


Phosphorus sorption on tropical soils with relevance to Earth system model needs

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Abstract. Phosphorus (P) availability critically limits the productivity of tropical forests growing on highly weathered, low-P soils. Although efforts to incorporate P into Earth system models (ESMs) provide an opportunity to better estimate tropical forest response to climate change, P sorption dynamics and controls on soil P availability are not well constrained. Here, we measured P and dissolved organic carbon (DOC) sorption isotherms on 23 soils from tropical Oxisol, Ultisol, Inceptisol, Andisol, and Aridisol soils using P concentrations from 10 to 500 mg P L⁻¹, and DOC concentrations from 10 to 100 mg DOC L⁻¹. Isotherms were fit to the Langmuir equation and parameters were related to soil characteristics. Maximum P sorption capacity (Q_{max}) was significantly correlated with clay content ($\rho = 0.658$) and aluminium (Al)- or iron (Fe)-oxide concentrations ($\rho = 0.470$ and 0.461 respectively), and the DOC Q_{max} was correlated with Fe oxides ($\rho = 0.491$). Readily available soil characteristics could eventually be used to estimate Q_{max} values. Analysis of literature values demonstrated that the maximum initial P concentration added to soils had a significant impact on the resultant Q_{max} , suggesting that an insufficiently low initial P range could underestimate Q_{max} . This study improves methods for measuring P Q_{max} and estimating Q_{max} in the absence of isotherm analyses and provides key data for use in ESMs.

Additional keywords: adsorption isotherm, clay, dissolved organic carbon, iron oxide, phosphorus adsorption.

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Introduction

Tropical rainforests play a key role in the uptake of carbon dioxide (CO₂) due to their substantial productivity (Pan *et al.* 2011; Yang *et al.* 2014). Many tropical soils are highly weathered, and tropical forests are generally considered P limited, such that the extent to which tropical forests can continue to take up CO₂ in the future is critically influenced by P availability (Walker and Syers 1976; Elser *et al.* 2007; Pan *et al.* 2011; Yang *et al.* 2014; Wieder *et al.* 2015; Sun *et al.* 2017). However, the P cycle has only recently been incorporated into Earth system models (ESMs) (Wang *et al.* 2010b; Goll *et al.* 2012; Yang *et al.* 2014). Reed *et al.* (2015) identified critical P dynamic processes controlling soil P availability that could be better represented in ESMs, with particular emphasis on P interactions with mineral soils.

Strong adsorption of inorganic phosphate anions (PO₄³⁻) to mineral soils exerts a key control on the availability of P to plants and microbes (Lloyd *et al.* 2001). Phosphate anions initially attach to the highest energy binding sites and then fill lower energy sites (McGechan and Lewis 2002). As P anions accumulate at binding sites, the soil particle surfaces become

increasingly negative, decreasing the affinity for P anions as P concentrations increase (Barrow 1978). The prioritisation of higher energy sites before lower energy sites, and a decreasing binding affinity with increasing concentrations results in a nonlinear isotherm where P removal is very strong at low concentrations (Barrow 1978; McGechan and Lewis 2002). Traditionally, the sorption properties of soils have been estimated through two parameters in the Langmuir equation, the maximum sorption capacity (Q_{max}) and the binding energy coefficient (k) (Barrow 1978; Anghinoni *et al.* 1996). At least three current ESMs include a P cycle, and all assume sorption capacity is higher in weathered and reactive soils common to the tropics, e.g. Oxisols and Andisols (Wang *et al.* 2007; Goll *et al.* 2012; Yang *et al.* 2014; Yang *et al.* 2016). However, there is a lack of P sorption studies related to tropical soils (Fontes and Weed 1996; Sato and Comerford 2005; Munhoz *et al.* 2011) compared with other environments (Anghinoni *et al.* 1996; Gichangi *et al.* 2008; Cannon 2010; Bastounopoulou *et al.* 2011).

A wide spectrum of Q_{max} and k values in P isotherm studies have been reported for both temperate and tropical soils.

For temperate soils, reported Q_{\max} values for North American Ultisols ranged from a mean value of 243 mg P kg⁻¹ (Cannon 2010) to a mean value of 2222 mg P kg⁻¹ (Anghinoni *et al.* 1996) (Table S1, available as Supplementary Material to this paper). The same variability among and within soil orders exists for tropical soils. Phosphorus Q_{\max} values ranged from 305 to 4487 mg P kg⁻¹ in Brazilian Oxisols (de Campos *et al.* 2016), and from 3237 mg P kg⁻¹ in an Ultisol to 78616 mg P kg⁻¹ in an Inceptisol (Poudel and West 1999). The specific causes of wide variability have yet to be pinpointed, but there are three sparsely discussed but critical aspects of P sorption. First, Q_{\max} can be underestimated due to low initial P concentrations added to the soils (Harter 1984). Tropical soils are particularly prone to this potential source of error due to their high P sorption capacities (Walker and Syers 1976; Fontes and Weed 1996; Poudel and West 1999; Elser *et al.* 2007; Auxtero *et al.* 2008; Yang *et al.* 2014; de Campos *et al.* 2016). Further, there is an absence of reported parameter uncertainties in the current literature, such as standard error or confidence intervals (Ryden *et al.* 1977; Fox 1982; Anghinoni *et al.* 1996; Fontes and Weed 1996; Gichangi *et al.* 2008; Bastounopoulou *et al.* 2011; Munhoz *et al.* 2011). Without these uncertainty values, it is difficult to compare sorption parameters from different studies in the same context. Finally, sorption isotherms are often fitted to the Hanes–Woolf linearised form of the Langmuir equation (Ryden *et al.* 1977; Fox 1982; Anghinoni *et al.* 1996; Fontes and Weed 1996; Gichangi *et al.* 2008; Bastounopoulou *et al.* 2011; Munhoz *et al.* 2011). The axes of a linearised isotherm are not truly independent of one another because the sorbed concentration (y -axis) is calculated from the equilibrium solute concentration (x -axis). A nonlinear fit is now recommended to avoid an overestimation of correlation between axes (Bolster and Hornberger 2007).

ESMs could readily exploit quantitative relationships between more widely measured soil physicochemical properties and phosphate sorption, if such relationships were available. Sorption of P in tropical soils has been shown to have a strong association with iron (Fe) and aluminium (Al) oxides (Fontes and Weed 1996), which is expected given that the content of Fe- and Al-oxide minerals and the buffering capacity of acidic soils are often directly proportional (McGechan and Lewis 2002). The small particle sizes and high specific surface areas of clays can enhance binding of P (McGechan and Lewis 2002). Soil pH may also impact soil P sorption parameters, as a lower pH results in a more positive charge on hydrous oxides, thus attracting P anions (Sparks 1995). The role of physical characteristics in P sorption is complex, but quantitative relationships between soil properties and sorption can be obtained (Kothawala *et al.* 2009; Mayes *et al.* 2012).

The goal of this work is to provide improved quantitative information on P sorption in tropical soils that can be used to improve parameterisation in ESMs. Our specific objectives were to generate P sorption isotherms and Langmuir parameters Q_{\max} and k of A and B horizon soils from locations across the tropical climate zone, and to determine whether any soil characteristics significantly contributed to the variation of observed soil P sorption parameters.

Materials and methods

Soil selection

Twenty-three tropical soils and one sub-tropical soil from both A and B horizons were selected for analysis from an archive of air-dried and sieved (2 mm) soils at Oak Ridge National Laboratory (ORNL) to provide a broad representation of tropical regions (Table 1). Five soil orders (Ultisols, Aridisols, Oxisols, Andisols, and Inceptisols) were obtained from the following sources (Ryan *et al.* 2004; Bruno *et al.* 2006; Porder *et al.* 2006; Russell *et al.* 2007; Wang *et al.* 2010a; Vieira *et al.* 2011; Yavitt *et al.* 2011; Mage and Porder 2013; Jagadamma *et al.* 2014; Mayor *et al.* 2014). Further information on soil characteristics (e.g. soil origin, climate, and parent material) and reference publications can be found in Table S2 (Supplementary Material).

Soil characterisation

Samples were air-dried at room temperature for 48 h, ground with mortar and pestle, and passed through a 2-mm sieve to remove roots and small rocks. Soil pH was measured in a 0.005 M CaCl₂ solution at a 2:1 solution to solid ratio. Total Fe and Al oxides were extracted and determined by the dithionate-citrate-bicarbonate (DCB) method (Loeppert and Inskeep 1996) and analysed by inductively coupled plasma mass spectrometry (ELAN-1600, Perkin-Elmer Corporation, Waltham, MA, USA). Particle size was ascertained using the Buoycous hydrometer method (Gee and Or 2002). For carbon (C), nitrogen (N), and total organic carbon (TOC) content, soil samples were oven-dried overnight at 70°C, ground to a fine powder, and analysed on a LECO TruSpec elemental analyser.

Table 1. Subsoils used in this study

Additional information on soil origin can be found in Table S2 (Supplementary Material)

Location	Soil order	Identifier	Horizon	Depth (cm)
Kenya	Aridisol	KA-A	A	0–10
Hawaii	Andisol	HA-FA	A	10–20
Hawaii	Andisol	HA-FB	B	55–65
Brazil	Inceptisol	BR-B	A	0–10
Brazil	Inceptisol	BR-G	A	0–10
Brazil	Inceptisol	BR-N	A	0–10
Puerto Rico	Inceptisol	IC-V	A	0–10
Puerto Rico	Inceptisol	IC-RT	A	0–10
Brazil	Oxisol	BO-A	A	0–12
Brazil	Oxisol	BO-B	B	42–65
Costa Rica	Oxisol	CRO-A	A	0–15
Costa Rica	Oxisol	CRO-B	B	50–75
Puerto Rico	Oxisol	EV-V	A	0–10
Puerto Rico	Oxisol	EV-RT	A	0–10
Panama	Oxisol	P-22	A	0–10
Panama	Oxisol	P-23	A	0–10
Panama	Oxisol	P-30	A	0–10
Panama	Oxisol	P-35	A	0–10
Brazil	Ultisol	BU-BA	A	0–10
Brazil	Ultisol	BU-BB	B	37–50
China	Ultisol	CU-HSA	A	0–5
China	Ultisol	CU-HSB	B	5–10
Costa Rica	Ultisol	CRU-V	A	0–10
Costa Rica	Ultisol	CRU-RT	A	0–10

(LECO Corporation, St. Joseph, MI, USA). The TOC was determined by removing inorganic C by treating the soil with 3 M HCl for 1 h and rinsing 3 times. Total P was prepared using a Lachat digestion block and measured by a Lachat in-line sample preparation and determination instrument (Hach, Loveland, CO, USA) following the Kjeldahl method 13–115–01–1-B (Lachat Instruments, Milwaukee, WI, USA). All concentrations are expressed as a function of soil dry weight.

Phosphorus sorption isotherms

Soils (3 g) were added to 50 mL glass vials along with a 30 mL aliquot of different KH_2PO_4 concentrations, ranging from 10 to 500 mg P L^{-1} , in duplicate and in a 0.01 M CaCl_2 matrix (Graetz and Nair 2000). Blank soil samples, conducted in triplicate, were exposed only to 0.01 M CaCl_2 . Separate glass vials without soil received 30 mL of each concentration of KH_2PO_4 in 0.01 M CaCl_2 to determine the concentration of added P. Two drops of toluene were added to each vial to inhibit microbial uptake (Gichangi *et al.* 2008). Vials were capped and placed on a shaker at room temperature for 24 h at 85 oscillations per minute, centrifuged at $453\times g$ for 10 min, filtered using a Millex 0.45- μm filter, and acidified before storage and analysis (Gichangi *et al.* 2008; Bastounopoulou *et al.* 2011). Phosphorus remaining in the supernatant was measured by the molybdenum blue method (Murphy and Riley 1962; Drummond and Maher 1995), utilising the Lachat as described above. Supernatant P, and resulting P sorption maximum values, were reported as mg of orthophosphate as phosphorus, or mg $\text{PO}_4\text{-P}$, per kg dry weight of soil. Dissolved P in the samples was confirmed to be in the form of PO_4^{-3} via ion chromatography (Dionex ICS-2100, Sunnyvale, CA, USA).

Dissolved organic carbon isotherms

Dissolved organic carbon (DOC) isotherms were determined using a C stock acquired from a stream in Georgetown, SC (Gu *et al.* 1994; Chen *et al.* 2002). A 30-mL aliquot of DOC concentrations, ranging from 2.5 to 100 mg C L^{-1} in 0.01 M NaCl, was added to glass vials containing 0.5 g of the <2 mm fraction soil, in duplicate (Mayes *et al.* 2012). Blank soil samples, conducted in triplicate, were exposed only to 0.01 M NaCl. Vials without soil also received 30 mL of each DOC concentration to determine initial DOC added. Vials were shaken and centrifuged as described above. The supernatant was analysed using a Shimadzu TOC-L CSH/CSN analyser (Shimadzu Corp., Kyoto, Japan).

Fitting to the Langmuir equation

Phosphorus and DOC sorbed concentrations were calculated using the Fox and Kamprath (1970) procedure, where the amount sorbed was calculated as the difference between the concentration added and the concentration remaining in the supernatant. Sorption data were fitted to the non-linear form of the Langmuir equation (Eqn 1) from Mayes *et al.* (2012) to provide a curve and sorption parameters, utilising a method developed by Bolster and Hornberger (2007), which also calculated the standard error (s.e.) for each parameter, and the goodness-of-fit for the entire equation. In this case, goodness-of-fit measured model efficiency (E), where $E=1$ (or 100%) indicated that the model perfectly fit the data.

Equations used to calculate s.e. and E can be found in Bolster and Hornberger (2007).

$$RE = (k \times Q_{\max} \times X_f) / (1 + (k \times X_f)) \quad (1)$$

where RE is the amount of P or DOC adsorbed or desorbed (mg kg^{-1} soil), X_f is the final measured equilibrium solution concentration (mg L^{-1} solution), Q_{\max} is the maximum sorption capacity (mg kg^{-1} soil), and k is the binding affinity coefficient ($\text{L solution mg}^{-1}$).

Statistical analysis

Data reported as percentage values were square-root transformed to account for constrained data and conformed to parametric data assumptions for analysis. Data were analysed in JMP 13.2.1 (SAS Institute Inc., Cary, NC, USA). For normally distributed data, analysis of variance (ANOVA) was applied to assess variance by soil order, where $P < 0.05$ indicated significant differences. A post-hoc Tukey's test was used to determine where those differences occurred. Variance in non-normal data was determined by a Wilcoxon rank test, where $P < 0.05$ indicated significant difference. A post-hoc Dunn's multiple comparison test for pairs was performed to determine where those differences occurred. A Spearman rank test was performed to assess the presence of any statistically significant correlations between Langmuir model sorption parameters (Q_{\max} and k) and soil characteristics. Correlations were considered statistically significant for correlation coefficients that had a $P < 0.05$, and where significant, the strength of correlation was shown by the Spearman correlation coefficient (ρ).

Results

By fitting the isotherms to the Langmuir equation, the resultant Q_{\max} values ranged from 733.8 mg $\text{PO}_4\text{-P kg}^{-1}$ (Kenya Aridisols, KA-A) to 3775 mg $\text{PO}_4\text{-P kg}^{-1}$ (Costa Rica Oxisol, CRO-A) (Table 2), and the mean Q_{\max} value for all soils was 2060 mg $\text{PO}_4\text{-P kg}^{-1}$ (standard deviation (s.d.) = 767.7). Hawaii Andisols did not reach a sorption maximum over the range of initial P concentrations used in this study, so their isotherm was not represented using the Langmuir equation. To assess correlation and variance among sorptive and physical soil characteristics, soils were pooled together for correlation analysis, and by soil order for variance. Due to low sample size, only Inceptisol, Oxisol, and Ultisol soils were included in the variance analysis. Despite the broad range of values, P Q_{\max} values did not display any significant difference among soil orders (ANOVA, $P=0.07$) (Fig. 1).

KA-A and CRO-A also represented the lowest and highest Q_{\max} values for DOC sorption, establishing a DOC Q_{\max} range of 310.0–6212 mg C kg^{-1} and a mean of 1876 mg C kg^{-1} (Table 3). Although an initial Wilcoxon test indicated variance (Wilcoxon, $P=0.02$), a post-hoc Dunn's comparison test exhibited no significant differences among DOC Q_{\max} values by soil order (Dunn's, $P > 0.05$).

The sorption maxima for P and DOC were significantly positively correlated with each other (Fig. 2). There were no significant relationships among the binding coefficients (Table 4).

Table 2. Phosphorus sorption isotherm parameters

Phosphorus sorption isotherm maximum (Q_{max}), binding affinity coefficient (k), respective standard errors (s.e.), and goodness-of-fit (E) values estimated by fitting the isotherms to the Langmuir equation

Identifier	Soil order	Q_{max} (mg kg ⁻¹)	Q_{max} s.e.	k (L mg ⁻¹)	k s.e.	E (%)
KA-A	Aridisol	733.8	69.5	0.020	0.005	93.4
BR-B	Inceptisol	1793.6	120.9	0.061	0.012	94.9
BR-G	Inceptisol	2124.5	128.4	0.161	0.033	95.0
BR-N	Inceptisol	2044.4	153.0	0.080	0.017	93.7
IC-V	Inceptisol	2059.4	185.7	0.112	0.056	75.6
IC-RT	Inceptisol	1474.1	152.7	0.103	0.041	85.0
BO-A	Oxisol	2177.1	259.7	0.123	0.052	90.3
BO-B	Oxisol	2156.3	85.5	0.134	0.018	98.7
CRO-A	Oxisol	3775.3	411.2	0.031	0.011	85.3
CRO-B	Oxisol	3693.4	353.1	0.043	0.016	78.6
EV-V	Oxisol	2680.3	161.3	0.077	0.022	92.7
EV-RT	Oxisol	1769.4	208.8	0.120	0.051	84.5
P-1	Oxisol	2171.4	122.6	0.037	0.005	98.1
P-6	Oxisol	2303.6	151.4	0.055	0.010	96.0
P-22	Oxisol	2243.4	255.4	0.025	0.010	84.3
P-30	Oxisol	1845.0	139.0	0.042	0.009	95.5
BU-BA	Ultisol	1364.9	217.5	0.026	0.013	88.9
BU-BB	Ultisol	1046.5	83.2	0.079	0.032	90.3
CU-HSA	Ultisol	1556.8	372.8	0.015	0.009	86.7
CU-HSB	Ultisol	1228.8	240.7	0.067	0.059	69.2
CRU-V	Ultisol	3010.2	188.8	0.285	0.090	91.0
Mean values		2059.6	167.5	0.081	0.014	—

Clay content ranged from 2.25% (Hawaii Andisol, HA-FB) to 67.7% (Costa Rica Oxisol, CRO-B) (Table 5). An initial test of variance indicated that clay content varied by soil order (Wilcoxon, $P=0.02$), though a post-hoc Dunn's comparison did not illustrate significant difference (Dunn's, $P > 0.05$). Andisols were primarily composed of sand-sized particles (mean = 65.1%, s.d. = 5.60%), and Oxisols had significantly less sand than both Inceptisols and Ultisols (Tukey, $P < 0.05$).

To determine correlative relationships between Q_{max} and reactive soil properties, the pooled soils were regressed against particle size, pH, Al- and Fe-oxide content, P, C, and TOC (Kothawala *et al.* 2009; Mayes *et al.* 2012). Phosphorus sorption maxima exhibited a significant positive correlation with clay content, and a negative correlation with sand content (Table 6, Fig. 3), but no correlations with particle size were found for DOC sorption maxima (Table 6).

Although Al- and Fe-oxide concentrations did not exhibit significant differences by soil order (ANOVA, $P=0.19$ and 0.33 respectively), both covered a wide range of values, with Andisols representing the highest observed Al- and Fe-oxide concentrations. The greatest Al-oxide concentration (9.93 mg g⁻¹, Hawaii Andisol, HA-FA) was greater than the lowest observed concentration (0.35 mg g⁻¹, Puerto Rico Ultisol, IC-V) by a factor of 28, and the greatest Fe-oxide concentration (90.5 mg g⁻¹, Hawaii Andisol, HA-FB) was greater than the lowest observed concentration (1.55 mg g⁻¹, Brazil Ultisol, BU-BA) by a factor of 58 (Table 5). Total P, Al- and Fe-oxides were all positively correlated with P Q_{max} values (Table 6, Fig. 4), whereas Fe-oxides were the only physical characteristic correlated with DOC Q_{max} values (Table 6).

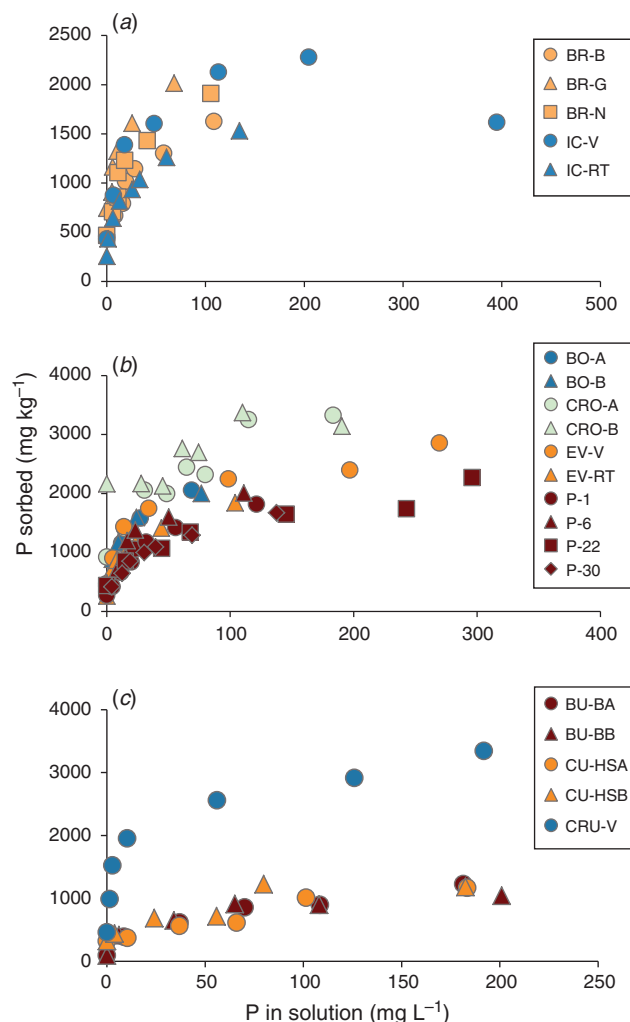


Fig. 1. Scatter plots depicting the shape of phosphorus (P) sorption isotherms for (a) Inceptisols, (b) Oxisols, and (c) Ultisols. Legends indicate soil identifiers listed in Table 1.

The C content ranged from 0.65% (Brazil Ultisol, BU-BB) to 10.5% (Hawaii Andisol, HA-FB) (Table 5). The TOC was lowest in the Kenya Andisol (KA-A, 50.8 mg kg⁻¹), and greatest in the Panama Oxisol P-23 (465 mg kg⁻¹) (Table 5). Neither C content nor TOC displayed variance by soil order (ANOVA, $P=0.75$; Wilcoxon, $P=0.45$ respectively). Total P, however, was sensitive to soil order (Tukey, $P=0.02$); Oxisols in our database (mean = 612 mg P kg⁻¹, s.d. = 219, $n=10$) had significantly more total P than Ultisols (mean = 295 mg P kg⁻¹, s.d. = 193, $n=5$) (Table 5). No correlations were observed between sorption maxima and C, TOC, or P in the pooled soils (Table 7).

The soils were acidic, with a mean pH of 4.70 (s.d. = 0.73) (Table 5), which was not sensitive to soil order, though Hawaii Andisols exhibited the highest observed pH values (5.90 and 5.84, HA-FA and HA-FB respectively), and Costa Rica and China Ultisols the lowest (3.58 and 3.66, CRU-V and CU-HSA respectively). No correlations were observed between sorption maxima and pH in the pooled soils (Table 6).

Table 3. Dissolved organic carbon (DOC) sorption isotherm parameters

DOC sorption isotherm maximum (Q_{max}), binding affinity coefficient (k), respective standard errors (s.e.), and goodness-of-fit (E) values estimated by fitting the isotherms to the Langmuir equation

Identifier	Soil order	Q_{max} (mg kg ⁻¹)	Q_{max} s.e.	k (L mg ⁻¹)	k s.e.	E %
KA-A	Aridisol	310.0	47.3	0.089	0.044	81.5
HA-FA	Andisol	4338.6	277.0	0.053	0.007	99.4
HA-FB	Andisol	1426.2	310.7	0.024	0.010	93.9
BR-B	Inceptisol	1691.9	118.3	0.042	0.007	98.5
BR-G	Inceptisol	1220.8	37.8	0.123	0.012	99.0
BR-N	Inceptisol	1239.3	153.6	0.042	0.012	94.6
IC-V	Inceptisol	1215.9	101.9	0.109	0.028	94.2
IC-RT	Inceptisol	1278.7	179.2	0.080	0.032	89.3
BO-A	Oxisol	1264.5	176.4	0.037	0.012	94.9
BO-B	Oxisol	1858.0	290.0	0.067	0.028	90.8
CRO-A	Oxisol	1929.1	160.4	0.068	0.015	97.0
CRO-B	Oxisol	6212.4	240.9	0.100	0.008	99.7
EV-V	Oxisol	2012.6	230.6	0.103	0.034	92.8
EV-RT	Oxisol	2560.1	505.6	0.028	0.010	95.5
P-1	Oxisol	1375.8	154.0	0.042	0.011	95.2
P-6	Oxisol	2214.9	407.6	0.022	0.008	95.2
P-30	Oxisol	2559.8	347.9	0.017	0.004	98.2
P-36	Oxisol	1528.7	182.0	0.061	0.019	92.1
BU-BA	Ultisol	673.2	227.2	0.015	0.009	91.3
BU-BB	Ultisol	1087.6	60.5	0.132	0.026	97.3
CU-HSA	Ultisol	975.9	172.3	0.017	0.006	96.0
CU-HSB	Ultisol	2297.6	234.4	0.016	0.003	99.1
Mean values		1876.0	271.5	0.059	0.008	–

Some correlations between physical properties were observed. The C content was positively correlated with TOC, Al-oxides, and Fe-oxides, but not with total P, although total P was correlated with TOC (Table 7). Total P, Al- and Fe-oxides were also all positively correlated with one another (Table 7).

Discussion

Langmuir sorption parameters

The Langmuir isotherm fits provided adequate representations of the P and DOC isotherms, with acceptable s.e. and E values. Both DOC and P isotherms were also fit to the Freundlich equation because it has been shown to provide a better fit than Langmuir for P (Bolster and Hornberger 2007); however, our Langmuir fits were superior with lower s.e. and higher E values (Brenner *et al.* 2018). Consequently, only Langmuir fits are discussed here. Despite the wide range of P Q_{max} values in this study, there was no significant difference among soil orders. Studies have shown that highly weathered soils (i.e. Oxisols and Ultisols) have greater P sorption capacities than less weathered soils (i.e. Inceptisols) (Oades *et al.* 1989; Yang and Post 2011), and soils with higher amounts of variable charge minerals (i.e. Oxisols and Andisols) also typically have greater P sorption capacities (Oades *et al.* 1989). Although the absence of significantly different P sorption maxima observed here was unexpected based on the existing literature, it is likely due to the small sample size of the individual soil orders studied, and the relatively high variation in sorption values, particularly the Ultisols (Fig. 1c).

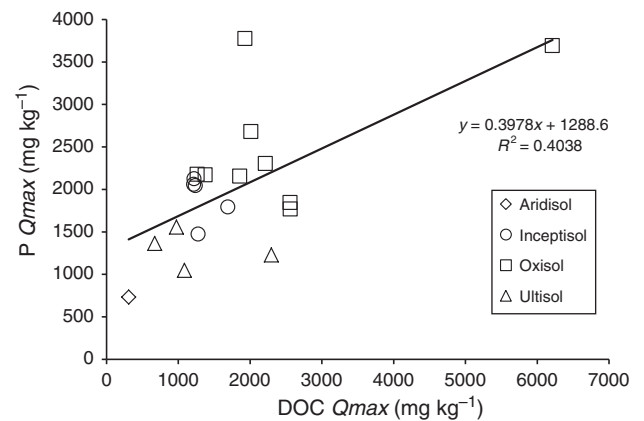


Fig. 2. Linear regression displaying the relationship between Langmuir-derived sorption maxima (Q_{max}) of dissolved organic carbon (DOC) and phosphorus (P).

Table 4. Spearman correlation coefficients (ρ) among Langmuir-derived sorption parameters

Phosphorus (P) and dissolved organic carbon (DOC) sorption isotherm maxima (P and DOC Q_{max} respectively), and P and DOC binding affinity coefficient (P and DOC k respectively) estimated by the Langmuir equation. * $P < 0.05$

	Q_{max} (P)	k (P)	Q_{max} (DOC)	k (DOC)
Q_{max} (P)	–			
k (P)	0.152 ^A	–		
Q_{max} (DOC)	0.483* ^B	0.132 ^B	–	
k (DOC)	0.193 ^B	0.361 ^B	–0.137 ^C	–

^A $n = 21$, ^B $n = 19$, ^C $n = 22$.

Correlation of Langmuir parameters with soil physiochemical properties

Phosphorus sorption maxima were significantly correlated with both Al- and Fe-oxides, which is in agreement with others that have assessed sorption parameter relationships (Lopez-Hernandez and Burnham 1974; Sakadevan and Bavor 1998; Börling *et al.* 2001; McGeachan and Lewis 2002). However, when graphing the relationship between P sorption maxima and either Al- or Fe-oxides, only 12% and 7.6% of the variation in P sorption maxima could be explained by the resulting linear regression equation respectively (Fig. 4). Gichangi *et al.* (2008) described the relationship between P Q_{max} values and DCB-extracted Al- and Fe-oxides with a quadratic function, explaining 89% and 70% of variation in P Q_{max} values respectively, indicating that these parameters provide a reliable estimation for P sorption. A quadratic function minimally improved the R^2 values for describing the relationship between P sorption maxima and either Al- or Fe-oxides (23% and 11% respectively), but since a quadratic fit is unsupported by a mechanistic rationale, the fits are not shown. The low R^2 in our linear regressions are likely a result of the small overall sample size and global distribution of soil samples; a larger sample size could potentially provide a statistically reliable equation for estimating P Q_{max} from DCB-extracted Al- and Fe-oxide concentrations.

Table 5. Selected properties of analysed soils

Carbon and nitrogen content (C, N), total organic carbon (TOC), total phosphorus (P), dithionate-citrate-bicarbonate extracted aluminium- and iron-oxides (Al-oxides and Fe-oxides respectively), pH in CaCl₂. Dashes indicate no data

Identifier	Soil order	Sand (%)	Silt (%)	Clay (%)	C (%)	N (%)	TOC (mg kg ⁻¹)	P (mg kg ⁻¹)	Al-oxides (mg g ⁻¹)	Fe-oxides (mg g ⁻¹)	pH
KA-A	Aridisol	62.60	23.88	13.53	0.78	0.032	50.76	278.75	0.54	1.64	5.64
HA-FA	Andisol	61.10	32.50	6.40	9.33	0.494	461.40	891.25	9.93	54.9	5.90
HA-FB	Andisol	69.03	28.72	2.25	10.40	0.699	452.00	896.25	8.27	90.5	5.84
BR-B	Inceptisol	45.80	21.00	33.10	3.30	0.300	235.62	–	3.67	18.5	5.21
BR-G	Inceptisol	63.40	16.80	19.90	2.60	0.220	187.68	–	5.71	17.9	4.81
BR-N	Inceptisol	63.40	17.80	18.90	2.90	0.240	145.02	–	7.29	41.2	5.16
IC-V	Inceptisol	24.45	59.54	16.00	2.77	0.178	194.28	348.75	0.35	7.40	4.10
IC-RT	Inceptisol	50.66	32.34	17.00	3.90	0.238	194.06	255.00	2.10	6.54	3.87
BO-A	Oxisol	13.38	56.56	30.06	4.78	0.316	274.84	558.75	4.48	36.4	4.39
BO-B	Oxisol	43.40	28.98	27.62	2.29	0.080	156.48	548.75	1.95	48.6	4.68
CRO-A	Oxisol	11.72	44.19	44.09	4.82	0.474	513.00	510.00	3.81	9.40	4.40
CRO-B	Oxisol	7.21	25.10	67.69	1.38	0.125	173.34	468.75	2.26	13.9	4.36
EV-V	Oxisol	15.37	54.39	30.24	2.81	0.250	133.30	348.75	0.54	4.33	4.29
EV-RT	Oxisol	30.05	48.35	21.60	7.21	0.616	272.56	494.38	3.40	27.3	3.73
P-22	Oxisol	28.33	42.75	28.92	3.87	0.431	196.22	1013.75	2.40	7.47	5.61
P-23	Oxisol	10.39	49.65	39.95	3.51	0.371	464.80	453.75	1.78	27.1	4.03
P-30	Oxisol	16.00	57.03	26.97	4.23	0.464	218.80	900.63	1.70	27.8	5.57
P-35	Oxisol	33.80	43.31	22.89	4.32	0.472	319.68	817.50	4.77	27.9	4.77
BU-BA	Ultisol	39.99	38.82	21.19	2.30	0.171	223.38	276.25	0.36	1.55	5.35
BU-BB	Ultisol	36.24	35.06	28.70	0.64	0.008	141.62	146.25	0.74	4.36	5.00
CU-HSA	Ultisol	56.02	27.87	16.11	5.00	0.336	196.00	228.75	2.13	6.94	3.66
CU-HSB	Ultisol	46.66	37.77	15.56	0.93	0.054	168.54	193.13	0.78	7.70	4.12
CRU-V	Ultisol	32.85	42.75	24.40	5.54	0.543	425.60	628.75	4.06	46.1	3.58
CRU-RT	Ultisol	20.68	32.22	47.10	4.63	0.427	430.80	493.75	1.53	28.2	3.98

Table 6. Spearman correlation coefficients (ρ) for relations among soil properties and phosphorus (P) and dissolved organic carbon (DOC) sorption maxima (Q_{max})

* $P < 0.05$

	Q_{max} (P)	Q_{max} (DOC)
Sand	–0.618* ^A	–0.373 ^A
Silt	0.256 ^A	0.223 ^A
Clay	0.658* ^A	0.284 ^A
C	0.358 ^A	0.302 ^A
TOC	0.342 ^A	0.281 ^A
P	0.686* ^B	0.480 ^B
Al-oxides	0.470* ^A	0.337 ^A
Fe-oxides	0.461* ^A	0.491* ^A
pH	–0.186 ^A	–0.068 ^A
Q_{max} (P)	–	0.483* ^A
Q_{max} (DOC)	0.483* ^A	–

^A $n = 19$, ^B $n = 16$.

Although some studies have found that Al plays a more significant role than Fe in P sorption mechanics for both temperate soils (Lopez-Hernandez and Burnham 1974; Sakadevan and Bavor 1998; Börling *et al.* 2001) and tropical soils (Fontes and Weed 1996; Poudel and West 1999; Hartono *et al.* 2005; Gichangi *et al.* 2008; Alleoni *et al.* 2012; Chimdi *et al.* 2013; de Campos *et al.* 2016), our study found that DCB-extracted Al- and Fe-oxides were similarly correlated with the P Q_{max} values ($\rho = 0.470$ and 0.461 respectively). Considering the low R^2 values for these parameters in

describing P Q_{max} , this lack of discrepancy in parameter influence is not surprising. Nonetheless, our data did indicate that particle size had a stronger influence on P sorption maxima than Al- or Fe-oxides. Clay was strongly correlated with P Q_{max} values, where 56% of the variation could be explained by the corresponding linear regression equation (Fig. 3). The high weathering rate of tropical soils leads to an abundance of clay minerals, providing a high surface area and numerous binding sites (McGechan and Lewis 2002). For ESMs, this provides evidence that information about clay content could significantly aid in the estimation of P sorption parameters for tropical soils (Lopez-Hernandez and Burnham 1974; McGroddy *et al.* 2008; Bruland and DeMent 2009; Moazed *et al.* 2010; Alleoni *et al.* 2012). Although P sorption isotherms are not often performed in routine soil analyses, particle size is a frequently measured parameter. Therefore, ESMs could derive sorption parameters via measured clay content, or even estimated clay content based on soil weathering rates, if a solid correlative relationship was available. Other researchers who have assessed relationships with physicochemical parameters disagree about which parameter has the greatest influence. Lopez-Hernandez and Burnham (1974) found that Al- or Fe-oxides had significantly more influence on P sorption than clay content in tropical Oxisols and Ultisols. Hartono *et al.* (2005) found that Al- and Fe-oxides and clay content were similarly influential in tropical Ultisols, as did de Campos *et al.* (2016) in a study that analysed tropical Alfisols, Entisols, Inceptisols, Histosols, Mollisols, Oxisols, and Ultisols.

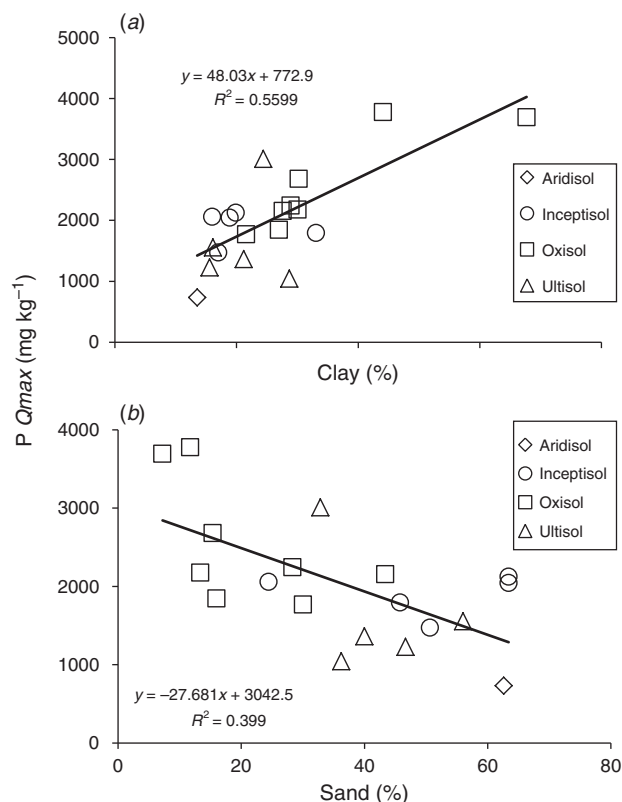


Fig. 3. Linear regression displaying the relationship between Langmuir-derived phosphorus sorption maxima ($P Q_{max}$) and (a) clay content, and (b) sand content.

The varying influence of soil physical and chemical parameters on $P Q_{max}$ values, as well as the variance of $P Q_{max}$ values themselves, may be further influenced by the soil order or parent material. This was illustrated in particular by the Hawaii Andisols, which never reached a sorption maximum. The Andisols were primarily composed of sand (Table 5), even though sand was negatively correlated with $P Q_{max}$ values throughout the dataset (Table 6, Fig. 3). The isotherm was approximately linear, indicating strong sorption, which is consistent with documented high sorption capacities of Andisols (Dahlgren *et al.* 2004; Oades *et al.* 1989; Fox and Searle 1978; Parfitt 1978). Therefore, it appears that the influence of Al- and Fe-oxides outweighed the influence of particle size among Andisols (Liptzin and Silver 2015; Dahlgren *et al.* 2004; McGeachan and Lewis 2002; Anghinoni *et al.* 1996; Mehadi and Taylor 1988; Parfitt 1978).

The relationship between P and DOC sorption maxima, though positively correlated, does not tell a straightforward story. Dissolved organic matter and humic acids can compete with P for sorption sites, which can lead to the release of sorbed P, or P can be incorporated into the sorbed complex (Tiessen *et al.* 1994; Lloyd *et al.* 2001; Frizano *et al.* 2003; Guppy *et al.* 2005). The correlation between DOC and $P Q_{max}$ values suggests that similar binding sites could be involved; however, the vast difference between DOC and $P Q_{max}$ values for different soils (ranging from 41.1 mg kg⁻¹ to 2519 mg kg⁻¹) confirms a more complex relationship. This is further complicated

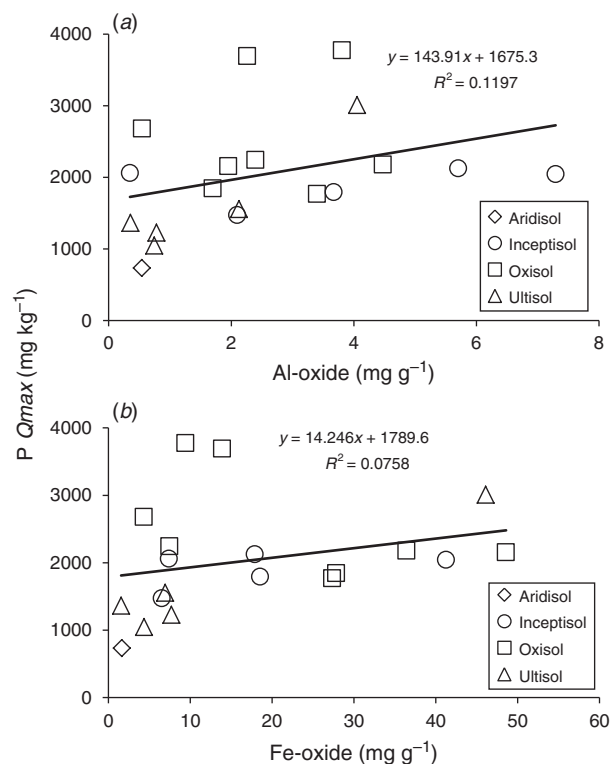


Fig. 4. Linear regression displaying the relationship between Langmuir-derived phosphorus sorption maxima ($P Q_{max}$) and (a) aluminium (Al) oxide content, and (b) iron (Fe) oxide content.

Table 7. Spearman correlation coefficients (ρ) for carbon content (C), total organic C (TOC), total phosphorus (P), and aluminium (Al) and iron (Fe) oxides

* $P < 0.05$

	C	TOC	P	Al-oxides	Fe-oxides
C	—				
TOC	0.639 ^{*A}	—			
P	0.443 ^B	0.552 ^{*B}	—		
Al-oxides	0.489 ^{*A}	0.500 ^{*A}	0.654 ^{*B}	—	
Fe-oxides	0.748 ^{*A}	0.496 ^{*A}	0.737 ^{*B}	0.748 ^{*A}	—

^A $n = 23$, ^B $n = 20$.

by the different correlations between the Q_{max} parameters and other soil properties. Although $P Q_{max}$ values were significantly correlated with sand content, clay content, and Al- and Fe-oxides, DOC Q_{max} values were only significantly correlated with Fe-oxides. However, because our DOC and P sorption maxima were measured separately, the extent of competitive interactions is not known.

Comparison of Q_{max} values with literature Q_{max} values

Our Langmuir-calculated P sorption maxima exceeded many of the Q_{max} values used by Yang *et al.* (2014) in their ESM (Anghinoni *et al.* 1996; Gichangi *et al.* 2008; Bastounopoulou *et al.* 2011; Munhoz *et al.* 2011; Wang and Liang 2014). These studies also used notably different maximum P concentrations

to calculate the P sorption isotherm, which could lead to an underestimation of P Q_{max} values (Harter 1984). However temperate soils have been shown to have smaller P sorption maxima (Anghinoni *et al.* 1996; Cannon 2010; Bastounopoulou *et al.* 2011; Yang and Post 2011), so a smaller range of initial P concentrations might be appropriate for the soils in those studies. For example, an initial maximum P concentration of 50 mg P L⁻¹ was used for temperate Appalachian soils (Anghinoni *et al.* 1996). However, because tropical soils are high in oxides and clay-sized particles and tend to have higher P sorption capacities (Walker and Syers 1976; Fontes and Weed 1996; Poudel and West 1999; Elser *et al.* 2007; Auxtero *et al.* 2008; Yang *et al.* 2014; de Campos *et al.* 2016), higher initial P concentrations may be required to reach the plateau of the isotherm and appropriately fit the Langmuir Q_{max} parameter. Despite the need for high initial P concentrations, many studies with tropical soils used maximum P concentrations as low as 100 mg P L⁻¹ for soils in Indonesia (Hartono *et al.* 2005). In our study, the maximum initial P concentration, and resulting Q_{max} values, was five times as high as concentrations in Hartono *et al.* (2005). A study by Tiessen *et al.* (1994) that generated P sorption isotherms for volcanic Oxisols observed Q_{max} values ranging from 10 to 360 mg PO₄-P kg⁻¹, which were notably lower than those observed in our study (Table 2). This discrepancy is most likely due to the low maximum concentration of P added to create their isotherm: 50 mg P L⁻¹, the same maximum concentration used for temperate soils in the study by Anghinoni *et al.* (1996). In some cases, we found no evidence of P remaining in the supernatant in our study, even with an initial concentration as high as 100 mg P L⁻¹, indicating that the range of initial P concentrations for tropical soils should probably always exceed 100 mg P L⁻¹. An example of our P sorption isotherms can be seen in Fig. 5, where the Q_{max} and standard error are illustrated for a Puerto Rico Oxisol (EV-V). For this soil, P in solution was below the limit of detection for initial P concentrations ranging from 5 to 50 mg P L⁻¹. Once enough P had been added to the soils to allow P to be detectable in the supernatant, initial

P concentrations of 100 and 150 mg P L⁻¹ still only contributed to the linear portion of the isotherm; it was not until an initial P input of 200 mg P L⁻¹ that the isotherm began to curve, therefore confidently establishing a plateau and enabling fitting of Q_{max} .

Studies that used a maximum P concentration comparable to or exceeding our own also found higher P Q_{max} values. Alleoni *et al.* (2012) used an initial maximum P concentration of 1200 mg P L⁻¹ for P sorption isotherms in Brazilian Oxisols, and their resulting P Q_{max} ranged from 2400 to 2600 mg PO₄-P kg⁻¹. Poudel and West (1999) analysed tropical volcanic Oxisols, Ultisols, and Inceptisols from the Philippines using initial maximum P concentration of 1000 mg P L⁻¹ and found a mean P Q_{max} of 12 856 mg PO₄-P kg⁻¹. A Spearman rank test on the surveyed literature (Table S1) further cemented the influence that initial P concentration has on final P sorption maxima ($\rho = 0.687$, $P < 0.0001$), indicating that Q_{max} values increase when a higher maximum initial P concentration is used. The need for a greater range of initial P concentrations was also illustrated by our inability to produce a P sorption maximum for the Hawaii Andisols. Their high sorption capacity supports the need to carefully estimate sorption maxima in soils of volcanic origin and in soils with notable concentrations of clays and Al- and Fe-oxides.

Relevance of P isotherms to Earth system models

As ESMs begin to incorporate the P cycle (Wang *et al.* 2010b; Goll *et al.* 2012; Yang *et al.* 2014; Reed *et al.* 2015), it is important to provide more thorough information on soils in tropical regions, where soil P is low and forest productivity is generally considered high. The studies used by Yang *et al.* (2014) to estimate P sorption maxima (Anghinoni *et al.* 1996; Gichangi *et al.* 2008; Bastounopoulou *et al.* 2011; Munhoz *et al.* 2011; Wang and Liang 2014) represent P sorption parameters of non-tropical soils based on isotherms with lower maximum P concentrations, and therefore lower Q_{max} values may have underrepresented P sorption maxima for tropical ecosystems. Better estimates of P sorption capacity can help to predict plant productivity in highly weathered soils of tropical regions, thus increasing model efficacy. Furthermore, a thorough analysis of the relationships among Q_{max} , k , particle size, and Al- and Fe-oxides across a wide range of tropical soils could offer stronger linear regressions for estimating sorption parameters, thereby reducing the need for niche P sorption isotherm studies. ESMs could instead obtain sufficient information from more readily available studies that include particle size and Al- and Fe-oxide concentrations.

Conclusions

The Langmuir equation provided a suitable description of P and DOC sorption properties of the tropical soils. Sorption isotherms are infrequently utilized in soil characterization analyses, but this study demonstrated that clay content could be a significant predictor of P Q_{max} values, offering a strong potential for ESMs to estimate P sorption parameters with more widely available data. To expand the efficacy of this proposed method, it would be useful to analyse these correlations among larger sample sizes from different soil orders, so that

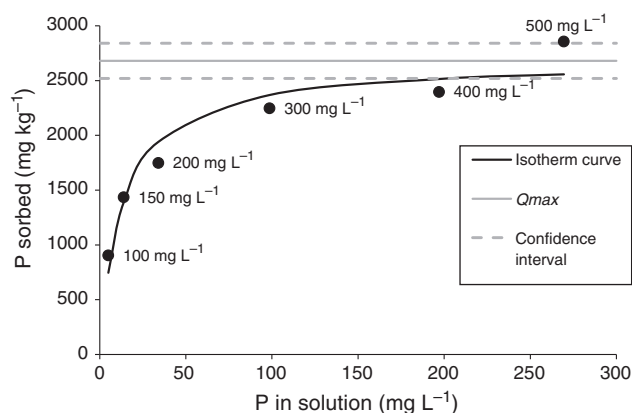


Fig. 5. Langmuir-derived P sorption isotherm for one of the soils analysed in this study, a Puerto Rico Oxisol (EV-V). P sorption maximum capacity (Q_{max}) is indicated by a solid grey line, with the standard error confidence interval depicted by dotted grey lines. Initial P concentrations (mg P L⁻¹) for resulting data points are labelled alongside markers.

the differing influence of soil order and parent material could be better accounted for in ESMs. Our results also suggested that the initial maximum P concentration used in generating isotherms is critical for appropriately estimating P Q_{max} values. Previous studies may have underestimated P sorption maxima due to insufficient initial P input concentrations. The high sorption capacity of weathered, tropical soils necessitates a maximum concentration that properly approximates the sorption plateau of the isotherm.

Conflicts of interest

The authors declare no conflicts of interest.

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