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Wheat yield prediction by zero sink and equilibrium-type soil phosphorus tests

Running title: WHEAT YIELD PREDICTION BY A ZERO SINK P TEST (DGT)

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ABSTRACT

Diffusive gradients in thinfilms (DGT) have been shown to outperform other phosphorus (P) tests in soils with strong P sorption while this is not confirmed for moderately weathered European soils. We tested the performance of DGT to predict wheat grain yield in Swedish long-term fertility experiments compared to standard intensity (water extraction, P-H_2O), and quantity (ammonium-lactate-extractable P, P-AL) tests. A Mitscherlich-type model was used to fit wheat yield response to P application rates (0, 15, 30 or 35, and 45 kg P ha^{-1} y^{-1}) in each individual trial replicate to estimate maximum yield. For trials with clear plateau-type yield response and model fits of $R^2 > 0.75$ relative yields (RY) were calculated for each P treatment and plotted against the soil P test results ($N = 143$). The goodness of Mitscherlich-type fits decreased in the sequence P-DGT ($R^2 = 0.35$) > P-H_2O ($R^2 = 0.18$) > P-AL ($R^2 = 0.13$). When excluding soils with a P-AL:P-DGT ratio > 0.1, *i.e.*, high distribution coefficients (Kd), the goodness of fits (R^2) considerably improved to 0.55 for P-AL, 0.46 for P-H_2O, and 0.65 for P-DGT ($N = 61$). At 95% of maximum yield the upper limit of P deficiency for P-DGT is 44.8 (low Kd soils) and 61.9 µg L^{-1} (all soils), respectively, falling within the range reported for other European and Australian soils (6.0--142 µg L^{-1}). We show that in the investigated Swedish soils DGT performs better than the quantity and intensity tests, which is attributed to its ability to capture P diffusion and resupply from soil solid phase, similar to plant roots in the rhizosphere.

Key Words: ammonium lactate extractable phosphorus, diffusive gradients in thin films (DGT), long-term field experiment

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INTRODUCTION

Phosphorus (P) is one of the essential macronutrients in crop production (Ma *et al.*, 2009). Globally, low P status of soil is considered as a main limiting factors of productivity, resulting in yield gaps relative to the yield potential if not supplied in appropriate amounts (Foley *et al.*, 2011). On the other hand, long-term input of P at high fertilization rates has been related to environmental problems including eutrophication of waterways (Carpenter, 2008), inefficient agronomic use, and unsustainable mining of limited resources of rock phosphate (Jedelhauser and Binder, 2015).

Depending on natural soil quality and fertilizer input rates, large variation in soil P status is observed, with 29% of the global cropland displaying P deficits while 71% show luxury P levels (MacDonald *et al.* 2011). Among other factors, accurate assessment of P availability in soil is considered as prerequisite for improving P efficiency and reducing environmentally detrimental P losses from soil (Hamilton *et al.*, 2017; Jordan-Meille *et al.*, 2012).

Generally, P is strongly adsorbed to the soil solid phase, resulting in small P concentrations in soil solution. Consequently, P transport rates in soil and availability to plants is limited while the plant demands for this macronutrient and related uptake rates are high, commonly leading to P depletion in the rhizosphere (Degryse *et al.*, 2009). Depletion and the formation of steep P concentration gradients in the rhizosphere trigger resupply (desorption and dissolution) from the solid phase, and diffusion of P towards the root surface (Barber, 1995; Dunham and Nye, 1976; Fox, 1981; Hinsinger *et al.*, 1011; Menezes-Blackburn *et al.*, 2016; Peaslee and Phillips, 1981). Therefore, P uptake is generally considered to be controlled by uptake-driven diffusion and desorption rather than mass flow (Degryse *et al.*, 2009).

The concept of nutrient availability in soil can be expressed in terms of (1) capacity, (2) quantity, (3) intensity, and (4) (rate of) resupply and buffering (Fox 1981; Peaslee and Phillips 1981). The potential of a given soil to store a nutrient in plant-available (labile) form is termed capacity, the realization of this potential is referred to as quantity, typically measured by equilibrium-based soil extraction. The nutrient concentration in soil solution is generally considered as a measure of intensity (Fox 1981).

A multitude of soil P tests has been employed to assess the P availability in soil, and to provide indices for P deficiency and fertilizer requirements (MacDonald *et al.*, 2011, Neyroud and Lischer, 2003). The majority of P availability indices can be categorized in quantity and intensity tests, and are based on equilibrium-type soil extraction (Neyroud and Lischer, 2003, Wuenscher *et al.*, 2015; Zbíral and Nemec, 2002). Among the most popular and widely used P quantity tests, Olsen (Olsen *et al.*, 1954), Colwell (Colwell and Esdaile, 1968), Mehlich-3 (Mehlich, 1984), Bray-1 (Bray and Kurtz, 1945), ammonium lactate (AL; Egner *et al.*, 1960), and calcium-acetate-lactate (CAL; Schüller, 1969) should be named. Commonly used intensity tests include 0.01 M $CaCl_2$ (Houba *et al.*, 2000) and water extraction (Jarosch *et al.*, 2018). All these methods are based on chemical extraction for a period long enough to attain a quasi-equilibrium between the solid and liquid phase. During extraction, desorption and dissolution reactions occur against a declining concentration gradient. Mechanistically, this opposes the P uptake by plant roots that act like a zero sink, creating increasingly steep concentration gradients in the rhizosphere (Barber, 1995). Therefore, Amer *et al.* (1955) introduced the first zero-sink procedure using resin beads to better simulate P uptake conditions, followed by modifications (Sibessen, 1967) and the development of similar methods (Chardon *et al.*, 1996; Freese et al.,1995;

Schoenau and Huang, 1991; van der Zee *et al.*, 1987). Alternatively consecutive water extractions using large solution: solid ratios have been used (Jarosch *et al.*, 2018). All these zero sink procedures involve shaking of the P-binding material in a soil suspension and the need for subsequent separation.

A simple yet more sophisticated approach, initially developed for measuring metal fluxes in water and sediments (Davison and Zhang, 1994), is using geometrically defined devices consisting of a thin hydrogel layer containing finely dispersed sorbent material acting as zero sink, overlain by a diffusive gel that does not interact with the analyte of interest. In typical routine applications, these so-called diffusive gradients in thin films (DGT) are applied to soils or sediments with a moisture content that is brought close to saturation prior to deployment (Zhang *et al.*, 1998). The combination of a zero sink with a diffusive layer mechanistically resembles the plant root and its associated P depletion zone. Degryse *et al.* (2009) explored the theoretical similarities of nutrient uptake in plants and DGT fluxes, and concluded that in diffusion-limited conditions DGT fluxes (or concentration) are expected to correlate strongly with plant uptake. Moreover, DGT fluxes may still correlate well with plant uptake if diffusion is not the limiting factor, given that the uptake is not saturated.

Although the mass of soil from which P is extracted by DGT is variable, depending on soil properties and moisture content, assuming an average sampling depth of 2 mm for European soils, Nawara *et al.* (2017) calculated that standard DGT (24 hours deployment) would extract similar amounts as obtained by 0.01 M $CaCl_2$. Based on this, and a strong correlation of P-DGT with 0.01 M $CaCl_2$ they refer to DGT as mere intensity test (Nawara *et al.*, 2017). This view is opposed by the theoretical foundation of DGT (Davison and Zhang, 1994; Degryse *et al.*, 2009; Zhang *et al.*, 1998), and experimental and modelling evidence indicating that after only one hour deployment DGT measurements tend to be a function of the P resupply capacity of the soil solid phase (Menezes-Blackburn *et al.*, 2016). The same authors conclude that, in contrast to equilibrium-type P extraction methods, DGT captures differences in P diffusion and resupply from the solid phase. Further evidence for considerable contribution of resupply to standard DGT measurements is provided by Moody *et al.* (2013) for Australian soils, and Almas *et al.* (2017) who showed that DGT also captured to some extent slowly-desorbing P fractions accumulated during long-term fertilization.

Apart from its intriguing mechanistic similarity to diffusion-limited nutrient uptake in plants, DGT measurements appear to be less affected by soil properties such as carbonate content, pH and ion concentrations than batch extraction (Mason *et al.*, 2008), and could be sent to laboratories after relatively simple on-site deployment instead of shipping soils. This is of utmost importance if sanitary regulations and/or shipping costs prohibit or limit the transport of soil samples between the sampling locations and laboratories. However, like any other soil test, DGT measurements do not account for root activities such as exudation of protons and organic acids, and related changes in P availability.

Yet, limited information on the performance of DGT as predictor of soil P availability to crops is available. Most calibration studies were conducted on highly weathered soils from tropical and subtropical regions (Australia, Africa, South-East Asia) known for their high P-fixation potential (Dubus and Becquer, 2001). Based on field and pot experiments, it was found that P-DGT was generally superior to various equilibrium-type quantity (Colwell, Olsen, Mehlich-3, Bray-1) and intensity (0.01 M $CaCl_2$) tests in explaining yields of wheat (Mason *et al.*, 2010; Speirs *et al.*, 2013), maize (Six *et al.*, 2012; Six *et al.*, 2013; Six *et al.*, 2014), tomato (Menzies *et al.*, 2005), but not of rice (Six *et al.*, 2013) and pastures (Burkitt *et al.*, 2016).

Calibration studies for less developed European soils formed under temperate climate are still scarce. While some greenhouse studies confirm the expected better performance of DGT for predicting yields and P uptake in spring barley (Tandy *et al.*, 2011) and rye (Duboc *et al.*, 2017) as compared to equilibrium-type P tests, others report diverging results between field and pot experiments (Mundus *et al.* (2017). The most comprehensive study was conducted by Nawara *et al.*

(2017), who compared the prediction of RY response of several crops (wheat, maize, barley, sugar beet, potato, flax) using archived samples from long-term experiments in Northern and Western Europe (Belgium, Germany, France, U.K., Sweden) by various soils tests. Their calibrations integrating all sites and crops into one equation showed better predictive power of the quantity tests Olsen (49%) and P-AL (46%) as compared to P-DGT (37%) and the intensity test (0.01 M $CaCl_2$; 31%). This was attributed to the less pronounced fixation of P in moderately weathered European (temperate zone) soils and the related greater importance of P quantity for P supply to crops (Nawara *et al*., 2017).

In summary, on highly weathered soils DGT appears to perform generally better than equilibrium-type soil P tests in predicting RY of wheat in long-term field experiments, and that of maize in greenhouse pot studies. A superior performance of DGT for predicting yield and P uptake of various crops could not be confirmed in European field experiments.

Given the mechanistic advantages but differential performance of DGT in soils with low and high P fixation potential, and the dependence on crop type and experimental setting, further studies are required to allow for more consistent evaluation of DGT based on broader evidence. Moreover, the hypothesis that P availability in less developed European soils is controlled primarily by P quantity (Nawara *et al*., 2017) is challenged by consistent evidence for diffusion-controlled P supply in P-depleted rhizospheres (Santner *et al*., 2012; Kreuzeder *et al*., 2018). Further, the majority of published work on P pools captured by DGT supports the theoretical concept of DGT (Davison and Zhang, 1994; Degryse *et al*., 2009; Zhang *et al*., 1998) as a measure of P diffusion and resupply from soil solid phase, including highly fertilized soils (Almas *et al*., 2018; Jarosch *et al*., 2018; Menezes-Blackburn *et al*., 2016; Moody *et al*., 2013). In line with this, we hypothesize that DGT should predict crop yield in most situations, including less developed soils such as in Europe, better than equilibrium-based quantity or intensity tests.

To test this hypothesis, we report on comparative calibration of P-DGT, P-H_2O and P-AL in low to moderately weathered soils using archived soils and wheat yield data from Swedish long-term fertilization experiments. Based on the information discussed above, we hypothesize that DGT should perform better than the equilibrium-based quantity (P-AL) and intensity (P-H_2O) tests. We further make attempts to derive upper limits of P deficiency ("critical values") for both soil tests.

MATERIALS AND METHODS

Experimental sites and soils

We obtained archived soil samples and grain yield data of wheat (*Triticum aestivum* L.) from six long-term experiments in southern and central Sweden. These experiments have been documented in detail in previous publications (Carlgren and Mattson, 2001; Kirchmann, 1991; Kirchmann and Erikkson, 1993; Kirchmann *et al*., 1999). The sites differ in climate conditions, with mean annual temperatures ranging between 7.1–8.1 °C at the southern sites, and 5.0–5.5 °C at the central sites. Annual precipitation varies between 590--777 mm at the southern sites, and 528--635 mm at the central sites. Soil properties of the sites are compiled in Table I.

TABLE I

Soil characteristics for the experimental sites in southern and central Sweden

Site	Soil group b)	Layer	OC a)	$CaCO_3$ equivalent b)	Clay a)	Clay b)	Silt b)	Sand b)	Textural class (FAO) c)	CEC b)	pH (H_2O) a)	Alo d)	Feo d)	P-total a)	P-AL a)	P-HCl a)	K-AL a)	K-HCl a)
			g kg^{-1}							cmol$_c$ kg^{-1}		mg kg^{-1}						
Fjärdingslöv	Haplic Phaeozem	0--20	14	8.4	170	150	770	80	Silt loam	12.1	7.5	809	2230	6900	33	260	42	620
		20--50			170						7.7				25	250	36	600
		50--100			130						8.0				49	490	52	850
Orup	Haplic Phaeozem	0--20	24	0.0	130	230	250	520	Sandy clay loam	15.0	6.2	1570	3690	1900	24	530	38	470
		20--50			150						6.6				16	460	44	710
		50--100			120						7,.1				109	640	43	810
Örja	Eutric Cambisol	0--20	11	0.6	150	370	350	280	Clay loam	10.6	7.2	782	2740	1600	59	360	80	1150
		20--50			190						7.3				29	270	59	1090
		50--100			320						7.7				21	310	110	2200
Ekebo	Eutric Cambisol	0--20	31	0.0	140	190	360	450	Loam	8.70	6.8	1570	2800	5700	67	370	54	560
		20--50			150						5.4				7.0	190	36	680
		50--100			170						5.7				5.0	280	50	950
Kungsängen	Gleyic Cambisol	0--20	21	0.0	560	570	260	170	Clay	24.5	7.1	1400	8430		37	560	140	4400
Fors	Calcaric Phaeozem	0--20	22	35	180	130	420	450	Loam	14.0	7.7	863	1450		106	730	90	2520

a) Initial soil characteristics (Karlgren and Mattson, 2001).

b) Taken from Kirchmann (1999), Kirchmann and Eriksson (1993), Kirchmann *et al*. (1999).

c) Classification based on sand, silt and clay contents provided by Kirchmann (1999), Kirchmann and Eriksson (1993), Kirchmann *et al*. (1999).

d) Ammonium oxalate-extractable Al and Fe, taken from Börling *et al*. (2004) and Gustafsson *et al*. (2012).

To minimize the effect of adverse growth conditions as a limiting factor we selected soil samples at each site only from years with high yields and wheat as main crop. For the same reason, only P treatments at the highest nitrogen fertilization rate (150 and 125 kg N ha^{-1} y^{-1} at the southern and central sites, respectively; Carlgren and Mattson, 2001) of each site were included in our study. This resulted in samples from seven years (1967, 1979, 1991, 1999, 2003, 2011, 2015) selected at each of the four southern, and three years (1967, 1979, 1999) at each of the two central sites. Each site x year combination consists of a control and three P treatments, *i.e.*, 15 (= replacement of P removal), 35 (central sites) or 30 (southern sites), and 45 kg P ha^{-1} y^{-1}, applied as mineral fertilizer (in the form of mono superphosphate until 1991 and 1994 in the southern and central sites, respectively, thereafter as triple superphosphate; Carlgren and Mattson, 2001)

For the years 1967, 1979 and 1991 soils and yield data from two individual replicates were available while only composite samples could be obtained for the years thereafter. For the years 1999, 2011 and 2015 at the southern sites the missing replicates were replaced by plots that had received 20 t ha^{-1} of livestock manure every 4th year, as P response differed only marginally between mineral and organic fertilizer treatments. At the central sites, plots that had received 20 t manure ha^{-1} every 6th year were included only for 1999. The P input with manure had been accounted for by adjusting the mineral fertilization rate to obtain a total P input equalling that of the plots without manure application.

This approach resulted in a total number of 64 individual trial replicates with four treatments each, yielding 256 pairs of soil samples and grain yield data. As we could not obtain the replacement treatments (15 kg P ha^{-1}) for any of the two replicates at the two central sites for 1967, the final number of soil x yield data pairs equals 252. The experimental design along with the average yield data is compiled in Table II.

TABLE II

Experimental design and average measured yields (arithmetic means of two replicates of all sites at the indicated P fertilization rate)

Region	P rate	Average measured yield in the year:[c)]						
		1967	1979	1991	1999	2003	2011	2015
	kg ha^{-1} y^{-1}	kg ha^{-1} y^{-1}						
Southern sites[a)]	0	4256	3589	5430	5666	5292	4532	6723
	15	4670	4046	5368	6228	6377	5215	7285
	30	4776	4213	4867	6443	6542	5286	6862
	45	4687	3972	4909	6334	6530	5416	7392
Central sites[b)]	0	5669	4344		3541			
	15		5147		4188			
	35	6030	5114		4572			
	45	5939	4877		4577			

[a)] Sites Fjärdingslöv, Orup, Örja and Ekebo

[b)] Sites Kungsängen and Fors

[c)] From 1999 each one of the two repclicates was fertilized with mineral fertilizer and manure, respectively

Soil analysis

P-AL

Ammonium-lactate-extractable P (P-AL) of the archived soil samples had been measured by Otabbong *et al.* (2009) using ammonium lactate solution (0.1M NH_4 – lactate + 0.4 M HOAc, adjusted to pH 3.75). This method has been widely adapted in EU countries including Sweden (Otabbong *et al.*

2009). We obtained the data from the database of the Swedish long-term fertility experiment. P-AL is considered as P quantity test (Nawara *et al*., 2017).

P-DGT

Using the diffusive gradients in thin films technique (Zhang and Davison, 1994; Zhang *et al*., 1998), we determined the DGT-measured P concentrations (P-DGT), i.e., the time-averaged solute concentration at the DGT – soil interface of the experimental soils.

Diffusive gel preparation. Prior to casting, a glass mould was assembled by placing Teflon spacer (0.5 mm diffusive gels and 0.25 mm for binding gels) in between two acid washed and dried glass plates. A plastic clip was then placed in both sides and the bottom of the glass plates and spacer assembly. The diffusive gel was casted by pouring a mixture of gel solution (15% polyacrylamide and 0.3% agarose derived cross-linker), ammonium persulfate (10%) and TEMED catalyst (99% N, N, N′, N′- Tetramethylethylenediamine) following the Zhang *et al*. (1995) procedure in the mould previously prepared using a pipette. The glass plates with the gel were then placed in the oven at 45 °C. After an hour the mould bearing the gel was removed from the oven and left to cool down. When the temperature of the plates was at room temperature, the gel was collected by lifting the other side of the mould with a blade. The gel was rinsed with high-quality (HQ) water (18 MΩ cm, prepared by a Millipore Elix 3 water purification system) to detach it from the glass plate. For hydration, the collected gel was soaked for 9 hours in HQ water which was replaced every 3 hours. After hydration, the thickness of the diffusive and binding gels increased to 0.8 mm and 0.4 mm, respectively. The gels were soaked in 0.01M $NaNO_3$ and stored in the refrigerator.

Ferrihydrite gel preparation. Ferrihydrite gels were prepared following Santner *et al*. (2010). 2.7 g of $FeCl_3 \cdot 6H_2O$ (97% ACS Reagent, Sigma Aldrich) was dissolved by adding 40 ml of HQ water in a 120 ml vial. Four thin gels (0.25 mm gels) were put in the solution and the vial was filled with HQ water up to 100 ml. The gels were soaked in $FeCl_3 \cdot 6H_2O$ solution for 2 h to allow even distribution of Fe in the gel. After soaking, the gels were individually put in 100 ml 0.05 M M 2-(N-morpholino)-ethanesulfonic acid (MES) at pH 6.7 to precipitate the Fe in the gel. The gel was gently stirred with tweezers upon soaking in MES for 30 to 60 seconds for homogenous precipitation and was shaken in a plate shaker at low agitation for 30 min. After shaking, the gels were washed by soaking them in HQ water for 6 h (HQ was replaced every 2 h), subsequently stored in a container with 0.03 M $NaNO_3$ solution, and placed in a refrigerator.

Gel cutting. Both diffusive and ferrihydrite gels were spread on a plexi-glass plate moistened with HQ water. Excess water was removed by tilting the plexi-glass plate, and after cutting, the gel discs were stored in a container with 0.03 M $NaNO_3$ solution and kept in a refrigerator (4 °C).

DGT sampler assembly. Custom-made, plastic housings (Quernmore, Lancaster, U.K., www.dgtresearch.com) were used in assembling the DGT sampler. The housing material has two components, a backing cylinder and a cap with an exposure window of 1.7 cm. The samplers were assembled by placing a ferrihydrite gel (0.25 mm gels) on top of the backing plate. To avoid sticking to the diffusive gel disc, polycarbonate membrane (pore size 0.2 µm, thickness 10 µm; Nuclepore, GE Healthcare, Freiburg, GER) was placed on top of the ferricellulose nitrate filter disc (pore size 0.45 µm, thickness 130 µm; Supor, Pall GmbH, Dreieich, GER). The interlayered gels and membranes on top of the cylinder were locked-up together with the plastic cap.

Preparation of soil paste. Prior to soil paste preparation, maximum water holding capacity of the dried soil samples was determined by visual inspection according to Rhodes (1996). Soil pastes were prepared by saturating the soil samples to 85% of maximum water holding capacity. The soil samples were then allowed to incubate in a moist environment for 24 hours at 20 °C (approximately 5 g of dried soil sample was required for each sampler).

DGT deployment. A plexi-glass mould was attached on top of the DGT sampler before loading the soil paste to assure a standardized volume of soil paste in contact with the window of the sampler. After 24 hours of incubation, the soil pastes were carefully placed on top of the DGT sampler to ensure full contact with the window of the sampler. The samplers bearing the soil paste were then placed in the incubator for 24 h at 20 °C. Subsequently, the soil paste was removed and the samplers were disassembled. The ferrihydrite gel was then removed, and eluted with 5 ml 0.25 M H_2SO_4 in a plate-shaker at low agitation for at least 2 hours.

P-H_2O

Using a solution: soil ratio of 1:10 (Demaria *et al*., 2005), 2.5 g of dried soil sample was weighed in 100 ml vials. After adding 25 ml of HQ water, the samples were shaken for 14 h at 90 rpm and subsequently filtered with filter paper (Munktell 14/N, Munktell, Bärenstein, Germany), followed by syringe filtration (0.45-µm; Rotilabo ®-syringe filter, Nylon, unsterile, Carl Roth Gmbh+Co.KG) to remove the colloids from the extracted solution. The samples were then acidified with 0.25 M H_2SO_4.

Colorimetric P measurement

Colorimetry was used to measure the P concentration in the DGT eluates and water extracts (Murphy and Riley, 1962). Staining reagent was made by mixing 3 ml of 0.009 M ammonium heptamolybdate (99%, Merck Millipore), 1 ml of 0.004 M potassium antimony (III) tartrate hydrate (99.95%, Sigma Aldrich) and 10 ml HQ water. Subsequently, 0.14 ml of staining reagent, 1 ml of eluate and 0.06 ml of 0.1 M ascorbic acid (≥ 99% ACS Reagent, Sigma Aldrich) were loaded subsequently into the cuvette and were left to react for 15 to 20 min. The P concentration in the samples was then measured using a Hitachi U-2000 UV/VIS spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan) at a wavelength of 881 nm.

Model fitting, statistics and calculations

Simple linear regression was used to assess the relation between the three extraction methods. Using non-linear regression, a Mitscherlich-type model (Eq. 1) was fitted individually for each trial replicate to the measured absolute wheat grain yield data and the corresponding rate of P application to determine the maximum yield.

$$y = y0 + a\left(1 - e^{-bx}\right) \qquad \text{(Eq. 1)}$$

where y is the yield at P application rate x, $y0$ refers to the computed yield of the control, and $y0 + a$ to the calculated maximum yield (Mason *et al*. 2010), a and b are model parameters. The GRD non-linear module of the EXCEL (Version 15.33) Solver was used to solve the equation by minimizing the sum of chi squared. The goodness of fit was evaluated by the coefficient of determination, R^2. Trials with $R^2 < 0.75$ were excluded from further data analysis.

For each of the remaining trials we calculated the relative yields for all treatments (control, 15, 30 or 35, and 45 kg P ha^{-1} y^{-1}) according to Eq. 2:

$$RY\,(\%) = \frac{y}{y0+a} \times 100 \qquad \text{(Eq. 2)}$$

where RY refers to the relative yield.

The RY values were plotted against each of the three soil P test (P-AL, PH$_2$O, P-DGT) data, and the Mitscherlich model was fitted according to Equation 2, where $y0$ is the calculated RY (%) of the control (minimum), $y0 + a$ is calculated maximum RY and, x is the result of soil P tests. The goodness of fit was again evaluated by R^2.

In a first step, the model was fitted to all soil – P test pairs of the remaining trials. As plotting P-AL against P-DGT revealed two distinct data populations, separated by a P-AL:P-DGT ratio of 0.1, we fitted the Mitscherlich model also separately to each of the two data. Further, we calculated the distribution coefficients (Kd, ratio between quantity and intensity), defined as P-AL:P-H$_2$O, for all soils and the populations with a P-AL:P-DGT ratios of <0.1 and >0.1, to explore the possible effect of Kd on yield response to the soil tests.

The upper boundaries of P deficiency (often referred to as "critical values") of the soil P tests for wheat were obtained by the intercept of the fitted curve with 95% RY using an inverse prediction of Equation 1.

RESULTS

Soil P tests

The extraction yields of P-AL range between 1.00 and 227 mg kg^{-1}, with a mean of 29.3 mg kg^{-1}. The range of P-H$_2$O is 0.019 -- 19.9 mg kg^{-1}, with a mean of 3.14 mg kg^{-1}. DGT-available P (P-DGT) varied between 1.41--457 µg L^{-1}, with a mean of 80.8 µg L^{-1} (Table III). The coefficient of variation for the P tests was largest for P-AL (167%), followed by P-H$_2$O (125%) and P-DGT (112%).

TABLE III

Upper limits of P deficiency (95th percentile) of wheat for the soil test used in this study and comparison with published values (n = 143, all soils; n = 61, P-AL:P-DGT < 0.1 soils)

Soil P test	Unit	Mean of extracted P (this study)		Range of extracted P (this study)		Upper limit of P deficiency for wheat grain yield at 95% relative yield						
						This study		Nawara *et al.* (2017)a)	Mason *et al.* (2010)b)	McBeath *et al.* (2007)b)	Speirs *et al.* (2013)c)	
		All soils	K_d < 0.1 soils	All soils	K_d < 0.1 soils	All soils	K_d < 0.1 soils				Calca-rosols	Other soils
P-AL	mg kg^{-1}	29.3	6.26	1.00--227	1.10--18.7		3.29	69				
P-H$_2$O		3.14	4.11	0.019--19.9	0.237--17.2	2.30	1.28					
P-DGT	µg L^{-1}	80.8	107	1.41--457	14.5--457	61.9	44.8	28	66e)	59d)	76e)	34e)

a)Long-term field experiments, European soils.

b)Field experiments, Australian soils.

c)Greenhouse experiment.

d)At 80% relative yield.

e)At 90% relative yield.

The relations between the P concentrations obtained with the three extractants are shown as scatterplots in Fig. 1. We found linear correlation between P-DGT and P-H$_2$O (Panel A) with a coefficient of determination of 0.88. However, the scatterplots of P-AL (quantity test) versus P-H$_2$O

(Panel B) and P-DGT (Panel C), respectively, show separation of the datasets in two distinct populations, one with large, the other with low P-AL concentrations over the full range of P extracted either by H_2O or DGT. Given the obvious split in two populations we plotted the extracted P concentrations against the P-AL:P-DGT ratio and found a population cut-off at P-AL:P-DGT~0.1. For soils with P-AL:P-DGT ratio < 0.1, we found a relatively close linear relation between P-DGT and P-AL (R^2 = 0.79), and a weaker one between P-H_2O and P-AL (R^2 = 0.66). For the soils with P-AL:P-DGT ratio > 0.1, the coefficients of determination are low (< 0.45) for both. A detailed data analysis showed that 96% of the organic treatments is associated with the P-AL:P-DGT ratio > 0.1 population.

Fig. 1 Scatterplots of the P extraction yields of (A) P-H_2O versus P-DGT, (B) P-H_2O versus P-AL, (C) P-DGT versus P-AL; panel (D) shows the relation between K_d and the ratio of P-AL:P-DGT. In panels A and D potency regression lines were fitted to the data. Data in panels B and C are split in two populations separated by a corresponding ratio between P-AL and P-DGT of 0.1, representing low and high K_d soils.

The K_d values correlated well (R^2 = 0.90) with the P-AL:P-DGT ratio (Fig. 1, plot D), and ranged for all soils between 0.61 and 3470, with a mean of 90.7 and a median of 4.37 L kg^{-1}. For the subset of soils with P-AL:P-DGT < 0.1, the K_d values ranged between 0.61 and 11.4, with a mean of 2.62 and a median of 2.01 L kg^{-1}. The corresponding K_d values for the subset of soils with P-AL:P-DGT > 0.1 was 1.47--3470 (range), 156 (mean) and 16.5 (median) L kg^{-1}. The results show that the population of soils with P-AL:P-DGT < 0.1 represents the low K_d soils of our study.

Wheat grain dry yields

The measured mean dry yield of wheat grain of the trials with R^2 > 0.75 (N = 143 soil–RY pairs) for the Mitscherlich fit that were included in the subsequent soil test – yield response fitting is 5310 kg ha^{-1} y^{-1}, with a range of 2240--8450. The modelled RY of all P treatments of the considered trials ranged between 35.9 and 107%, with a mean of 91.8%. Measured dry yields of the population with P-AL:P-DGT ratio < 0.1 (N = 61) vary between 3270 and 8450 kg ha^{-1} y^{-1} with a mean of 5290, the corresponding modelled RY between 63.0 and 107% (mean 94.7%).

Grain yield response to soil tests

Figure 2 shows plots of the calculated RY of the responsive (R^2 > 0.75) trials for which yields approached a plateau over the P concentrations obtained with the three soil P tests. The lines show the Mitscherlich fit to the data. When all data of these trials are included (N = 143, Panels A-C), the goodness of fit (R^2) is generally low, decreasing in the order P-DGT (0.25) > P-H_2O (0.18) >P-AL (0.14). If data with a P-AL:P-DGT ratio ≥ 0.1 are excluded, R^2 increases to 0.55 (P-AL), 0.46 (P-H_2O) and 0.65 (P-DGT), respectively (N = 61, Panels D-F). The improved fits are associated with the preferential removal of later sampling dates (1999-2015).

Fig. 2 Relative yield (RY) as a function of soil P concentrations measured by the three soil P tests: (A) P-AL, (B) P-H_2O, (C) P-DGT;, all soils; (D) P-AL, (E) P-H_2O, (F) P-DGT, for soils with P-AL:P-DGT ratio < 0.1 only. The insert in panel (D) shows the data in the lower range (< 20 mg kg^{-1}) of P-AL. The triangles show individual observations; lines are predicted with the Mitscherlich model. The R^2 values indicate the goodness of the model fits.

Upper boundaries of P deficiency

Using inverse prediction of the Mitscherlich model (Equation 1) we calculated the upper limits of P deficiency at 95% RY. The deficiency limits were 2.30 mg kg^{-1} for P-H_2O and 61.9 µg L^{-1} for P-DGT, but due to the poor fit, it could not be determined for P-AL when all responsive trials were considered. For soils with P-AL:P-DGT < 0.1, the deficiency limits were 3.29 mg kg^{-1} for P-AL, 1.28 mg kg^{-1} for P-H_2O, and 44.8 µg L^{-1} for P-DGT.

DISCUSSION

For all responsive trials approaching a yield plateau, prediction of RY is generally poor, with somewhat better performance of P-DGT ($R^2 = 0.25$). This observation compares to previous investigations of European soils by Nawara *et al.* (2017), who reported $R^2 = 0.37$ for the RY response to P-DGT. The fit between P-H_2O and RY in our study ($R^2 = 0.18$) is below that for P in the similar $CaCl_2$ extract ($R^2 = 0.31$) reported by Nawara *et al.* (2017). However, in our study the Mitscherlich-type model fails even more clearly to predict RY based on P-AL ($R^2 = 0.14$; Fig. 2, Panels A-C) whereas Nawara *et al.* (2017) report a performance for P-AL ($R^2 = 0.46$) and other quantity tests superior to P-DGT. They suggested that intensity tests perform better only in soils with strong P retention such as in Australian soils (Mason *et al.*, 2010; McBeath *et al.*, 2007; Speirs *et al.*, 2013). As in low to moderately weathered European soils sorption of P is typically less pronounced, Nawara *et al.* (2017) argue that P availability is more likely controlled by quantity, resulting in similar or better performance of quantity tests.

The distribution coefficient, Kd, is generally considered as a measure of buffer power in soil, with large Kd indicating stronger fixation. In line with this, removing soils with large P-AL:P-DGT ratio, corresponding to high Kd (Fig. 1), is expected to improve the performance of quantity relative to that of intensity tests (Nawara *et al.*, 2017). Therefore, we fitted the Mitscherlich-type model to the subset of data with P-AL:P-DGT ratio < 0.1. We found substantial increase of the goodness of the Mitscherlich fit not only for the quantity test (P-AL, $R^2 = 0.55$) but also for P-DGT ($R^2 = 0.65$), and less pronounced, for P-H_2O ($R^2 = 0.46$). These changes (Fig. 2) are associated with the removal of most data representing high RY in the lowest range of P-DGT and P-H_2O, and low RY (< 80%) at small to moderate P-AL concentrations (Fig. 2). Moreover, all data with P-AL > 20 mg kg^{-1} were removed from the P-AL-RY plot, corresponding to soils that had received high fertilizer loads. Virtually all removed soils (*i.e.*, with P-AL:P-DGT ratio > 0.1) had been sampled in 1999 or later, allowing for a longer period of P accumulation in the treatments where fertilization (> 15 kg P ha^{-1} y^{-1}) exceeded P removal by crops, or depletion in the controls (Fig. 2). Accordingly, large Kd is caused either by P accumulation in the fertilized treatments, or very low P solubility in the strongly depleted controls. Whereas P-AL overestimates P availability in the latter (sampling 1999-2015, controls), the RY response on these soils is much better captured by P-H_2O (Fig. 2), indicating the importance of intensity for P uptake from P-depleted soils. Conversely, P-H_2O tends to overestimate P availability in a relevant number of fertilized soils (> 15 kg P ha^{-1} y^{-1}) obtained in earlier sampling years (1967--1991) which is in line with higher importance of P quantity. The generally better performance of P-DGT appears to be related to its mechanistic advantage to capture both intensity and quantity to some extent (Almas *et al.*, 2017; Degryse *et al.*, 2009; Menezes-Blackburn *et al.*, 2016). However, the predictive power of DGT was also limited (Fig. 2).

In soils with long-term legacy of fertilization, the cumulative P fertilization rates are considered directly proportional to the degree of soil saturation with P, and the related loss of P-retention capacity (Menezes-Blackburn *et al.*, 2016). Phosphorus saturation is expected to promote P diffusion into particles as steep gradients between the surface and the interior of minerals develop (Barrow, 2017), resulting in stronger P fixation, and increasing the fraction of slowly-desorbing P (Almas *et al.*, 2017). This may explain that the quantity test (P-AL), did not perform better than the intensity test (P-H_2O) in our study when soils with P-AL:P-DGT ratio > 0.1 are included. Upon removal of soils with P-AL:P-DGT ratio > 0.1, the quantity test is superior to the intensity test as proposed by Nawara *et al.* (2017). Experimental evidence also indicates that quick and slow P desorption can be captured to some extent by DGT even within the standard deployment time of 24 hours (Menezes-Blackburn *et al.*, 2016; Almas *et al.*, 2017). However, the data and modelling of Menezes-Blackburn *et al.* (2016) also show that short-term deployment (24 hours) of DGT does only partially account for P that becomes slowly available in high-Kd soils with low P intensity, but may be accessed by crops during a growth period of several months. This may explain the failure of DGT to predict P availability in these particular soils, i.e., those in the low P-DGT range but high RY, which had been heavily fertilized over long time (Fig. 2). This interpretation is consistent with the model proposed by Barrow (1983) predicting that P that has reacted with soil for a long period can be fixed in the interior of minerals by particle diffusion. This process is driven by long-term addition of high fertilizer loads, creating a steep P activity gradient between the surfaces and the interior of soil minerals. In the vicinity of active plant roots, the external P diffusion is decreased, resulting in reverse diffusion of the penetrated phosphate ions along a chemical P activity gradient (pH~5-7) or an electric potential gradient (pH < 5) (Barrow, 2017). Moreover, none of the P tests is able to capture additional mobilization of P by root exudates (Hinsinger *et al.*, 2011).

In contrast to the results of Nawara *et al.* (2017), P-DGT outperformed the predictive power of the quantity test (P-AL) whether or not soils with low Kd are included. P-DGT also performed better than the intensity test (P-H_2O). Menezes-Blackburn *et al.* (2016) concluded that DGT, in contrast to equilibrium-type methods (such as P-AL and P-H_2O), addresses dissimilarities in P diffusion and kinetics of P resupply from the soil solid phase. Theoretical considerations show that strong correlation between DGT and plant response is expected where diffusion from bulk soil to the soil-plant interface is the rate-limiting step (Degryse *et al.*, 2009; Six *et al.*, 2012). If this applies, DGT is likely to perform better than equilibrium-based quantity and intensity tests in predicting nutrient uptake and yield. DGT may correlate with plant uptake even if diffusion is not the rate-limiting step, given that nutrient uptake is not saturated (Degryse *et al.*, 2009), but in this case is not mechanistically superior to other soil tests.

As the observed outperformance of P-AL by DGT even in the soils with low Kd in our study is not in line with a mainly quantity-controlled P availability as proposed for European soils by Nawara *et al.* (2017), we suggest that this can be explained by diffusion and resupply as rate-limiting steps in P uptake. This is supported by chemical imaging of labile P around individual root segments of various crop plants including wheat, grown on temperate-zone soils, consistently showing strong depletion zones (Santner *et al.*, 2012; Kreuzeder *et al.*, 2018). The generally better performance of DGT compared to water extraction in predicting grain yield is expected as soil solid-phase buffering affects DGT and plant uptake flux in similar manner (Degryse *et al.*, 2009).

The upper boundary of P deficiency for wheat grain yield is 61.9 µg L^{-1} for all responsive soils of our study, and 44.8 µg L^{-1} if only soils with P-AL:P-DGT ratio < 0.1 are considered. This compares to a mean of 28 µg L^{-1} (range 6.1--110 µg L^{-1} at 95% RY) for various crops grown on European soils and values between 34 and 76 (at 80 or 90% RY) for Australian soils (Table III). Note that the upper boundaries of P deficiency for wheat reported by Nawara *et al.* (2017) vary considerably between the experimental sites, covering a range of 6 to 110 µg L^{-1}.

According to Nawara *et al.* (2017), the potential of a soil test to distinguish between soils can be evaluated by the coefficients of variation of the test results. For soils from different European long-term experiments, Nawara *et al.* (2017) report a CV of 69 for P-AL and a CV of 190 for P-DGT. They used P-$CaCl_2$ as intensity test, with a CV of 120. Accordingly, the distinctive potential decreased in the order P-DGT > P-$CaCl_2$ > P-AL. As pointed out by Santner *et al.* (2018), Nawara *et al.* (2017) used different deployment times deviating from the standard procedure for DGT, varying between 2 (for soils with P-$CaCl_2$ > 4.4 mg kg^{-1}) and 48 hours (for soils with P-$CaCl_2$ < 0.8 mg kg^{-1}). Recalculation of their data to the DGT standard deployment time of 24 hours shows that this narrows the CV for P-DGT to 140 (Nawara *et al.*, 2018). For the soils of the Swedish long-term experiments used in our study, the distinctive potential decreased in the order P-AL (171%) > P-H_2O (128%) > DGT (114%). The coefficients of variation decreased for the subsets of soils including only soils from responsive trials (112-167%), and soils with P-AL:P-DGT < 0.1 (73-106%). Overall, the difference between the soil tests was less pronounced than in the study of Nawara *et al.* (2017), and therefore of minor importance for the evaluation of the soil tests.

For the calibration based on soils with P-AL:P-DGT < 0.1, the success rate for predicting fertilizer response correctly based on soil test results below the critical value was 60% for P-DGT, and 63% for the other two soil tests. The failure rate for soil test results above the critical value was 15 (P-DGT), 4.8 (P-AL) and 7.1% (P-H_2O). Nawara *et al.* (2017) report success rates of 75 for P-DGT and 76% for P-AL. For the intensity test (P-$CaCl_2$) they found a success rate of 68%. The corresponding failure rates reported by Nawara *et al.* (2017) are 31 (P-DGT), 28 (P-AL) and 30% (P-$CaCl_2$). While the success rates are somewhat lower in our study, the failure rates are clearly smaller. Note that the failure and success rates reported by Nawara *et al.* (2017) could be biased by the differential DGT deployment times used in their study (Santner *et al.*, 2018). Overall, the success and failure rates indicate additional factors involved in nutrient uptake that are not captured by the soil tests. As nutrient diffusion in the rhizosphere is also controlled by moisture content, climate factors such as aridity indices should be considered to further improve the predictive power of P indices.

CONCLUSIONS

Our work adds to the available information on DGT calibration for soil P testing. It shows that DGT can well explain the variation in RY of wheat in temperate zone, moderately weathered soils of Scandinavia, and outperform both quantity and intensity tests likely because of its ability to integrate intensity, diffusion and resupply from solid phase into one measurement. This is in line with diffusion-controlled P uptake by crops grown on temperate zone soils and the related vast evidence for P depletion in the rhizosphere. We conclude that DGT is a promising technique for soil P testing and fertilization management but additional information such as climate data may be required to develop a P index and upper boundaries of P deficiency that can be applied in different environmental conditions. Moreover, it appears that all soil tests fall short if extremely depleted soils and/or soils with high cumulative P accumulation are included in the calibration.

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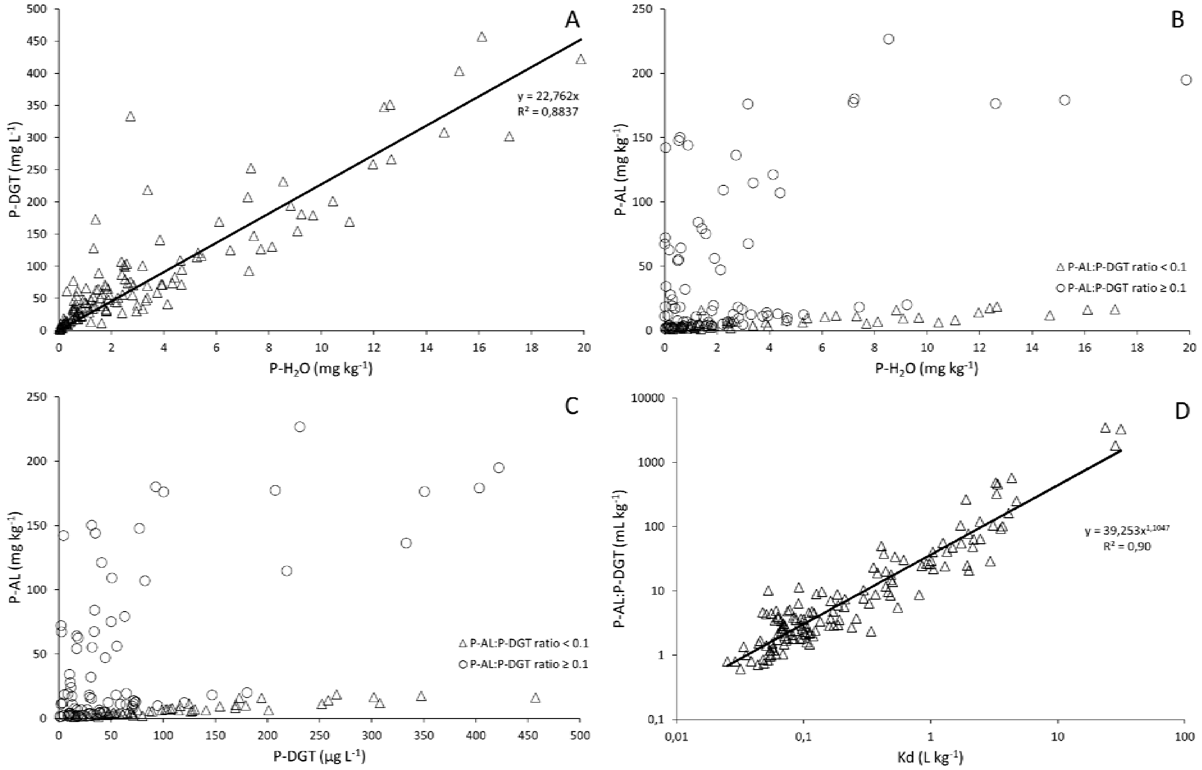

Fig. 1

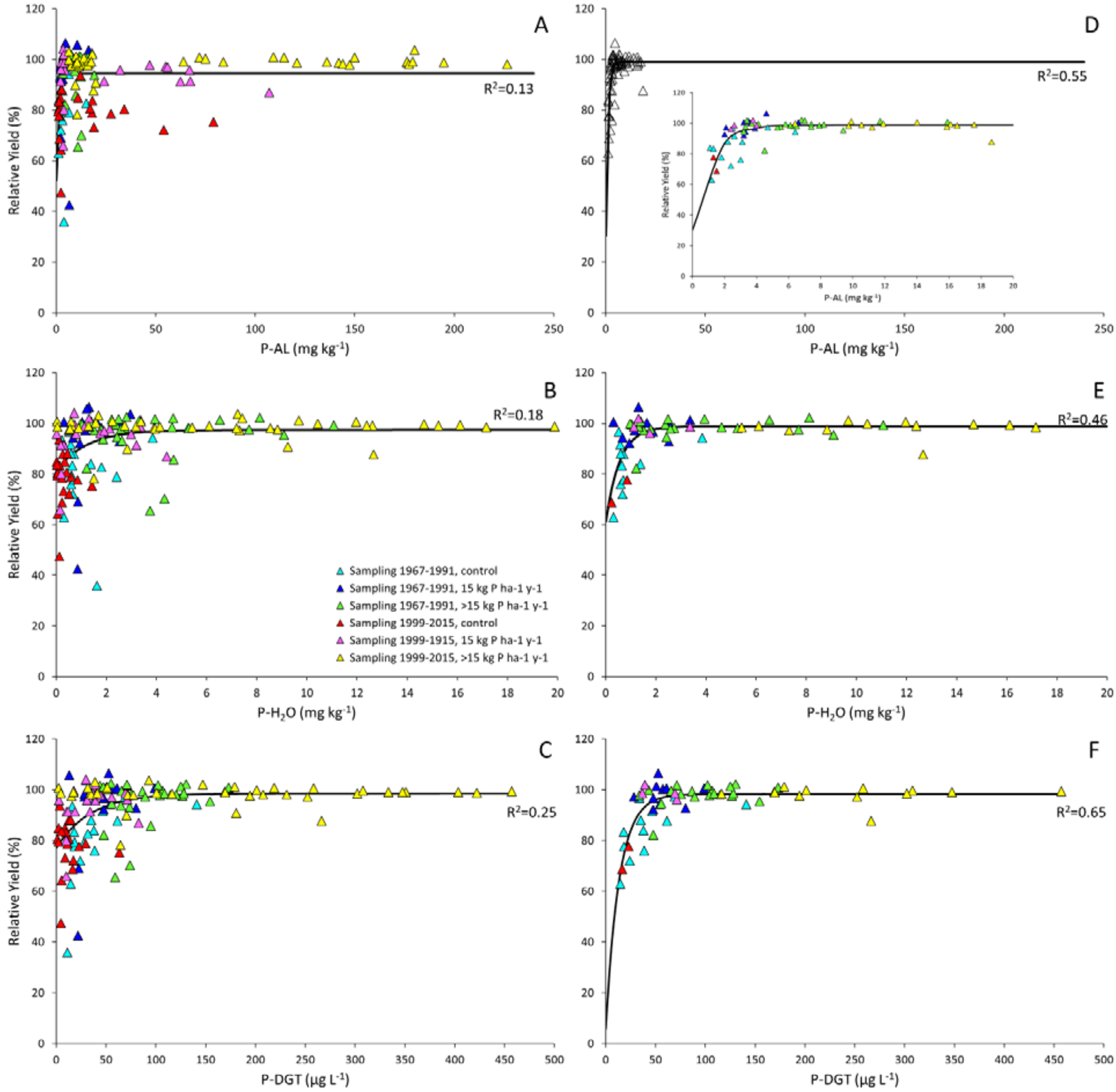
A
R²=0.13
Relative Yield (%)
P-AL (mg kg⁻¹)
0
20
40
60
80
100
120
0
50
100
150
200
250
D
R²=0.55
Relative Yield (%)
P-AL (mg kg⁻¹)
B
R²=0.18
Relative Yield (%)
P-H₂O (mg kg⁻¹)
0
2
4
6
8
10
12
14
16
18
20
Sampling 1967-1991, control
Sampling 1967-1991, 15 kg P ha-1 y-1
Sampling 1967-1991, >15 kg P ha-1 y-1
Sampling 1999-2015, control
Sampling 1999-1915, 15 kg P ha-1 y-1
Sampling 1999-2015, >15 kg P ha-1 y-1
E
R²=0.46
P-H₂O (mg kg⁻¹)
C
R²=0.25
Relative Yield (%)
P-DGT (µg L⁻¹)
0
50
100
150
200
250
300
350
400
450
500
F
R²=0.65
P-DGT (µg L⁻¹)

Fig. 2