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Phosphorus desorption and isotope exchange kinetics in agricultural soils

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Abstract

To improve phosphorus (P) fertilization and environmental assessments, a better understanding of release kinetics of solid-phase P to soil solution is needed. In this study, Fe (hydr)oxide-coated filter papers (Fh papers), isotopic exchange kinetics (IEK) and chemical extractions were used to assess the sizes of fast and slowly desorbing P pools in the soils of six long-term Swedish field experiments. The P desorption data from the Fh-paper extraction of soil (20 days of continual P removal) were fitted with the Lookman two-compartment desorption model, which estimates the pools of fast (Q_1) and slowly (Q_2) desorbing P, and their desorption rates k_1 and k_2. The amounts of isotope-exchangeable P (E) were calculated ($E_{1\text{min}}$ to $E_{>3\text{ months}}$) and compared with Q_1 and Q_2. The strongest relationship was found between $E_{1\text{ min}}$ and Q_1 ($r^2 = .87$, $p < .01$). There was also an inverse relationship between the IEK parameter n (the rate of exchange) and k_1 ($r^2 = .52$, $p < .01$) and k_2 ($r^2 = .52$, $p < .01$), suggesting that a soil with a high value of n desorbs less P per time unit. The relationships between these results show that they deliver similar information, but both methods are hard to implement in routine analysis. However, Olsen-extractable P was similar in magnitude to Q_1 (P-Olsen $= 1.1 \times Q_1 + 2.3$, $r^2 = .96$), n and k_1 were related to P-Olsen/P-$CaCl_2$, while k_2 was related to P-oxalate/P-Olsen. Therefore, these extractions can be used to estimate the sizes and desorption rates of the different P pools, which could be important for assessments of plant availability and leaching.

KEYWORDS
fertiliser, long term trials, modelling, phosphate, soil analysis, soil improvement, soil use and management

1 | INTRODUCTION

Crop phosphorus (P) uptake is dependent on the continuous replenishment of P from the soil solid phase to the soil solution (Pierzynski et al., 2005). The supply of P from the solid to the solution phase largely occurs via (a) desorption of P from mineral surfaces, (b) dissolution of P-containing minerals and (c) mineralization of organic P by microorganisms (Frossard et al., 1995). Commonly, pools of soil P exist on a continuum of 'availability' to plants (Holford, 1997). The short-term plant P uptake and the risk of P leaching are a function of several factors including: soil P concentration, time, P speciation and soil properties such as pH and the mineralogy of the clay fraction (Penn & Camberato, 2019; Pierzynski et al., 2005). Solid-phase P can be divided into a number of different pools and defined by the rate of which it can resupply soil solution P (Fardeau, 1995). The pool of soil P available for plant uptake during a growing season, henceforth referred to as the 'labile' P, is typically evaluated with a single-step chemical extraction method (or 'test'), which differ among regions (Jordan-Meille et al. 2012). A better understanding of the P release from solid to solution, and its connection to soil properties and chemically extractable P fractions, may greatly improve the interpretation of the results from routine methods used to assess both the size of the labile P pool and the risk of P leaching.

As is the case in a number of other countries (e.g. Norway, Hungary, Slovenia, Flanders), the current Swedish guidelines on estimating pools of labile P in surface soils are based on the acid ammonium acetate lactate (pH 3.75, P-AL) extraction (Börling et al., 2017; Egnér et al., 1960). As a result of excessive P fertilizer use, approximately half of the arable land in Sweden has concentrations of labile P in surface soils that are considered 'high' or 'very high' based on current guidelines (Djodjic et al., 2004; Eriksson et al., 2010). However, the P-AL extraction can overestimate the pool of plant-available P in soils with large concentrations of calcium phosphate (Ca-P) (Braun et al., 2019; do Horta et al., 2010; Eriksson et al., 2016). Alternatively, the sodium bicarbonate (0.5 mol·L^{-1} $NaHCO_3$ at pH 8.5) extraction of Olsen (1954) can be used, as is the case in Denmark, England, France and Italy. However, these single-step chemical extraction methods are not able to accurately determine pools of labile P in all soil types, and they do not account for the slow release of P to the soil solution (McLaren et al., 2014).

The release of P from a soil can be described considering three factors: the intensity factor (the concentration of P in solution), the quantity factor (the amount of P that can be released from the soil solid phase and reach the solution within a given time) and the buffer capacity (the ability of a soil to maintain the concentration of P in solution when the quantity varies, e.g. because of fertilization or plant uptake) (Pierzynski et al., 2005). Some information about these factors can be obtained using a combination of chemical extractions, such as dilute $CaCl_2$ for the intensity (van Raij, 1998; Six et al., 2012), AL or Olsen for the quantity factor within a growth season (Demaria et al., 2005; van Rotterdam et al., 2012), and the ratio of quantity to intensity to estimate the buffer capacity (Reijneveld et al., 2014; van Rotterdam-Los, 2010). However, before such an approach can be implemented, the suitability of the extraction methods to measure the quantity and intensity factors needs to be validated by kinetic methods.

In general, the amount of desorbable P can be described using two discrete P pools, one fast desorbing pool (Q_1), which is largely considered to comprise of P bound to the active soil surfaces in direct contact with the soil solution, and one slowly desorbing pool (Q_2), which is largely considered to comprise of P-containing minerals and of P that has penetrated into the inner domains of adsorbing particles (Lookman et al., 1995). Each pool has its own P release kinetics, and the sum of the two pools can be approximated with oxalate-extractable P (Frossard et al., 2014; Lookman et al., 1995). Frossard et al. (2014) used a flow-through cell experiment to show that ryegrass was able to take up P from both the Q_1 and Q_2 pools. However, a correct estimation on the size of the fast desorbing P pool is by itself not sufficient to assess the labile P pool, as the release kinetics of more stable P species also needs to be taken into consideration.

Highlights

- Fh papers and IEK can both be used to estimate the size of the fast desorbing P pool.
- Soils with a high rate of isotopic exchange desorb less P per time unit.
- The amount of Olsen-extractable P was similar in size to the pool of fast desorbing P.
- The P-Olsen/P-$CaCl_2$ ratio estimates the rate of desorption from the fast desorbing P pool.
- The P-oxalate/P-Olsen ratio estimates the rate of desorption from the slowly desorbing P pool.

'Infinite' P sinks such as Fe (hydr)oxide-coated filter papers (referred hereafter as Fh papers, as ferrihydrite is the most likely mineral phase that forms on these papers) can be used to improve our understanding of the amount of P available for desorption within different time periods and of the soil P buffering capacity across a diversity of soil types (Chardon et al., 1996; McLaren et al., 2014; van Rotterdam et al., 2009, 2012; Sharpley, 1991). If the papers in the soil suspension are continuously replaced, information about long-term desorption can be obtained.

The rates of soil P sorption/desorption can also be studied using isotopic exchange kinetics (IEK) (Aigner et al., 2002; Fardeau, 1995; Frossard et al., 2011), where a small amount of radioactive labelled PO_4 is added to a soil suspension. The removal of the radioactive PO_4 (by exchange with native PO_4) from the soil solution over time is fitted with an IEK model (Fardeau et al. 1985). The fitted parameters from this model can then give information on the P sorption capacity of the soil, the soil solution P turnover (K_m) and the amount of isotopically exchangeable soil P at a given time (the E value) (Fardeau, 1995; Frossard & Sinaj, 1997; Helfenstein et al., 2018). For agronomic applications, the amount of exchangeable P can be divided into different compartments, which is defined by the time it takes for P to leave the solid phase and enter the solution (Fardeau, 1995). Commonly, $E_{1\ min}$ represents the pool of free P ions that is considered immediately available to plants, $E_{1\ day}$ - $E_{1\ min}$ represents the amount of P exchangeable during a period considered to be equivalent to the life time of a single root hair or mycorrhizal hyphae, and $E_{3months}$- $E_{1\ day}$ represents the amount of P exchangeable during a period considered to be equivalent to the life time of a root system of an annual crop (Frossard & Sinaj, 1997). The amount of P removed by a single Fh paper over 16 hr was shown to be highly correlated with E_{1min} (Aigner et al., 2002), and the amount of P desorbed after 14 days using a flow-through reactor with dilute $CaCl_2$ solution was highly correlated with E_{1min}, $E_{60\ min}$ and $E_{14\ days}$ (Frossard et al., 2014). Schneider and Morel (2000) estimated the inorganic P that participates in the soil-solution dynamics in a French Haplic Luvisol using both desorption (anion exchange resin) and IEK methods and found these concentrations to be equal. However, no study has compared the kinetics of isotope exchange with the kinetics of desorption in the presence of an infinite sink for P for a wide range of soils. The two kinetic methods used in the current paper are minimally invasive. Further, they provide information on the rate at which P is transferred across the soil–solution interface, and on the amount of sorbed P that may be available for desorption after a given time period. The isotope exchange method is used to assess fluxes of exchangeable P between the solid phase and the solution in a system at steady state, while the Fh paper method assesses the P desorption rate in the presence of an infinite sink. Since both methods are focused on the transfer of P between the solid and solution phases, it may be hypothesized that the information they deliver are similar even though they are based on different principles.

The objective of this paper was to compare the time-dependent release of P to the soil solution using both an infinite sink method (Fh papers) and isotopic exchange kinetics. Further, the results were compared with those obtained using classical soil P extractions, to see whether the latter can provide insights into the short-term P dynamics in soils. Soils were chosen that represent extremes in terms of P status because of long-term P depletion or excessive P inputs.

2 | MATERIALS AND METHODS

2.1 | Site background and characterization

Soil samples were collected from six long-term field experiments located across Sweden, which included the following sites: Ekebo, Fjärdingslöv, Fors, Högåsa, Kungsängen and Vreta Kloster. The sites covered a wide variation in soil properties and soil P status. Selected soil properties are shown in Table 1. All long-term field experiments have been in operation for at least 50 years (Carlgren & Mattsson, 2001). Each experiment consists of treatments with sixteen different combinations of nitrogen (N), potassium (K) and P applications. For this study, soils were sampled from plots with the combination of the highest N fertilization level (an average of 125 kg N $ha^{-1}yr^{-1}$ for the Fors, Kungsängen, Vreta Kloster and Högåsa soils, and 150 kg N ha^{-1} yr^{-1} for the Ekebo and Fjärdingslöv soils), and either the lowest or highest levels of PK fertilization. These plots had received either no P or K fertilizer (A3), or received P and K equal to that removed by the previous crop plus an additional 30 kg P ha^{-1} yr^{-1} and 80 kg K ha^{-1} yr^{-1} (D3). Fertilizer P was added as single superphosphate (9% P) until 1991 (Ekebo and Fjärdingslöv) or 1994 (other sites), and thereafter as triple superphosphate (20% P). For each field trial, the cumulative net mass balance of P between the start year and 2017 was calculated as the P added as fertilizer minus P removed by harvest. Soil sampling and sample preparation were described in detail by Braun et al. (2019).

Details of soil extraction methods are given in Table 2. All P extractions except total inorganic P were carried out in duplicate, and all extracts were filtered (< 0.2 μm) prior to analysis. The choice of ICP-MS as analytical method for AL was based on the Swedish standard analytical protocol (Börling et al., 2017), and the choice of colorimetric analysis of molybdate-reactive P for Olsen was based on the Danish standard protocol (Rubæk & Kristensen, 2017). To get an idea about the distribution of P between the sorbed and dissolved phases, the P-Olsen/P-$CaCl_2$ ratio was calculated. Determinations of total carbon and total inorganic carbon (measured after combustion at 550 ºC for 2 hr) were carried out by dry combustion using a LECO TruMac CNS Analyzer.

2.2 | Desorption experiment

Successive removal of P from soil suspensions using Fh papers was studied for all soils, based on the method of van Rotterdam et al. (2009). Briefly, Whatman no. 100 filter papers were cut into 2 × 5 cm strips, submerged in 0.4 mol·L^{-1} $FeCl_3$ solution for 30 s, air-dried for 1 hr and then submerged in 2.68 mol·L^{-1} ammonia solution for 30 s. The papers were then rinsed thoroughly with water to remove any loose iron (hydr)oxide particles. A mass of 4 g of air-dried soil was weighed into a 50-mL polypropylene centrifuge tube, which then received 40 ml 0.005 mol·L^{-1} $CaCl_2$ solution. Two papers with a total active area of 40 cm^2 were placed in a nylon mesh bag (Chardon et al., 1996), which was then placed in the centrifuge tube. The tubes were shaken for a certain period of time on an end-over-end shaker at 20 rpm. The papers were removed and fresh papers were placed in the tubes after 2, 4, 8, 26, 48, 78, 145, 221 and 316 hr of shaking time counted from the start of the

TABLE 1 Selected properties of the top soil (0–20 cm) at the investigated sites

			Clay	Silt	Sand	Inorganic C	Organic C	Al_{ox}[a]	Fe_{ox}[a]	
Location	**Treatment**	**pH**	**% of mineral fraction**			**g kg^{-1}**		**mmol kg^{-1}**		**FAO soil order**[b]
Ekebo	A3	6.87	14.7	36.6	48.8	<1	24.2	62.6	39.5	Haplic Phaeozem
	D3	6.84	13.9	36.5	49.6	<1	23.4	94.2	37.2	
Fjärdingslöv	A3	6.98	17.7	26.9	55.5	<1	12.3	30.8	37.8	Haplic Phaeozem
	D3	6.88	16.0	25.8	58.2	<1	18.4	29.8	25.1	
Fors	A3	8.33	16.6	58.2	25.4	4.7	15.6	30.7	25.2	Calcaric Phaeozem
	D3	7.73	15.0	59.0	26.1	7.7	17.1	30.4	29.3	
Högåsa	A3	5.82	6.25	16.8	77.0	<1	19.2	67.8	53.5	Arenic Umbrisol
	D3	6.29	7.40	23.1	69.6	<1	20.6	86.2	56.9	
Kungsängen	A3	6.59	55.0	41.8	3.30	<1	22.3	54.1	162	Gleyic Cambisol
	D3	6.56	53.6	43.1	3.35	<1	20.7	55.9	176	
Vreta	A3	6.78	41.4	51.3	7.3	<1	18.7	59.9	29.2	Haplic Phaeozem
Kloster	D3	6.82	48.6	42.6	8.9	<1	20.2	63.6	32.4	

[a] Al_{ox} = oxalate-extractable Al, Fe_{ox} = oxalate-extractable Fe. For references see Table 2.

[b] Kirchmann et al., 1999; Ekebo and Fjärdingslöv), Kirchmann (1991; Fors and Kungsängen), Kirchmann et al. (2005; Högåsa and Vreta Kloster).

TABLE 2 The soil phosphorus (P) extraction techniques used in the study

Extractants	Duration of extraction	L:S ratio[a]	Analytical method of P measurement	Reference
$CaCl_2$ (0.005 mol·L^{-1})	2 hr	10	ICP-MS	Houba et al., (2000)
Olsen (0.5 mol L^{-1} $NaHCO_3$, pH 8.5)	0.5 hr	20	Molybdenum blue	Olsen, (1954)
AL (0.01 mol·L^{-1} acid ammonium lactate and 0.4 mol·L^{-1}acetic acid, pH 3.75)	4 hr	20	ICP-MS	Egnér et al., (1960)
Oxalate (0.2 mol·L^{-1} oxalate buffer, pH 3.0)	4 hr	100	ICP-OES	van Reeuwijk, (1995)
Total inorganic P (0.5 mol·L^{-1} H_2SO_4 on non-ashed soils)	16 hr	50	Malachite green	Walker and Adams, (1958)

[a] Liquid to soil ratio based on weight.

experiment. After 481 hr, the experiment was stopped and the last papers removed. Removed papers were rinsed with water and then submerged in 40 ml of 0.1 mol·L^{-1} H_2SO_4 solution and shaken for 1 hr to dissolve all P (van Rotterdam et al., 2009). In the eluents, molybdate-reactive P was determined using a Seal AA3 AutoAnalyzer (Seal Analytical, Germany). An initial pilot study was carried out to determine the P sorption capacity of the Fh papers, which involved Fh papers and solution P concentrations of 50 and 500 μg P L^{-1}. The Fh papers recovered between 95% and 100% of the added solution P.

Phosphorus desorption was described by using the model of Lookman et al. (1995), in which the desorption kinetics is described using two discrete pools:

$$Q_{des}\,(t) = Q_1\left(1 - e^{-k_1 t}\right) + Q_2\left(1 - e^{-k_2 t}\right) \tag{1}$$

where Q_1 and Q_2 are the amounts of fast and slow desorbing P (mg P kg^{-1} air-dried soil), respectively, k_1 is the rate of desorption per hour of P from Q_1, and k_2 is the rate of desorption per hour of P from Q_2. The sum of Q_1 and Q_2 was set equal to the

TABLE 3 Cumulative net mass balance of P (P added as fertilizer – P removed by harvest) and extractable P fractions of the top soil (0–20 cm), standard deviations are shown in parentheses

Location		Net P balance		P-Olsen	P-AL			P-Olsen/ P-CaCl$_2$
		kg P ha^{-1}	P-CaCl$_2$	mg P kg^{-1}		P-ox	P-inorg	
Ekebo	A3	−535	0.06 (0.001)	6.40 (1.76)	33.0 (6.68)	383 (7.9)	246	107
	D3	1559	1.03 (0.010)	56.0 (12.69)	258 (2.76)	788 (29.9)	638	54.2
Fjärdingslöv	A3	−482	0.06 (0.001)	2.08 (0.35)	11.2 (8.33)	139 (1.2)	145	35.0
	D3	1681	5.44 (0.245)	59.1 (5.29)	207 (6.25)	396 (8.3)	447	10.9
Fors	A3	−526	0.17 (0.012)	5.48 (0.23)	164 (29.38)	473 (7.3)	725	33.0
	D3	1578	11.3 (0.496)	84.5 (14.21)	306 (7.89)	641 (0.4)	925	7.45
Högåsa	A3	−335	0.11 (0.002)	16.7 (1.06)	36.9 (0.87)	406 (0.1)	308	154
	D3	1,453	1.17 (0.024)	67.7 (0.35)	157 (2.02)	663 (1.8)	552	57.9
Kungsängen	A3	−530	0.10 (0.015)	10.1 (0.12)	34.0 (1.04)	502 (2.1)	462	103
	D3	1,497	4.84 (0.421)	123.1 (0.47)	235 (14.99)	934 (26.5)	896	25.5
Vreta Kloster	A3	−453	0.09 (0.003)	2.33 (0.70)	43.6 (0.94)	326 (5.3)	309	25.1
	D3	1,485	7.86 (0.110)	87.2 (1.88)	205 (7.88)	622 (6.0)	742	11.1

Note: P-ox = oxalate-extractable P, P-inorg = H_2SO_4-extractable P.

amount of P extracted by ammonium oxalate, P-ox (Lookman et al., 1995):

$$Q_1 + Q_2 = P - ox \tag{2}$$

Parameter fitting for the Lookman model was carried out using the PEST software, which uses a Gauss–Marquardt–Levenberg algorithm to minimize the weighted sum of squared differences between the model and the observed data (Doherty, 2010).

2.3 | Isotope exchange kinetics

Isotopically exchangeable P was determined using the method described in Fardeau (1995). Briefly, 10 g air-dried soil was weighed into a 250 ml Nalgene bottle, which then received 99 ml of water. The bottles were shaken for 16 hr on an end-over-end shaker and then placed on a magnetic stirring plate. Each bottle then received a 1 ml aliquot of a carrier-free $^{33}PO_4$ solution containing ~ 0.1 MBq mL^{-1}. After 1, 4, 10, 30, 60 and 90 min following the addition of the radiotracer, approximately 2 ml of the soil suspension was removed with a syringe and filtered (0.2 μm). The filtrate was measured for its ^{33}P activity using a scintillation counter, and molybdate-reactive P was determined using the malachite green method (Ohno & Zibilske, 1991).

The decrease of radioactivity in solution as a function of time can be described as follows (Fardeau, 1995):

$$\frac{r(t)}{R} = m.\left\{t + m^{\frac{1}{n}}\right\}^{-n} + \frac{r(\infty)}{R} \tag{3}$$

$$\frac{r(\infty)}{R} = \frac{C_P}{P_{max}} \tag{4}$$

where R is the total amount of added radioactivity (MBq), $r(t)$ is the radioactivity in solution at time t (MBq), $r(\infty)$ is the radioactivity remaining in solution at infinity (MBq), t is the time in minutes, m and n are parameters determined by nonlinear regression, C_P is water-extractable P (mg P kg^{-1} soil) and P$_{max}$ is P extractable either with 0.2 mol·L^{-1} oxalate buffer or with 0.5 mol L^{-1} H_2SO_4 (mg P L^{-1}) on dry soil samples (mg P kg^{-1} soil). The quantity $E(t)$ (mg P kg^{-1} soil), that is the isotopically exchangeable P at time t, can then be calculated using the following equation (Frossard & Sinaj, 1997):

$$E(t) = C_p.\frac{R}{r(t)} \tag{5}$$

Two sets of calculations were performed, one in which P-ox was used as a representation of the total pool of exchangeable P (P$_{max}$), and one in which P$_{max}$ was represented by P-inorg (total inorganic P, see Table 2), in agreement with Frossard et al. (1994). The difference between the two calculation methods was small. To be comparable with the results obtained by the Lookman model, the values calculated with P-ox were used for all comparisons.

2.4 | Statistical analyses and graphics

The Fh paper experiments were carried out in duplicate, whereas the IEK experiments were not duplicated because of time constraints. However, one soil sample from each location was tested in triplicate to assess the variation between replicates, including an internal soil standard, which revealed minor differences (Appendix S1: Table S1). Regression analysis was made by calculation of Pearson's correlation coefficient *r*. A two-sided *t* test was used to check whether *r* was significantly different than zero. The difference in E values calculated with P_{max} set to either P-ox or P-inorg, and the differences in model parameter values between treatments, were tested with a paired *t* test. Data analysis and parameter fitting were made in R (R Studio Team 2016), PEST (Doherty, 2010) and in Microsoft Excel 2016.

3 | RESULTS

3.1 | Soil characteristics

Soils collected across the six field sites had a wide variation in soil properties (Table 1). The cumulative net mass P balances between the start of the field trial and 2017 were between −535 and −335 kg P ha^{-1} for the A3 treatments, and between 1,453 and 1681 kg P ha^{-1} for the D3 treatments (Table 3), suggesting considerable soil accumulation of P in the D3 treatments, and P depletion in the A3 treatments, which is in agreement with previously reported results from soil P extractions (Bergström et al., 2015). Soils from the Kungsängen and Vreta Kloster field sites were dominated by clay, whereas soils from the other field sites were sandy or silty loam. The pH of the sampled plots ranged between 5.8 and 8.3. Concentrations of inorganic C were low except at Fors, which contained calcium carbonate. Fors also had the highest concentrations of $CaCl_2$- and AL-extractable P for both the unfertilized and fertilized treatments (Table 3), and it was the only soil with a pH higher than 7. By contrast, Högåsa had the highest concentration of P-Olsen for the unfertilized treatments, and it was also the most acidic (pH 5.8–6.3) of the soils included in this study. For the fertilized treatments, the highest concentration of P-Olsen was found at Kungsängen.

Concentrations of P-ox in the 0–20 cm soil layer ranged from 139 to 502 mg kg^{-1} for the unfertilized treatments and from 396 to 934 mg kg^{-1} for the fertilized treatments. For both treatments, Fjärdingslöv had the lowest concentration of P-ox while Kungsängen had the highest. The ratio P-Olsen/P-$CaCl_2$ ratio was between 2.0 and 4.4 times higher in the unfertilized treatment than in the fertilized treatment for all soils (Table 3).

3.2 | Phosphorus desorption

The cumulative desorption of P over a time period of 20 days for the unfertilized and fertilized treatments is shown in Figure 1. For the unfertilized treatments, the total amount of desorbable P removed by the Fh papers (P-Fh) ranged from 8.9 to 27 mg P kg^{-1} soil, and for the fertilized treatments, it ranged from 99 to 200 mg P kg^{-1} soil. For all soils, more than 50% of total P-Fh was removed during the first five days, and at least 80% of total P-Fh was removed after a further 7 days. The difference between the fertilized and unfertilized treatments in the proportion of P-Fh removed at each time was minor across all soils, except for that at Fors where a larger percentage of P-Fh was removed early in the experiment for the fertilized treatment (Appendix S1: Figure S1). During the first three days of the Fh paper experiment, the relationship between time and the amount of P removed was nonlinear and had a steeper slope reflecting a rapid release of P during this phase. Afterwards, the rate of P removed by the Fh paper was reduced and took a linear form. No plateau was reached for the P removal within the 481-hr experiment.

The parameters Q_1, Q_2, k_1 and k_2 of the two-compartment Lookman model are presented in Table 4. There was a close 1:1 relationship between the Lookman model parameter Q_1 and P-Olsen ($r^2 = .96$, $p < .001$, Figure 2a) and a weaker but still significant relationship between Q_1 and P-AL ($r^2 = .63$, $p < .01$, Figure 2b) across all soils. The fast desorbing pool Q_1 was not related to any soil properties, but the slow desorbing pool Q_2 was related to the sum Al-ox + Fe-ox and to the soil organic C content (linear and power, $r^2 = .35$ and 0.47, respectively, $p < .05$). The r^2 and p values for all relationships between the Lookman parameters and both soil properties and IEK parameters can be found in Appendix S1: Tables S3 and S4.

The amount of P removed by the Fh papers did not exceed Q_1 until at the earliest 55 hr of shaking, and after 125 hr, the amount of P removed exceeded Q_1 for all samples. Long-term fertilization was found to affect the size of the Q_1 and Q_2 pools disproportionately. The percentage of Q_1 ranged between 1% and 3% of P-ox in the unfertilized treatments, and between 4% and 13% of P-ox in the fertilized treatments. The Fors soil had the largest proportional increase of Q_1 (from 1% to 13% of P-ox), and Ekebo the smallest (from 2% to 4%). Both Q_1 and Q_2 where related to the net mass P balance, but with a much stronger relationship for Q_1 (linear, $r^2 = .70$, $p < .001$ for Q_1 and $r^2 = .41$, $p < .05$ for Q_2).

The desorption rate for the fast desorbing pool, k_1, was consistently much higher than for the slowly desorbing pool, k_2. Additionally, k_1 was related to the ratio of organic C to Al-ox + Fe-ox (linear, $r^2 = .72$, $p < .001$), inversely related to Al-ox + Fe-ox (power, $r^2 = .64$, $p < .01$) and inversely related to the P-Olsen/P-$CaCl_2$ ratio (power, $r^2 = .67$, $p < .01$, Figure 3a). Finally, k_2 was related to the net mass P balance (linear, $r^2 = .86$, $p < .001$) and inversely related to P-ox/P-Olsen (linear, $r^2 = .91$, $p < .001$).

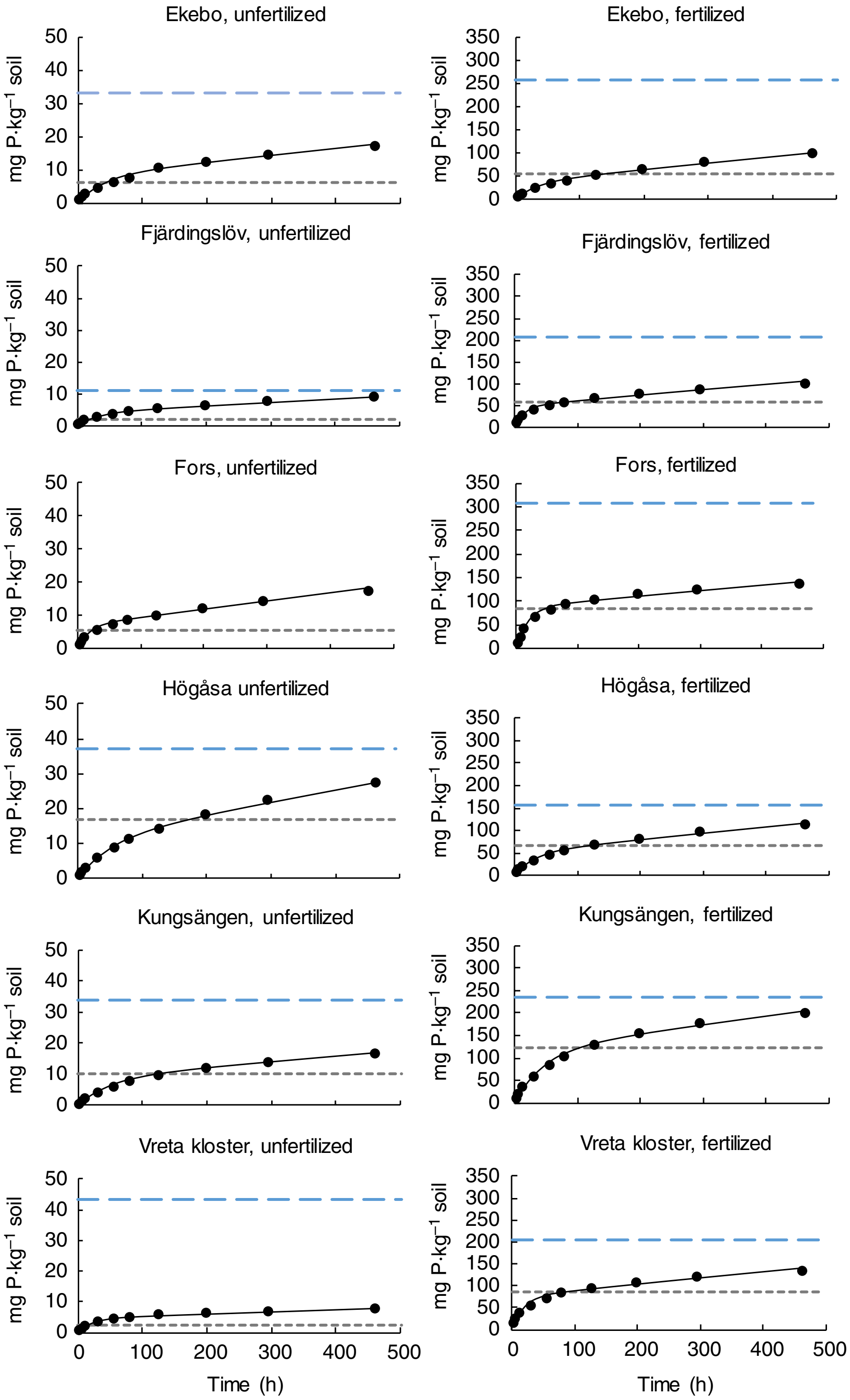

FIGURE 1 Cumulative P removal by Fh papers over a period of 481 hr in the 0–20 cm soil layer of unfertilized and fertilized treatments of six field sites located in Sweden. Filled circles show the cumulative removal of P by Fh papers (each symbol represents a paper). The black line (solid) shows the best fit for the Lookman model. The blue line (long dash) represents the measured P-AL whereas the grey line (short dash) depicts the measured P-Olsen value. For the unfertilized Fors site, the P-AL value is outside the scale of the y axis (164.2 mg P kg^{-1} soil)

3.3 | Isotopically exchangeable phosphorus

The parameters of the IEK model and the calculated E values for P_{max} = P-ox are presented in Table 5 (for P_{max} = P-inorg see Appendix S1: Table S2), and the r^2 and p values for all relationships between the IEK parameters and both soil properties and the pools and desorption rates from the Lookman model are found in Appendix S1: Tables S5 and S6. Consistently, fertilized treatments had higher values for C_p, m and E, and lower values for n, compared with the corresponding values from the unfertilized treatment ($p < .05$). The $E_{1\ min}$ was related to Q_1 (power, $r^2 = .87$, $p < .01$), and $E_{1\ day}$-$E_{1\ min}$ was related to both Q_1 and Q_2 (power and linear, $r^2 = .75$ and 0.65, respectively, $p < .01$). Further, for all soils except the fertilized treatment at the Fors site, $E_{1\ day}$-$E_{1\ min}$ was larger than Q_1. There was a relationship between $E_{3\ months}$-$E_{1\ day}$ and Q_2 (linear, $r^2 = .57$, $p < .01$). Additionally, both were related to Al-ox + Fe-ox and to organic C, suggesting that they are in part controlled by similar soil properties. There was

TABLE 4 Fitted desorption parameters k_1, k_2, Q_1 and Q_2 with 95% confidence intervals for the Lookman model according to PEST

Location		Q_1 (mg kg^{-1})	Q_2 (mg kg^{-1})	ln k_1 (h^{-1})	ln k_2 (h^{-1})	R^2
Ekebo	A3	8.1 (5.6, 10.5)	375 (373, 378)	−3.7 (−4.3, −3.1)	−9.7 (−10.1, −9.4)	0.991
	D3	34.7 (27.3, 42.1)	754 (746, 761)	−3.5 (−4.0, −3.0)	−8.5 (−8.7, −8.4)	0.997
Fjärdingslöv	A3	4.3 (3.4, 5.3)	135 (134, 136)	−3.4 (−3.6, −2.9)	−9.4 (−9.7, −9.1)	0.995
	D3	46.8 (38.1, 55.4)	350 (341, 358)	−2.7 (−3.2, −2.1)	−7.8 (−8.1, −7.6)	0.985
Fors	A3	6.8 (5.6, 7.7)	466 (465, 467)	−2.9 (−3.4, −2.3)	−9.8 (−10.0, −9.7)	0.993
	D3	86.4 (76.2, 96.6)	554 (544, 564)	−2.9 (−3.3, −2.6)	−8.4 (−8.7, −8.1)	0.992
Högåsa	A3	11.2 (8.7, 13.6)	395 (393, 398)	−4.0 (−4.4, −3.6)	−9.3 (−9.5, −9.1)	0.998
	D3	49.6 (38.1, 60.7)	613 (602, 625)	−3.4 (−4.0, −2.9)	−8.3 (−8.5, −8.0)	0.994
Kungsängen	A3	8.7 (6.8, 10.5)	494 (492, 496)	−3.9 (−4.3, −3.5)	−10.2 (−10.5, −9.9)	0.997
	D3	113 (84.2, 142)	821 (792, 850)	−3.8 (−4.3, −3.4)	−8.3 (−8.7, −7.9)	0.995
Vreta kloster	A3	4.7 (4.0, 7.7)	322 (319, 322)	−3.1 (−3.5, −2.7)	−10.7 (−11.0, −10.4)	0.991
	D3	73.4 (60.4, 96.6)	548 (525, 561)	−2.9 (−3.4, −2.4)	−8.2 (−8.5, −7.8)	0.986

also a strong relationship between $E_{>3\text{ months}}$ and Q_2 (linear, $r^2 = .84$, $p < .001$).

Regarding the parameters that are related to the mass transfer rates of P, there was an inverse relationship between the IEK parameter n and the rate of desorption from both the fast and the slowly desorbing P pools k_1 (linear, $r^2 = .53$, $p < .01$, Figure 4a) and k_2 (linear, $r^2 = .52$, $p < .01$, Figure 4b). There was also an inverse relationship between n and Q_1 (linear, $r^2 = .52$, $p < .01$), a relationship between m and Q_1 (power, $r^2 = .40$, $p < .05$) and another relationship between C_p and Q_1 (power, $r^2 = .91$, $p < .001$).

As for the relationships between IEK parameters and extractable P, there was a relationship between n and the P-Olsen/P-$CaCl_2$ ratio (power, $r^2 = .87$, $p < .01$, Figure 3b). Additionally, the soil properties pH, organic C, Al-ox, Fe-ox and the ratio of organic C to Al-ox + Fe-ox all had significant relationships to various E values (r^2- and p values in Appendix S1: Tables S5 and S6).

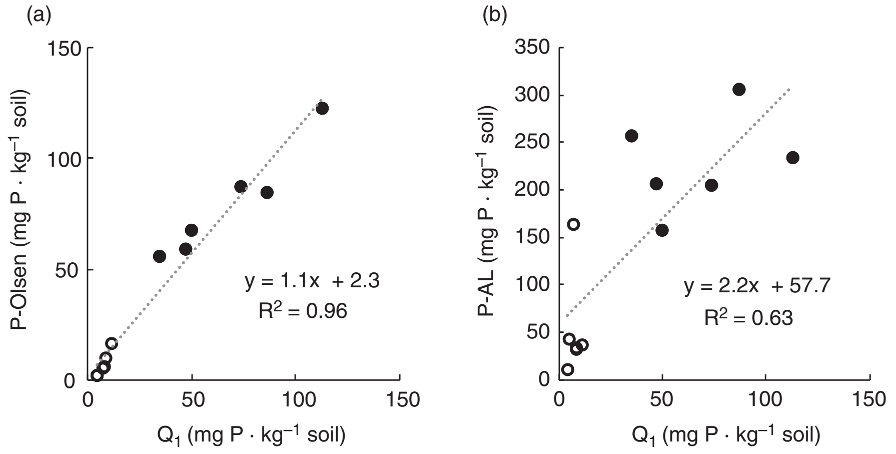

FIGURE 2 The amount of fast desorbing P, Q_1, derived from the Lookman model versus (a) P-Olsen and (b) P-AL. Filled circles represent treatments that received P fertilizer (D3), and unfilled circles represent treatments with no P fertilizer (A3)

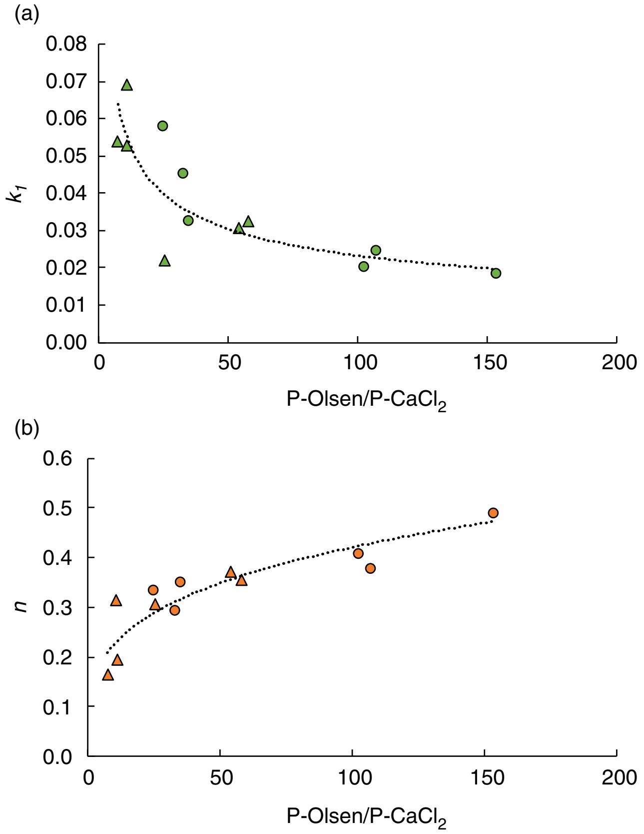

FIGURE 3 The ratio of P-Olsen/P-CaCl$_2$ as related to (a) the k_1 parameter of the Lookman model (Equation 2) and (b) the IEK parameter *n* (Equation 4). Circles denote unfertilized treatments, and triangles denote fertilized treatments

4 | DISCUSSION

4.1 | The relationships between desorption and isotopic exchange

Our analysis showed that the Fh paper method and the IEK method deliver similar information in terms of P pools. There were significant relationships between the parameters describing the fast reacting P such as the size of the fast desorbing pool (Q_1), and the pools of isotopically exchangeable P ($E_{1\text{ min}}$, and $E_{1\text{ day}}$-$E_{1\text{ min}}$), showing that even if these methods are based on different principles, the IEK method can be used to estimate the size of the fast desorbing P pool. However, since the maximum amount of P available for desorption or exchange in the Lookman and IEK models was estimated with P-ox, the strong relationships between this pool and the slowly desorbing pool (Q_2) or $E_{>3\text{ months}}$ should not be given much significance. Similarly, the relationship between Q_2 and $E_{>3\text{ months}}$ is mostly explained by the fact that both accounted for a major part of P-ox.

As for the rates of mass transfer, the significant relationships between *n* and the rates of desorption, k_1 and k_2, show that a soil with a low value for *n* has a faster rate of desorption. The parameter *n* describes the rate of removal of radioactivity from solution after 1 min (Fardeau, 1993), and a low value for *n* indicates a soil with high concentrations of ‘available’ (or fast desorbing) P (Frossard et al., 1989), consistent with the observations of lower values for *n* in the fertilized treatments in the current study. Additionally, the k_2 values in the fertilized treatments were significantly higher than for the corresponding unfertilized treatments. This can be explained by the decrease of the net charge of the adsorbing soil particles that results from diffusive penetration of PO_4 oxyanions into the particle and their subsequent adsorption (Barrow, 1983, 2015). With time, this decrease in net charge also decreases a soil's ability to adsorb added P, leading to a larger fraction of soil P in solution (Barrow & Debnath, 2014). After long-term addition of high amounts of fertilizer P the net diffusive penetration of P into soil particles will be reduced, which reduces P sorption (Barrow & Debnath, 2014). As a consequence, a soil with a long history of high P fertilizer addition is more likely to have a larger fraction of soil P in solution and to release P quickly. By contrast, the values for k_1 were not governed by the net mass P balance, but were instead inversely related to the solid–solution partitioning of the fast desorbing P as estimated by P-Olsen/P-CaCl$_2$, and by the soil properties Fe-ox, Al-ox + Fe-ox and the (Al-ox + Fe-ox)/organic C ratio. This suggests that the desorption rate of the fast desorbing pool is mostly governed by the partitioning of P between the dissolved and sorbed phases, which in turn is determined by soil properties related to P sorption such as the soil content of Al and Fe (hydr)oxides and organic C. However, as long-term P fertilization will affect the solid–solution partitioning of P, as previously discussed, it should indirectly affect the rate of desorption of the fast desorbing pool as well.

Morel et al. (1989) and Frossard et al. (1992) claimed that the parameter *m* (describing the fraction of radioactivity remaining in solution after 1 min of exchange) was more dependent on soil type and soil contents than on the agricultural history of the soils. However, in the current study the *m* values were consistently higher for the fertilized plots compared with the unfertilized ones at the same site. This suggests that changes in P fertilizer management do change the value of *m* over time, in agreement with the results of Morel et al. (1994). A probable explanation is that long-term fertilization causes an enrichment of P in the soil system, which leads to an increased saturation of P on the surfaces of soil (hydr)oxides, and therefore to fewer free or unsaturated binding sites (Bache and Williams 1971). Since the *m* parameter is inversely related to the sorption capacity of the soil (Morel et al., 1994; Sen Tran et al., 1988), it will be affected by this change as well. In contrast to a number of earlier studies (Frossard et al., 1992; Demaria 2004; Achat et al., 2016), we were

TABLE 5 IEK parameters C_p, m, and n, and the isotopically exchangeable P (E) at 1 min, 20 days, 1 min to 1 day, 1 day to 3 months and > 3 months of exchange

Location		C_p	m	n	E_{1min}	$E_{20\ days}$	E_{1day} - E_{1min}	$E_{3\ month}$ - $E_{1\ day}$	$E_{>3\ months}$
							mg P·kg soil^{-1}		
Ekebo	A3	0.05	0.17	0.34	3.09	77.0	29.3	80.3	271
	D3	0.48	0.33	0.31	14.6	241	103	207	464
Fjärdingslöv	A3	0.04	0.19	0.31	2.12	37.4	15.5	33.8	87.5
	D3	2.02	0.54	0.17	37.4	140	60.6	66.4	232
Fors	A3	0.06	0.45	0.29	1.37	25.6	9.74	27.3	435
	D3	2.95	0.79	0.13	36.7	114	45.9	50.9	507
Högåsa	A3	0.09	0.50	0.46	1.56	127	40.5	150	214
	D3	0.85	0.84	0.30	8.88	171	72.4	154	428
Kungsängen	A3	0.04	0.15	0.39	2.27	99.1	33.5	118	349
	D3	1.09	0.35	0.24	31.0	255	115	180	608
Vreta Kloster	A3	0.04	0.34	0.32	1.24	31.0	11.3	34.9	279
	D3	3.88	0.59	0.17	65.3	233	99.7	106	351

not able to find any significant correlations between *m* and soil properties. Possibly this can be explained by the relatively small number of samples and by the small variation between soils in terms of Al-ox and Fe-ox (Table 1). Achat et al. (2016) found significant relationships between the IEK parameters C_p, *m* and *n*, and the ratio of organic C to Al-ox + Fe-ox for grasslands, but not for croplands. Consistent with the above reasoning, no such relationships were found in the current study.

4.2 | Routine assessment of desorbable P

Neither of the two kinetic methods used in the current study are suitable for routine soil testing, so to what extent can pools and rates of mass transfer be predicted using commonly used soil tests and extractions? Firstly, the close correspondence between the Lookman model parameter Q_1 and P-Olsen is striking. It confirms previous studies (Guo et al., 1996; Menon et al., 1991; Moody et al., 2013) showing that P-Olsen approximates the pool of fast desorbing P, although the latter was determined in slightly different ways than in the current study. The AL test was more weakly related to Q_1 (Figure 4b) and is likely to include slowly desorbing soil P in addition to that of the fast desorbing P pool. Consistent with this, Braun et al. (2019) showed that the AL test solubilized a larger fraction of P that is not isotopically exchangeable, particularly for soils dominated by calcium phosphates. There were strong relationships (i) between P-Olsen and the fast desorbing P pool, Q_1, and (ii) between the P-Olsen/P-$CaCl_2$ ratio and both the rate of desorption from the fast desorbing pool and the rate of isotopic exchange at $t = 1$ min. In addition, there was an inverse relationship between k_2 and the P-ox/P-Olsen ratio. Together, P-CaCl2, P-Olsen and P-ox could provide information on the size and availability to desorption of the fast and slowly desorbing P pools, which could not be obtained by the use of a single extraction.

5 | CONCLUSIONS

The two studied kinetic methods, P desorption in the presence of Fh papers and ionic exchange kinetics, were hypothesized to deliver similar types of information on the size of the fast desorbing pool and the rates of mass transfer between the solid and the solution phase. This was shown to be correct by the relationships found between the model parameters optimized for each method, most importantly between $E_{1\ min}$ and the fast desorbing pool, Q_1, and between the IEK parameter *n*, describing the rate of exchange at $t = 1$ min, and the rates of desorption, k_1 and k_2, of the Lookman model. Our results also show that soils with higher values of *n* have a lower rate of desorption, a connection that was not previously known. Additionally, relationships were found between model parameter values and the results from classical chemical P extractions, which can be used to improve the interpretation of routine soil P testing results. A 'package' of routine tests consisting of extractions with $CaCl_2$, Olsen and oxalate could provide information on the intensity factor (P-$CaCl_2$), the pool of fast desorbing P (P-Olsen), the rate of P desorption for the fast desorbing pool (the P-Olsen/P-$CaCl_2$ ratio) and the rate of P desorption for the slowly desorbing pool (the P-ox/P-Olsen ratio). The implementation of this package in Swedish routine soil P assessment would provide a more accurate assessment of the size and availability of soil

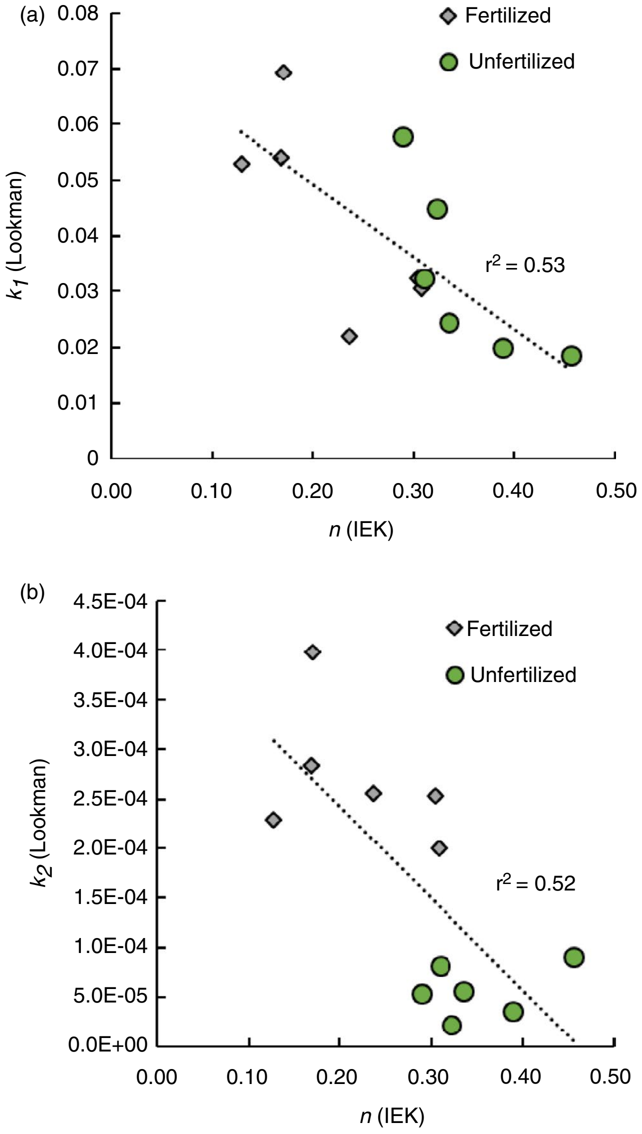

FIGURE 4 Relationships between the IEK parameter *n* (unitless) and (a) the Lookman parameter k_1 (hr^{-1}), (linear, $r^2 = .53$) and, (b) the Lookman parameter k_2 (hr^{-1}), (linear, $r^2 = .52$)

P for plant uptake and leaching, than the currently used AL extraction.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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