.

Table 1. Soil properties as average (n= 32) for the whole trial filed are listed together with the P_{AL} values (n=2) for each specific plot sampled for this investigation.

Measurement: whole filed	Units	Value
Total C		2.9
Total N		0.25
Clay	%	26
Silt		38
Sand		36
pH		5.7
Fe-Oxalate		5.99
Al-Oxalate		2.46
Fe-Total	g kg ⁻¹	24.5
Al-Total		34.8
Measurement: investigated plots		
P _{AL} , P1		27.0
P _{AL} , P2		80.5
P _{AL} , P3	mg kg ⁻¹	104.5
P _{AL} , P4		160.0

Table 2. The table lists the input parameters characterizing each of the four soils (n=2) investigated in our DIFS exercises. The estimated T_c values are shown as output.

Parameter (unit)	P1	P2	P3	P4
Input				
R (P_{DGT}/P_{CO})	0.7	0.04	0.04	0.04
K_{d-L} ($L\ kg^{-1}$)	291	124	71	56
K_{d-AL} ($L\ kg^{-1}$)	1193	751	656	595
P_c ($g\ cm^{-3}$) *			2.8	
(Tortuosity) **			2.44	
D_0 ($cm^2\ s^{-1}$)			5.57×10^{-6}	
D_s ($cm^2\ s^{-1}$)			2.29×10^{-6}	
Por_d			0.95	
Por_s *			0.49	
C_0 ($mg\ L^{-1}$) ***	0.45	2.14	3.92	5.32
D time (h.)			120	
$\Sigma\Delta g$			0.095	
times		0.05, 0.1, 0.2, 0.4, 0.6, 1		
Output & ratios				
T_{c-L} (s)	28220	87810	0.01	0.0014
T_{c-AL} (s)	24760	88540	88530	88480
K_{d-AL}/K_{d-L}	4	6	9	10

* These parameters are values measured in soils ** Estimated by equation 5 *** C_0 -values are provided as $mmol\ l^{-1}$ for DIFS modeling.

Table 3. Langmuir sorption isotherm parameters as outlined by equation 4. Estimated K_d values are seen in table 3.

	Units	P1	P2	P3	P4
K_L		1.18	0.57	0.27	0.23
b	mg kg ⁻¹	245	201	264	248

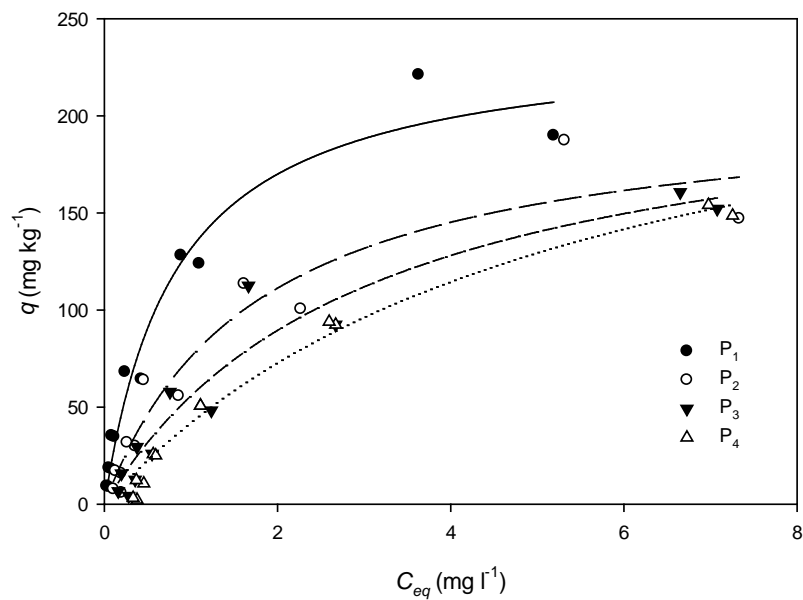


Figure 1

The adsorption of P to soil as affected by 4 long term application rates of P (P1=0, P2=16, P3=32 and P4=48 kg P haa⁻¹ yr.⁻¹) from an equilibrium solution (2.5 mM CaCl₂) containing increasing concentrations of P.

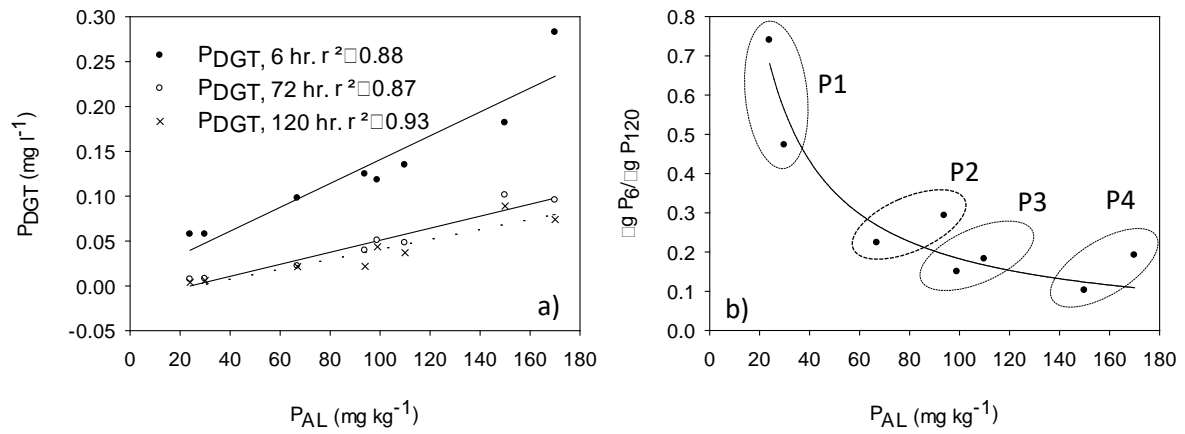


Figure 2. The figures shows the relationships between P_{AL} in soil with a) P_{DGT} and b) the mass ratio of P ($\mu\text{g P}$) accumulated in the DGT after 6 and 120 hours deployment time.

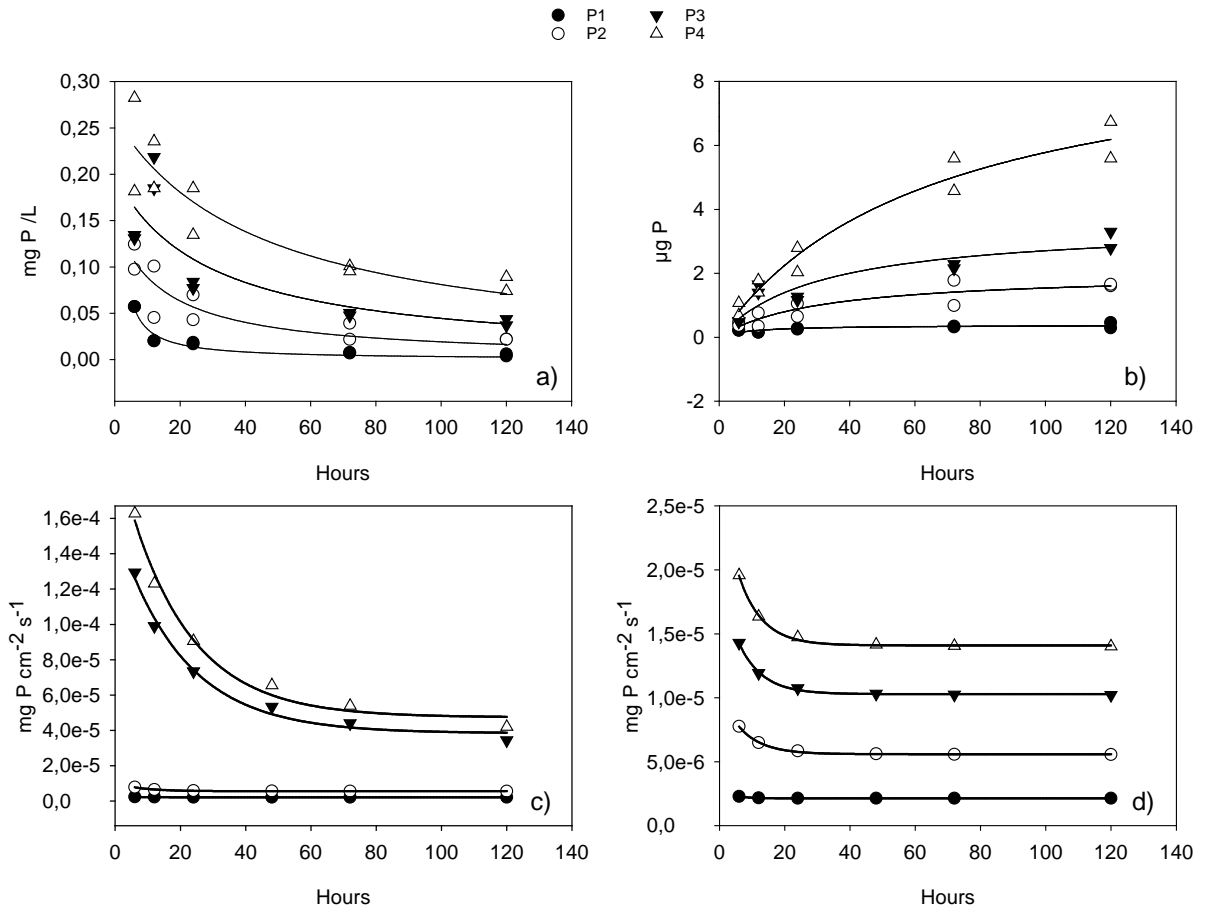


Figure 3. The figures show the concentrations of a) P_{DGT} and b) mass of P in DGTs exposed to the 4 different P-treated soil as affected by increasing contact between DGT and soil. The fluxes of P derived from c) K_{d-L} and d) K_{d-AL} as affected by P treatments and increasing deployment time between DGT and soils are also shown.

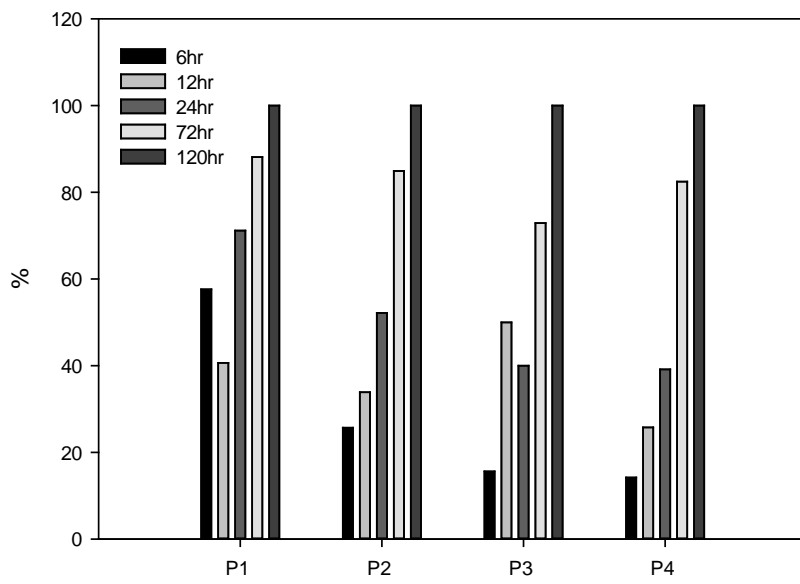


Figure 4. The columns show the relative distribution of P between the DGT's exposed to soil from 6 to 120 hours as affected by the rates of P applications (P1=0, P2=16, P3=32 and P4=48 kg P haa⁻¹ yr.⁻¹)

1)

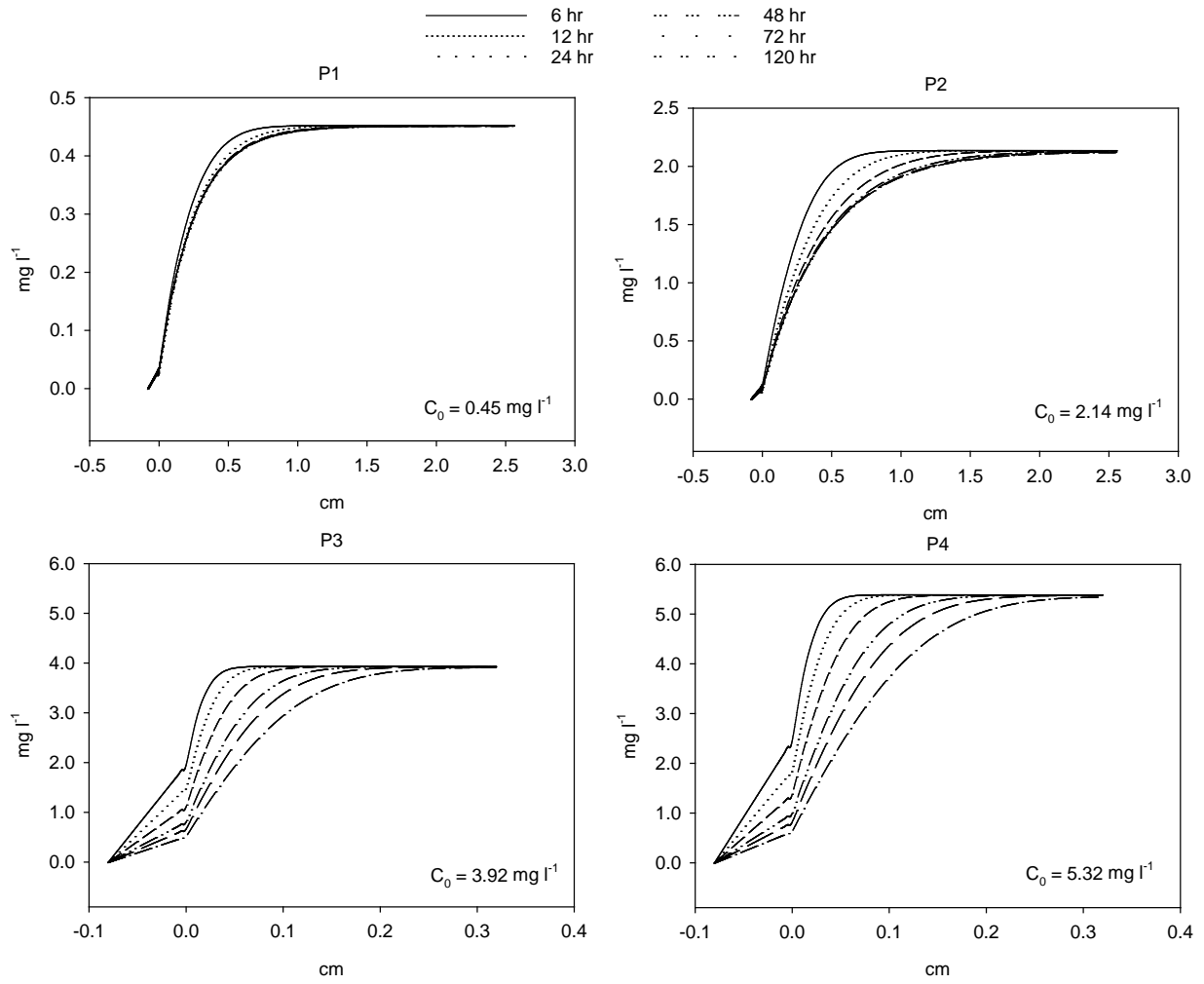


Figure 5. The DIFS estimated development of P concentrations at increasing distance from the DGT surface as affected by P treatments (P1=0, P2=16, P3=32 and P4=48 kg P haa⁻¹ yr.⁻¹), while deployment time increases from 6 to 120 hours. The K_{d-L} was used as an input parameter.

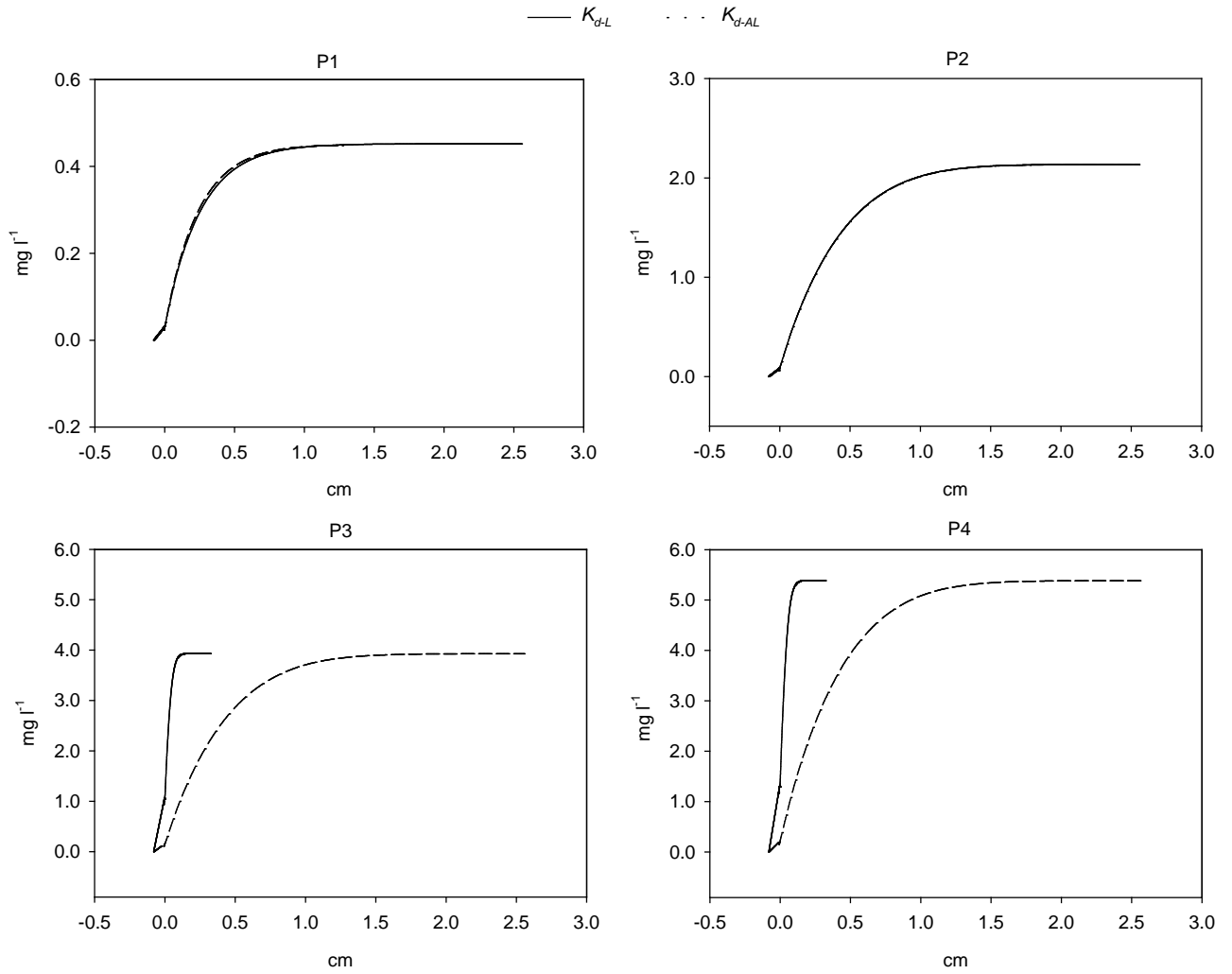


Figure 6. The graphs show the effects of changing from K_{d-L} to K_{d-AL} as input parameter on the DIFS estimated development of P concentrations at increasing distance from the DGT surface as affected by P treatments (P1=0, P2=16, P3=32 and P4=48 kg P haa⁻¹ yr⁻¹) at 24 hours deployment time only.



For Graphical Abstract Only