Unified Weak and Strong Soil Tests to Estimate Intrinsic Plant Available Phosphorus Pools

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ABSTRACT

Novel approaches for defining and measuring intrinsic P were developed based on the soil P adsorption reactions kinetics in tropical soils. Weakly and tightly adsorbed P pools were proposed as latent variables to describe the internal soil P status. The Olsen extractable P by a weak soil test contained only the weakly adsorbed P pool, and the modified Truog extractable P by a strong soil test contained both pools. The objectives of this study were to develop and test a new method that estimates the tightly adsorbed P pool using mathematical models derived from the state–space modeling technique. Five fertilizer phosphate (0–800 mg P kg^{-1} soil) rates were applied to seven tropical soils. Soil P was then extracted with the Olsen and modified Truog methods at nine times during a 180 d incubation. Results showed that the extraction efficiencies by the modified Truog method decreased as soil P sorption site density increased. For the seven soils, 22% to 62% of the weakly adsorbed P pool was extracted by the modified Truog method, and it was 28.8% higher than the Olsen method. For soils with low P sorption capacity, 14% to 36% of the tightly adsorbed P pool was extracted by the modified Truog method whereas only small portions were extracted from soils with high P sorption capacity. This research can be used to develop a mechanistic approach for determining P recommendations designed to optimal yields and minimize the impact of agriculture on the environment.

Core Ideas

- Weakly and tightly adsorbed P pools referred to the surface complexes and P adsorption reaction.
- Modified Truog extractable P contained both two intrinsic P pools.
- Latent intrinsic P pools were not directly observed but rather inferred.
- Extraction efficiencies of the two P pools by the modified Truog method were related to P sorption site density.
- Two soil intrinsic P pools unify many soil P tests which can be grouped as two categories of weak extractants and strong extractants.

PHOSPHORUS SHORTAGE in highly weathered tropical soils is a major constraint on agricultural productivity (Uehara and Gillman, 1981). When managing P in a crop–soil system, it is often imperative to consider variables and models that display explicitly the internal elementary laws from physics, chemistry, plant physiology, etc. The mass of soil P with similar availability for plant uptake can be defined as a set of discrete pools.

The pools based on the strength of the chemical bonds between the phosphate molecule and the soil particles (Shuai et al., 2014). Phosphate is adsorbed at the soil particle surface to form monodentate and bidentate surface complexes through ligand exchange with surface hydroxyl groups bound to metal cations (Arai and Sparks, 2007; Atkinson et al., 1974; Bowden et al., 1980; Goldberg and Sposito, 1984a,b, 1985; Parfitt et al., 1975; Rahnemaie et al., 2007). The monodentate surface complex has one bond whereas the bidentate surface complex has two bonds to connect a P atom to the surface of soil hydroxides or oxides. The P atom in the bidentate surface complex is more tightly bonded than in the monodentate surface complex. Thus, proposed that a 2 pool model based on monodentate (weakly) and bidentate (strongly) sorption could explain P availability (Shuai et al., 2014). These two P pools were termed as "intrinsic" due to the following two reasons: (i) they are the actual mass of soil P to react at particle surfaces and are available for crop uptake, and the ratios of the crop P uptake to the change of the P pools are 1:1; and (ii) they are characterized as latent variable that cannot be measured directly but rather inferred.

Soil extractable P is the extraction of the intrinsic P pools with chemical extractants. The effect of an extraction process is quantified by the extraction efficiencies, which are the percentages (constants) of the two P pools extracted (Shuai et al., 2014). For a weak extractant, such as 0.5 mol L^{-1} sodium bicarbonate (Olsen et al., 1954; Wuenscher et al., 2015), soil extractable P becomes the product of the weakly adsorbed P pool and the extraction efficiency, and equivalently, the weakly adsorbed P pool can be obtained from the soil extractable P divided by the extraction efficiency. The estimation of the extraction efficiency was based on (i) P adsorption reaction kinetics to form different pairs of the two P pools over time and to measure the time series of soil

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Abbreviations: CEC, cation-exchange capacity; ECEC, effective cation-exchange capacity; PSSD, soil P sorption site density.

extractable P, and (ii) the mechanistic model to describe the P adsorption reaction and the extraction reaction through state–space modeling technique (Shuai et al., 2014, 2016).

There is a need to extract and estimate the tightly adsorbed P pool with an extraction method with strength greater than sodium carbonate. In Oxisols, the Truog method, which consists of 0.001 mol L^{-1} sulfuric acid and 3% ammonium sulfate, fits this requirement (Truog, 1930). Ayres and Hagihara (1952) increased the concentration of sulfuric acid to 0.01 mol L^{-1}, likely due to soils with high P sorption capacity of soils in Hawaii. Aqueous sulfate replaces the adsorbed phosphate due to their competition for the sorption sites on particles of soil (Geelhoed et al., 1997; Hawke et al., 1989; Parfitt, 1982; Yao and Millero, 1996). The modified Truog method is a stronger P extractant than the Olsen method (Hue and Fox, 2010). Other techniques are being used for other soils. For example, in the central United States, the Bray technique is used to extract P that is readily available (P1) to the plant, and the strong Bray is used to extract reserve P (P2) (Clay et al., 2017). What is missing from this analysis is a technique to combine the multiple extractions into a single recommendation.

The objectives of this study were (i) to measure the dynamics of the modified Truog extractable P in the experiments of kinetics of P adsorption in seven tropical soils; (ii) to develop a new method to estimate the tightly adsorbed P pool by the modified Truog method; and (iii) to predict the two pools for P management in tropical soils.

MATERIALS AND METHODS
Materials

Seven Hawaiian soils of significant agricultural importance were selected in this study. Soil samples were collected at 0–15 cm depth from an Andisol (Maile series), a Mollisol (Pulehu series), and five soils within the Oxisol series (Halii, Kapaa, Makapili, Molokai and Wahiawa) (Table 1). The Maile soil was allowed to dry sufficiently to pass through a 2-mm sieve without sticking, and the other six soils were completely air-dried to pass a 2-mm sieve. The P fertilizer used in this study was powdered calcium monobasic phosphate [Ca(H$_2$PO$_4$)$_2$] of analytical grade.

Since phosphate exchange reactions of surface hydroxyl groups in non-calcareous soils are independent of the bulk solid phase to which the hydroxyl groups are bound (Goldberg and Sposito, 1984b), the soil P sorption site density (PSSD) was estimated as the sum of the sorption sites associated with each of the four component minerals including goethite, halloysite, gibbsite, and kaolinite (Jackman et al., 1997; Sposito, 1984). The PSSD was used to describe soil sorption capacity (Jackman et al., 1997; Shuai et al., 2014, 2016). The Rietveld method is a technique used to characterize the crystalline structure using X-ray diffraction patterns (Taylor, 1991). The mineralogical composition of soils were as presented by Jackman et al. (1997). The Halii soil contained goethite and no detectable phyllosilicates. The Kapaa soil contained high concentrations of gibbsite and goethite and a relatively small concentration of halloysite. The Maile predominantly contained amorphous Fe and Al hydrous oxides, very fine-grained goethite, and no kaolinite. The Makapili soil contained equal amounts of kaolinite, halloysite, and goethite. The Molokai and Pulehu soils were kaolinitic and contained very small amounts

of Fe and Al hydrous oxides; and the Wahiawa soil displayed approximately equal amounts of kaolinite and halloysite.

Soil pH was measured on 1:1 soil:water mixtures with deionized water. Organic C was determined by dry combustion using a Leco Carbon Determinator (Wang and Anderson, 1998). The cation-exchange capacity (CEC) was determined by leaching the soils with 1 mol L^{-1} ammonium acetate buffered at pH 7.0 (Blakemore et al., 1987), and the effective cation-exchange capacity (ECEC) was estimated by summing the amounts of Na, Ca, Mg, and K (as determined by atomic absorption spectrometry) in the leachates. Specific surface area of the whole soil was determined by the retention of glycerol (Kinter and Diamond, 1958). The clay content was determined for all soils except the Maile soil (Soil Survey Laboratory Staff, 1991; Soil Survey Staff, 1994).

Phosphorus Adsorption Experiments

Phosphorus fertilizer was mixed thoroughly with the soils. The amounts of fertilizer P addition were determined from the P sorption capacities of soils. The P sorption capacities of the Molokai and Pulehu soils were low, i.e., PSSD was less than 0.1 mol$_c$ kg^{-1} clay. The P sorption capacities for the other five soils were medium to high, i.e., PSSD was between 0.1 and 0.3 mol$_c$ kg^{-1} clay. The five different amounts (mg P kg^{-1} soil) were 0, 25, 50, 100, and 200 for Molokai and Pulehu; 0, 50, 100, 200, and 400 for Halii, Kapaa, Makapili, and Wahiawa; and 0, 100, 200, 400, and 800 for Maile. Deionized water was added to bring the soils to field capacity which was estimated as the soil water content at a suction of 10 kPa. Two replicates of each soil–fertilizer mix were incubated at 20.3 ± 0.3°C for 180 d under aerobic conditions. The soil water content was maintained at a constant level by adding water. Details of the experiments are available in Jackman (1994) and Shuai et al. (2014).

Soils were subsampled at nine times (2, 4, 8, 16, 32, 64, 96, 128, and 180 d) during the incubation. Two soil subsamples were mixed with the modified Truog solution (Ayres and Hagihara, 1952) at a 1:100 soil: solution ratio. Two soil subsamples were mixed with Olsen solution (0.5 mol L^{-1} NaHCO$_3$ buffered at pH 8.5) at a 1:20 soil: solution ratio (Shuai et al., 2014). After 0.5 h shaking, the solution P concentrations were determined with ammonium molybdate reagent and ascorbic acid (Murphy and Riley, 1962).

Mathematical Models
Kinetics of Phosphorus Adsorption Reactions in Soils

The concentration of P in solution is in instant equilibrium with the weakly adsorbed P pool x_1 (mg P kg^{-1} soil), and the mass of P in solution is negligibly small compared with x_1 (Goldberg and Sposito, 1984a).

$$x_1 + \text{SOH} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} x_2 \qquad [1]$$

where SOH is the sorption site at soil surface, and k_a and k_d are the adsorption and desorption rate coefficients, respectively (Barrow and Shaw. 1975; Shuai et al., 2014, 2016).

When only a small amount of surface P sorption sites is occupied by the adsorbed P, the second order kinetics of reactions described in Eq. [1] is a pseudo-first-order reaction, and

Table 1. Classification and properties of soils investigated in this study.

Soil	Classification	pH (water)	Organic carbon (g kg⁻¹)	Specific surface area (m² g⁻¹)	Clay (g kg⁻¹)	P sorption site density (mol_c kg⁻¹ clay)	ECEC (cmol_c kg⁻¹)	CEC (cmol_c kg⁻¹)
Halii	Fine, ferritic, isothermic Anionic Acrudox	5.09	73.9	107	470	0.245	6.5	8.8
Kapaa	Very fine, sesquic, isohyper-thermic Anionic Acrudox	4.75	46.9	101	499	0.242	4.6	6.9
Maile	Hydrous, isomesic Acrudoxic Hydrudand	5.18	240	272	ND†	0.265	28.2	22.0
Makapili	Very fine, sesquic, isohyper-thermic Anionic Acrudox	7.10	22.1	101	620	0.294	11.8	ND
Molokai	Fine, kaolinitic, isohyperthermic Typic Eutrotorrox	7.56	24.0	92	398	0.011	8.5	8.5
Pulehu	Fine-loamy, mixed, isohyper-thermic Cumulic Haplustoll	7.70	28.0	125	205	0.041	12.4	12.4
Wahiawa	Very fine, kaolinitic, isohyper-thermic Rhodic Eutrustox	4.78	19.7	84	701	0.102	6.1	5.1

† Not determined

the dynamics of intrinsic P pools behave as linear differential equations (Sparks, 1988). The P adsorption kinetics are

$$\frac{dx_1(t)}{dt} = -k_a[\text{SOH}]x_1 + k_d x_2 + u(t) \quad [2]$$

$$\frac{dx_2(t)}{dt} = k_a[\text{SOH}]x_1 - k_d x_2 \quad [3]$$

where t is time (d), $u(t)$ is the amount of external P added at time t, and $[\text{SOH}]$ is the concentration of surface sorption sites represented by the PSSD (mol_c kg⁻¹ clay). The coefficient of u in Eq. [2] is 1, and thus, the pools are actual masses in the same manner as the external fertilizer P.

Extraction of Soil Intrinsic Phosphorus Pools

The Olsen method is a weak extractant (Wuenscher et al., 2015) and it was denoted as y_{Olsen} (Shuai et al., 2014). The relationship between weakly adsorbed P pool and the Olsen extractable P is

$$y_{\text{Olsen}}(t) = c_{1,\text{Olsen}} x_1(t) \quad [4]$$

where $c_{1,\text{Olsen}}$ is the extraction efficiency of the weakly adsorbed P pool by the Olsen method.

The modified Truog extractable P (mg P kg⁻¹ soil), denoted as y_{Truog}, contains portions of both the weakly adsorbed P pool (x_1) and the tightly adsorbed P pool (x_2)

$$y_{\text{Truog}}(t) = c_{1,\text{Truog}} x_1(t) + c_{2,\text{Truog}} x_2(t) \quad [5]$$

where $c_{1,\text{Truog}}$ and $c_{2,\text{Truog}}$ are the extraction efficiencies of the weakly adsorbed P pool and the tightly adsorbed P pool by the modified Truog method, respectively. The justification of Eq. [5] is as follows. Sulfate forms not only monodentate but also bidentate surface complexes to compete for sorption sites with P (Parfitt and Smart, 1977, 1978; Geelhoed et al., 1997; Peak et al., 1999, 2001; Wijnja and Schulthess, 2000; Sverjensky and Fukushi, 2006; Fukushi and Sverjensky, 2007; Kubicki et al., 2007; Gu et al., 2016). Due to the similarity between the sulfate surface complexes and P surface complexes mentioned in the section of Introduction, the Truog extractant can be strong enough to break some of the P bidentate surface complex of the tightly adsorbed P pool as well

as the P monodentate surface complex of the weakly adsorbed P pool. The extraction efficiencies are absolute constants determined solely by soil mineralogical composition.

State–Space Equations and the Analytical Solution

The combination of the individual Eq. [2–5] forms the state–space equations. The ordinary differential Eq. [2, 3] are termed as state equations and the Eq. [4, 5] are termed as observation equations in state–space modeling technique (Kailath, 1980; Dorf and Bishop, 2008). The weakly adsorbed P pool $x_1(t)$ and the tightly adsorbed P pool $x_2(t)$ are termed as state variables, the amount of external P added $u(t)$ is termed as input, and the Olsen extractable P $y_{\text{Olsen}}(t)$ and the modified Truog extractable P $y_{\text{Truog}}(t)$ are termed as output. The input, output, and the state variable form the system of P adsorption reaction and the extraction processes.

The importance of the state–space modeling is (i) the P adsorption reaction and the extraction process are integrated together, and (ii) that the two intrinsic P pools as state variables link the input-output together and display the internal dynamics explicitly.

For the ordinary differential equations (Eq. [2, 3]), the initial condition of the weakly adsorbed P pool and the tightly adsorbed P pool are $x_1(0)$ and $x_2(0)$, respectively. The input in Eq. [2] is

$$u(t) = u(0)\delta(t) \quad [6]$$

where $\delta(t)$ is Dirac delta function $\delta(t) = \begin{cases} \infty & t = 0 \\ 0 & t \neq 0 \end{cases}$ and $\int_{-\infty}^{\infty} \delta(t)dt = 1$.

The dynamic changes of the two intrinsic P pools in Eq. [2, 3] were derived as Eq. [A.5, A.6] in Shuai et al. (2014):

$$x_1(t) = \frac{k_d[x_1(0) + x_2(0) + u(0)]}{k_a[\text{SOH}] + k_d} + \frac{k_a[\text{SOH}]x_1(0) - k_d x_2(0) + k_a[\text{SOH}]u(0)}{k_a[\text{SOH}] + k_d} e^{-(k_a[\text{SOH}]+k_d)t} \quad [7]$$

and

$$x_2(t) = \frac{k_a[\text{SOH}][x_1(0) + x_2(0) + u(0)]}{k_a[\text{SOH}] + k_d} + \frac{-k_a[\text{SOH}]x_1(0) + k_d x_2(0) - k_a[\text{SOH}]u(0)}{k_a[\text{SOH}] + k_d} e^{-(k_a[\text{SOH}]+k_d)t} \quad [8]$$

Combining the Eq. [5, 7, 8] gives

$$y_{\text{Truog}}(t) = \frac{\left(c_{1,\text{Truog}}k_d + c_{2,\text{Truog}}k_a[\text{SOH}]\right)[x_1(0) + x_2(0)]}{k_a[\text{SOH}] + k_d} +$$
$$\frac{\left(c_{1,\text{Truog}} - c_{2,\text{Truog}}\right)[x_1(0)k_a[\text{SOH}] - x_2(0)k_d]}{k_a[\text{SOH}] + k_d}e^{-(k_a[\text{SOH}]+k_d)t} +$$
$$u(0)\left(\frac{c_{1,\text{Truog}}k_d + c_{2,\text{Truog}}k_a[\text{SOH}]}{k_a[\text{SOH}] + k_d}\right) +$$
$$u(0)\left[\frac{k_a[\text{SOH}]\left(c_{1,\text{Truog}} - c_{2,\text{Truog}}\right)}{k_a[\text{SOH}] + k_d}e^{-(k_a[\text{SOH}]+k_d)t}\right] \qquad [9]$$

In Eq. [9], there is a linear relationship between the modified Truog extractable P (y_{Truog}) as output and the external P added ($u(0)$) as input. This linear input-output relationship is important in this study because it defines and determines the linearity of the system described by Eq. [2–5] and it also can be verified by experiments. According to linear system theory (Kailath, 1980), the linear relationships among state variables, input and output are all valid.

The intercept term in Eq. [9] becomes a constant when the reaction (Eq. [1]) is at equilibrium at the initial time to satisfy $\frac{x_1(0)}{x_2(0)} = \frac{k_d}{k_a[\text{SOH}]}$. As long as the reaction (Eq. [1]) is not at equilibrium at the initial time, the intercept in Eq. [9] changes with time. Transformation of weakly adsorbed P pool into the tightly adsorbed P pool occurs and the intercept decreases with time if $\frac{x_1(0)}{x_2(0)} > \frac{k_d}{k_a[\text{SOH}]}$. Otherwise, the intercept in Eq. [9] increases with time.

Impulse Response of the State and Output Variables

When the initial values of the two intrinsic P pools are zeros and $u(0) = 1$, Eq. [7–9] describe the impulse responses of state variable (x_1 and x_2) and output (y_{Truog}), denoted as g_1, g_2, and g_{Truog}, respectively, and they are

$$g_1(t) = \frac{k_d}{k_a[\text{SOH}] + k_d} + \frac{k_a[\text{SOH}]}{k_a[\text{SOH}] + k_d}e^{-(k_a[\text{SOH}]+k_d)t}, [10]$$

$$g_2(t) = 1 - g_1(t), \qquad [11]$$

and

$$g_{\text{Truog}}(t) = \frac{c_{1,\text{Truog}}k_d + c_{2,\text{Truog}}k_a[\text{SOH}]}{k_a[\text{SOH}] + k_d} +$$
$$\frac{k_a[\text{SOH}]\left(c_{1,\text{Truog}} - c_{2,\text{Truog}}\right)}{k_a[\text{SOH}] + k_d}e^{-(k_a[\text{SOH}]+k_d)t}. \qquad [12]$$

The impulse response of the weakly adsorbed P pool $g_1(0) = 1$ is due to the input of Dirac delta function at the initial time.

Impulse response is very useful in the analysis of dynamic system (Kailath, 1980; Dorf and Bishop, 2008). The purpose of using impulse response in the study is to simplify the data analysis even though the initial values of the two P pools cannot be zeros.

Data Analysis

Estimation of Extraction Efficiencies $c_{1,\text{Truog}}$ and $c_{2,\text{Truog}}$ by Modified Truog Method

Because there are only three independent constant terms in Eq. [12], the four parameters $c_{1,\text{Truog}}$ and $c_{2,\text{Truog}}$, k_a, and k_d cannot be estimated simultaneously by the nonlinear least squares regression technique (Shuai et al., 2014). The following steps were used to estimate the extraction efficiencies of the pools by the modified Truog method.

Step 1. Estimation of the impulse response of modified Truog extractable P, $g_{\text{Truog}}(t_i)$. At each sampling time for each soil, Eq. [9] can be rewritten as a linear function of $u(0)$

$$y_{\text{Truog}}(t_i) = \beta_0(t_i) + u(0)g_{\text{Truog}}(t_i) \qquad [13]$$

where t_i ($i = 1, 2, ..., 9$) is the sampling time, $\beta_0(t_i)$ was the effect of initial condition of soil P pools in the P adsorption experiments. The impulse response of modified Truog extractable P, g_{Truog}, at each sampling time t_i was obtained from the above model using linear regressions with the SAS software (SAS Institute, 2012). The advantage of using impulse response $g_{\text{Truog}}(t_i)$ in data analysis was that the experimental errors were filtered by the linear regressions.

Step 2. Calculation of the impulse response of the weakly adsorbed P pools at each sampling time, $g_1(t_i)$. The values of the adsorption rate $k_a[\text{SOH}]$ and desorption rate k_d are listed in Table 2. Equation [10] was used to calculate the impulse response of the weakly adsorbed P pools at each sampling time t_i as

$$g_1(t_i) = \frac{k_d}{k_a[\text{SOH}] + k_d} + \frac{k_a[\text{SOH}]}{k_a[\text{SOH}] + k_d}e^{-(k_a[\text{SOH}]+k_d)t_i}. [14]$$

Step 3. Estimation of the extraction efficiencies $c_{1,\text{Truog}}$ and $c_{2,\text{Truog}}$. The combination of Eq. [10, 12] gives

$$g_{\text{Truog}}(t_i) = \left(c_{1,\text{Truog}} - c_{2,\text{Truog}}\right)g_1(t_i) + c_{2,\text{Truog}}. \qquad [15]$$

The coefficients $c_{1,\text{Truog}}$ and $c_{2,\text{Truog}}$ in Eq. [15] was obtained using linear regressions of the results of $g_{\text{Truog}}(t_i)$ and $g_1(t_i)$ in the two steps above with the SAS software (SAS Institute, 2012).

Measurement of the Two Intrinsic Phosphorus Pools for Field Condition

In the description above, the goal is to estimate the extraction efficiency $c_{1,\text{Truog}}$ of the weakly adsorbed P pool and the extraction efficiency $c_{2,\text{Truog}}$ of the tightly adsorbed P pool by the modified Truog method. In Shuai et al. (2014), the extraction efficiency of the weakly adsorbed P pool $c_{1,\text{Olsen}}$ by the Olsen method was estimated. These three extraction efficiencies can be used to calculate the intrinsic P pools.

Generally, two extractants can be selected to include a weak extract and a strong extractant in the same manner as the Olsen method and the modified Truog method, respectively. The two intrinsic P pools can be measured at commercial laboratories using the currently available soil P tests. The P extracted by the weak extractant, denoted as P_{weak}, contains a portion of the weakly adsorbed P pool

$$P_{\text{weak}} = c_{1,\text{weak}}x_1 \qquad [16]$$

Soil	Adsorption rates ($k_a \times$[SOH], d^{-1})	Desorption rates (k_d d^{-1})	Extraction efficiency ($c_{1,Olsen}$)
Halii	0.0271	0.0186	0.224
Kapaa	0.0566	0.0330	0.195
Maile	0.0280	0.0172	0.162
Makapili	0.0330	0.0152	0.121
Molokai	0.0184	0.0220	0.464
Pulehu	0.0319	0.0321	0.405
Wahiawa	0.0435	0.0313	0.353

where $c_{1,weak}$ is the extraction efficiency of the weakly adsorbed P pool by the weak extractant.

The P extracted by the strong extractant, denoted as P_{strong}, contains portions of both two intrinsic P pools

$$P_{strong} = c_{1,strong}x_1 + c_{2,strong}x_2 \quad [17]$$

where $c_{1,strong}$ and $c_{2,strong}$ are the extraction efficiencies of the weakly adsorbed P pool and the tightly adsorbed P pool by the strong extractant, respectively. From Eq. [16, 17], the two intrinsic P pools can be calculated as

$$x_1 = \frac{P_{weak}}{c_{1,weak}} \quad [18]$$

and

$$x_2 = \frac{1}{c_{2,strong}}\left(P_{strong} - \frac{c_{1,strong}}{c_{1,weak}}P_{weak}\right). \quad [19]$$

RESULTS AND DISCUSSIONS
Modified Truog Extractable Phosphorus

The modified Truog extractable P (output) and the amount of external P added (input) were related linearly (Fig. 1). This linear input-output relationship justified the linear system including the P adsorption reaction and the extraction process, and then, the procedure of data analysis in this study was valid.

The intercept of the linear relationship between the modified Truog extractable P and the amount of external P added in the Pulehu soil decreased with increasing time (Fig. 1). This decrease suggests that at time 0, in the Pulehu adsorption experiment, the two P pools were not at equilibrium, because in the no-fertilizer control treatment the concentration of P in the two pools were variable. For the other six soils, the intercepts of each soil showed no apparent change with time, and thus, the two intrinsic P pools were at equilibrium at the beginning of the adsorption experiments.

Impulse Responses of the Modified Truog Extractable Phosphorus and the Weakly Adsorbed Phosphorus Pool

The impulse response of the modified Truog extractable P of each soil shown in Fig. 2 was obtained from the linear regression of measured Truog extractable P with level of external P addition $u(0)$ (see Eq. [13] and the step 1 in the section of Data Analysis). The calculated impulse response of the weakly adsorbed P pool for each soil (see Eq. [14] and the step 2 in

the section of Data Analysis) is shown in Fig. 2. These impulse responses for each soil decreased with time and then reached asymptotic constants. These trends suggest that equilibrium was achieved at the end of the experiment.

Extraction Efficiencies of the Phosphorus Pools by the Modified Truog Method

There were linear relationships between the impulse responses of modified Truog extractable P and the weakly adsorbed P pool at the nine adsorption times (Fig. 3). The extraction efficiencies $c_{1,Truog}$ and $c_{2,Truog}$ of the two intrinsic P pools were estimated (Eq. [15]) and shown in Table 3.

The extraction efficiencies $c_{1,Truog}$ of the weakly adsorbed P pools ranged from 22 to 62% for the seven soils. The extraction efficiencies $c_{2,Truog}$ were between 14 to 36% for the three soils Molokai, Pulehu, and Wahiawa, known for their low PSSD. For the other soils with higher PSSD, extraction efficiencies $c_{2,Truog}$ were below 2.1%.

The extraction efficiency $c_{1,Truog}$ decreased with increasing soil P sorption site density (see Fig. 4), and the relationship was described by

$$c_{1,Truog} = -0.118\ln(PSSD) + 0.104, R^2 = 0.949. \quad [20]$$

The extraction efficiency $c_{2,Truog}$ (see Fig. 5) decreased with increasing soil P sorption site density, and the relationship was described by

$$c_{2,Truog} = -0.108\ln(PSSD) - 0.135, R^2 = 0.982. \quad [21]$$

The extraction efficiencies for the weakly adsorbed P pool by the modified Truog listed in Table 3 and those by the Olson method listed in Table 2 were linearly related:

$$c_{1,Truog} = 1.288c_{1,Olsen}, R^2 = 0.88, p < 0.001. \quad [22]$$

The modified Truog extractable P contained a 28.8% larger amount of the weakly adsorbed P pool than did the Olsen extractable P.

Predictions of the Two Phosphorus Pools from the Soil Phosphorus Sorption Site Density

The Olsen method was used as the weak extractant (Shuai et al., 2014). The extraction efficiency of the weakly adsorbed P pool was a linear function of PSSD (Shuai et al., 2014). Inserting this linear model in to Eq. [18] gave the following equation

$$x_1 = \frac{P_{weak}}{0.466 - 1.118PSSD}. \quad [23]$$

The modified Truog method was used as the strong extractant. Inserting Eq. [21, 22] into Eq. [19] gave the following equation to calculate the tightly weakly adsorbed P pool

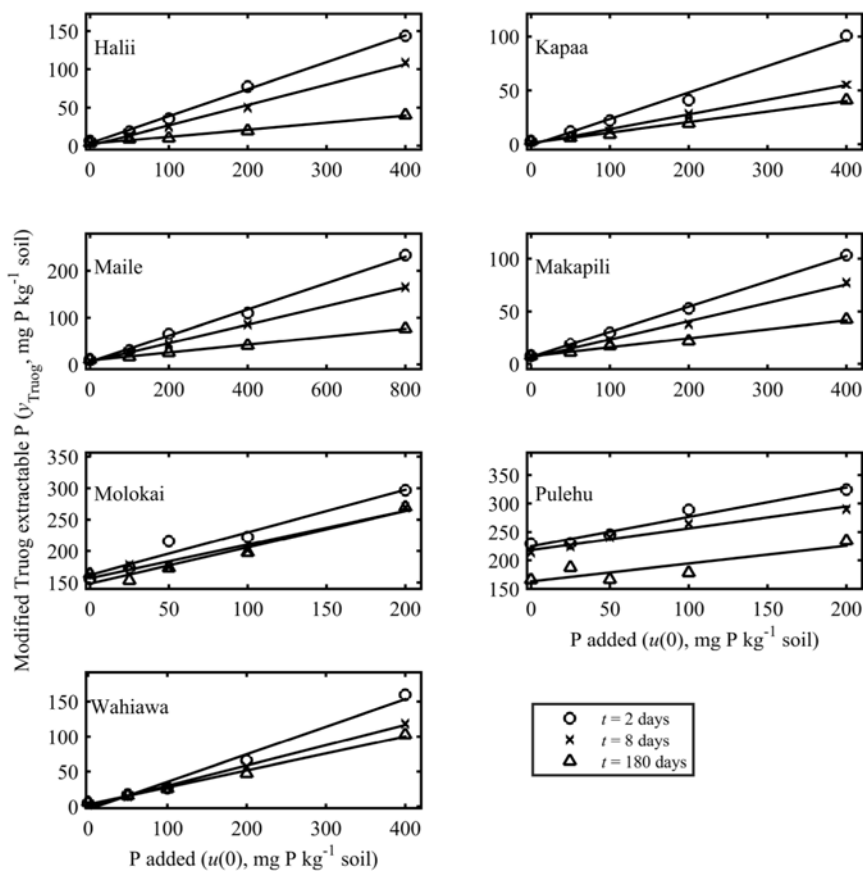$$x_2 = \frac{1}{-0.108\ln(PSSD) - 0.135}\left(P_{strong} - 1.288P_{weak}\right). \quad [24]$$

Fig. 1. Linear relationships between the modified Truog-P (y_{Truog}, mg P kg^{-1} soil) and added P ($u(0)$, mg P kg^{-1} soil) at three sampling times (2, 8, and 180 d) for the seven soils (see Eq. [13]).

These equations suggest that for a given soil, the weakly sorbed P increased with extractable P and that the tightly adsorbed P was proportional to the difference between the strong and weak P extractants.

Crop Phosphorus Uptake from the Tightly Adsorbed Phosphorus Pool

The tightly adsorbed P pool measured in this study was an improvement in predicting crop P uptake. According to Eq. [15] in Shuai et al. (2014), the tightly adsorbed P pool contributed 58.2% of the crop P uptake and the weakly adsorbed P pool contributed the remaining 41.8% in the Wahiawa soil; however, the change of the Olsen extractable P represented only 14.7% of the crop P uptake.

The difference between the two pools in terms of crop P uptake is that the weakly adsorbed P pools is readily available but the tightly adsorbed P pool is slowly available through desorption in the reaction [1]. When the desorption rate is greater than the rate of crop P uptake, the two P pools have no difference in P supply. However, when the desorption rate is less than the rate of crop P uptake, the tightly adsorbed P pool is less available than the weakly adsorbed P pool, and higher amount of the tightly adsorbed P pool will be required to meet crop P requirement. The dependence of the availability of the tightly adsorbed P pool on its desorption rate can help explain unexpected crop response to P fertilization. At some field sites, relatively high P rates are recommended based on Olsen P, and crop responses are predicted but actually not observed. The possible interpretation is that the fertilizer

P is transformed into the tightly adsorbed P pool and become unavailable for crop P uptake during crop growth due to the lower desorption rate than the rate of crop P uptake. As time goes on, the tightly adsorbed P pool will be desorbed and replenish the weakly adsorbed P pool and become available for crop P uptake as "residual effect" described in Uehara and Gillman (1981).

Phosphorus Fertilizer Recommendation based on the Two Intrinsic Phosphorus Pools

The traditional P fertilizer recommendation based on soil P tests heavily relies on the calibration of soil P tests with crop response to external P addition, which is well known as an empirical approach. The two intrinsic P pools can be used to modify the traditional P fertilizer recommendation. The one-dimensional critical level and initial extractable P in soil in the P fertilizer recommendation in Shuai et al. (2011) can be replaced with two-dimensional critical levels and initial P pools in soil. The pools complement other techniques that are based on changes in soil test P values or differences in soil depth to improve P recommendations (Alvarez and Steinbach, 2017; Conway et al., 2017).

A new mechanistic approach of P fertilizer recommendation can also be developed based the two intrinsic P pools. Phosphorus in crop–soil system is the interaction between soil P adsorption/desorption reaction and crop P uptake during the growth period. Then, P fertilizer recommendation can be a dynamic soil P management which matches the dynamics of soil P supply by the pools and crop P uptake aiming at crop optimal growth/yield.
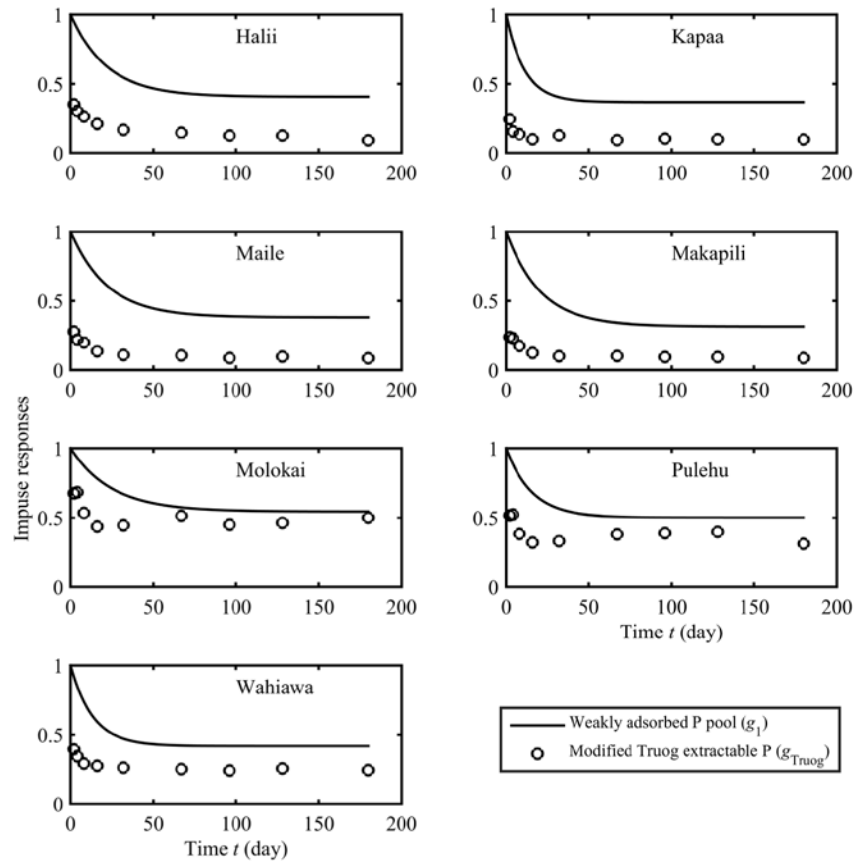
Fig. 2. Impulse responses of the weakly adsorbed P pool (g_1, curve) calculated by Eq. [14] and the modified Truog extractable P with time (g_{Truog}, circle) estimated from Eq. [13].
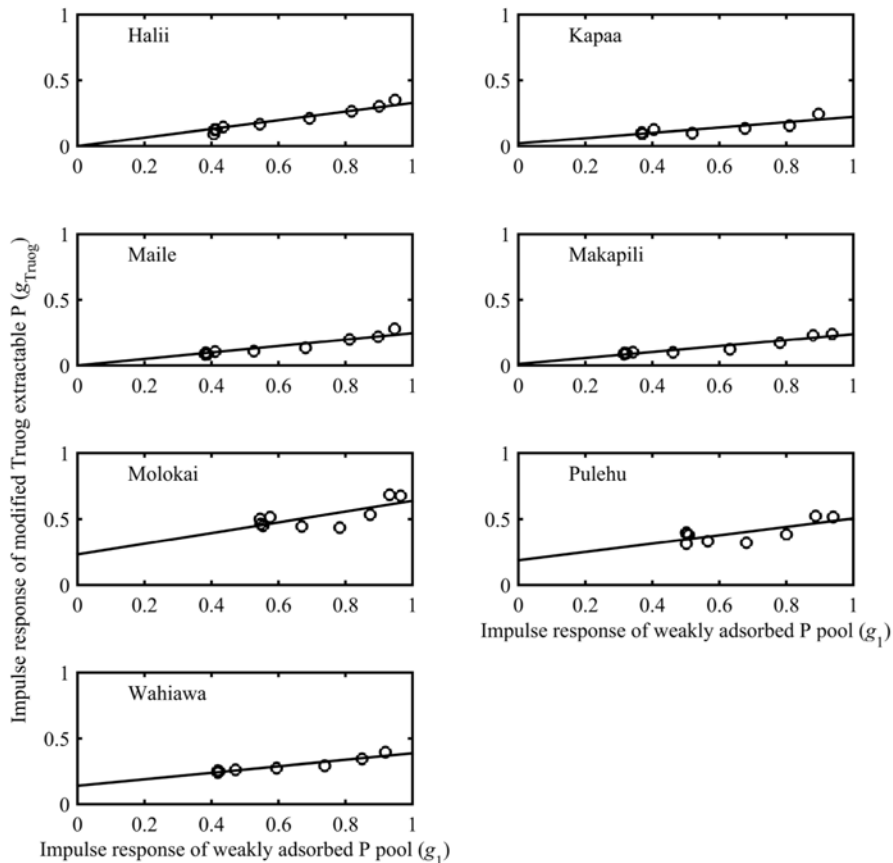

Fig. 3. Linear relationships between the impulse responses of the weakly adsorbed P pools (g_1) and the modified Truog extractable P (g_{Truog}) for the seven soils (see Eq. [15]).

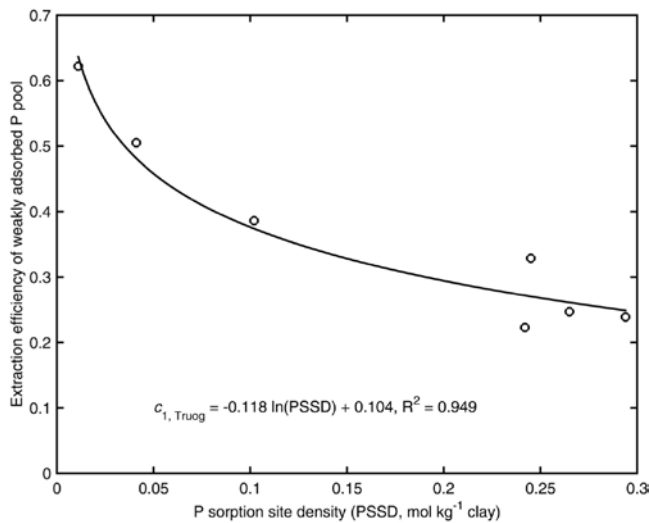| Soil	$c_{1,Truog}$	$c_{2,Truog}$	R^2	p-value
Halii	0.329	0.000	0.97	< 0.001
Kapaa	0.223	0.021	0.76	0.002
Maile	0.247	0.000	0.92	< 0.001
Makapili	0.239	0.011	0.92	< 0.001
Molokai	0.622	0.361	0.56	0.021
Pulehu	0.505	0.186	0.54	0.024
Wahiawa	0.386	0.140	0.90	< 0.001

Fig. 4. Change of the extraction efficiency of the weakly adsorbed P pool ($c_{1,Truog}$) by the modified Truog method with soil P sorption site density (PSSD) and the fitted curve for the seven soils.
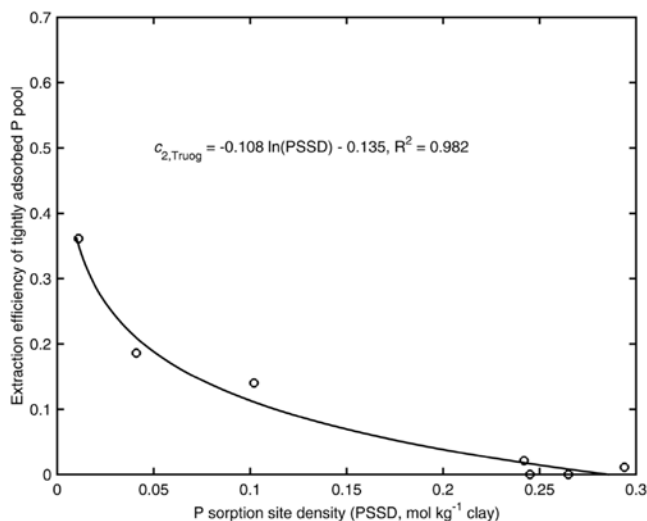

Fig. 5. Change of the extraction efficiency of the tightly adsorbed P pool ($c_{2,Truog}$) by the modified Truog method with soil P sorption site density (PSSD) and the fitted curve for the seven soils.

CONCLUSIONS

The extractable P by the strong modified Truog method contained portions of the weakly adsorbed P pool and the tightly adsorbed P pool. The coefficients of the linear relationship between the modified Truog extractable P and the two intrinsic P pools, i.e., extraction efficiencies, were estimated based on the dynamics of the modified Truog extractable P in P adsorption experiments using the new mathematical model derived from the state–space equations. The estimated extraction efficiencies of the two intrinsic P pools by the strong modified Truog method decreased with an increase in soil P sorption site density. The tightly adsorbed P pool for field soils could be measured from the modified Truog extractable P as long as the extraction efficiencies by the strong modified Truog method and the weak Olsen method were known.

The two intrinsic P pools unify all of the many soil P test methods developed and implemented at commercial laboratories for soil P management in the past over one hundred years. Any combinations of the pair of a weak extractant and a strong extractant among the many soil P test methods are expected to give the same estimates of the two intrinsic P pools of a soil.

REFERENCES

Alvarez, R., and H.S. Steinbach. 2017. Modeling soil test phosphorus changes under fertilized and unfertilized managements using artificial neural networks. Agron. J. 109:2278–2290. doi:10.2134/agronj2017.01.0014

Arai, Y., and D.L. Sparks. 2007. Phosphate reaction dynamics in soils and soil components: A multiscale approach. Adv. Agron. 94:135–179. doi:10.1016/S0065-2113(06)94003-6

Atkinson, R.J., R.L. Parfitt, and R.S.C. Smart. 1974. Infrared study of phosphate adsorption on goethite. J. Chem. Soc., Faraday Trans. I 70:1472–1479. doi:10.1039/f19747001472

Ayres, A.S., and H.H. Hagihara. 1952. Available phosphorus in Hawaiian soil profiles. The Hawaiian Planters'. Record (Washington) 54:81–99.

Barrow, N.J., and T.C. Shaw. 1975. The slow reactions between soil and anions: 3. The effects of time and temperature on the decrease in isotopically exchangeable phosphate. Soil Sci. 119:190–197. doi:10.1097/00010694-197503000-00002

Blakemore, L.C., P.L. Searle, and B.K. Daly. 1987. Methods for chemical analysis of soils. N.Z. Soil Bureau Scientific Rep. 80. N.Z. Soil Bureau, DSIRO, Lower Hutt, New Zealand.

Bowden, J.W., S. Nagarajah, N.J. Barrow, A.M. Posner, and J.P. Quirk. 1980. Describing the adsorption of phosphate, citrate and selenite on a variable charge mineral surface. Aust. J. Soil Res. 18:49–60. doi:10.1071/SR9800049

Clay, D.E., C. Robinson, and T.M. DeSutter. 2017. Soil testing and understanding soil testing results for precision farming. In: D.E. Clay, S.A. Clay, and S. Bruggeman, editors, Practical mathematics for precision farming. American Society of Agronomy, Madison WI.

Conway, L.S., M.A. Yost, N.R. Kitchen, and K.A. Sudduth. 2017. Using topsoil thickness to improve site-specific phosphorus and potassium management on claypan soil. Agron. J. 109:2291–2301. doi:10.2134/agronj2017.01.0038

Dorf, R.C., and R.H. Bishop. 2008. Modern control systems, 11th ed. Prentice Hall, Upper Saddle River, NJ.

Fukushi, K., and D.A.A. Sverjensky. 2007. A surface complexation model for sulfate and selenate on iron oxides consistent with spectroscopic and theoretical molecular evidence. Geochim. Cosmochim. Acta 71:1–24. doi:10.1016/j.gca.2006.08.048

Geelhoed, J.S., T. Hiemstra, and W.H. van Riemsdijk. 1997. Phosphate and sulfate adsorption on goethite: Single anion and competitive adsorption. Geochim. Cosmochim. Acta 61:2389–2396. doi:10.1016/S0016-7037(97)00096-3

Goldberg, S., and G. Sposito. 1984a. A chemical model of phosphate adsorption by soils: I. Reference oxide minerals. Soil Sci. Soc. Am. J. 48:772–778. doi:10.2136/sssaj1984.03615995004800040015x

Goldberg, S., and G. Sposito. 1984b. A chemical model of phosphate adsorption by soils. II. Noncalcareous soils. Soil Sci. Soc. Am. J. 48:779–783. doi:10.2136/sssaj1984.03615995004800040016x

Goldberg, S., and G. Sposito. 1985. On the mechanism of specific phosphate adsorption by hydroxylated mineral surfaces: A review. Commun. Soil Sci. Plant Anal. 16:801–821. doi:10.1080/00103628509367646

Gu, C.H., Z.M. Wang, J.D. Kubicki, X.M. Wang, and M.Q. Zhu. 2016. X-ray absorption spectroscopic quantification and speciation modeling of sulfate adsorption on ferrihydrite surfaces. Environ. Sci. Technol. 50:8067–8076. doi:10.1021/acs.est.6b00753

Hawke, D., P.D. Carpenter, and K.A. Hunter. 1989. Competitive adsorption of phosphate on goethite in marine electrolytes. Environ. Sci. Technol. 23:187–191. doi:10.1021/es00179a008

Hue, N.V., and R.L. Fox. 2010. Predicting plant-phosphorus requirements for Hawaii soils using a combination of P sorption isotherms and chemical extraction methods. Commun. Soil Sci. Plant Anal. 41:133–143. doi:10.1080/00103620903426949

Jackman, J.M. 1994. The phosphorus sorption potential of selected Hawaiian soils in relation to their mineralogy and chemistry. M.Sc. thesis. University of Hawaii, Honolulu.

Jackman, J.M., R.C. Jones, R.S. Yost, and C.J. Babcock. 1997. Rietveld estimates of mineral percentages to predict phosphate sorption by selected Hawaiian soils. Soil Sci. Soc. Am. J. 61:618–625. doi:10.2136/sssaj1997.03615995006100020035x

Kailath, T. 1980. Linear systems. Prentice Hall, Englewood Cliffs, NJ.

Kinter, E.B., and S. Diamond. 1958. Gravimetric determination of monolayer glycerol complexes of clay minerals. In: A. Swineford, editor, Clays and clay minerals. Nat. Acad. Sci.–Nat. Resour. Council Publ. 566. U.S. Gov. Office, Washington, DC. p. 318–333.

Kubicki, J.D., K.D. Kwon, K.W. Paul, and D.L. Sparks. 2007. Surface complex structures modelled with quantum chemical calculations: Carbonate, phosphate, sulphate, arsenate and arsenite. Eur. J. Soil Sci. 58:932–944. doi:10.1111/j.1365-2389.2007.00931.x

Murphy, J.P., and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27:31–36. doi:10.1016/S0003-2670(00)88444-5

Olsen, S.R., C.V. Cole, F.S. Watanabe, and L.A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. 939. U.S. Gov. Print. Office, Washington, DC.

Parfitt, R.L. 1982. Competitive adsorption of phosphate and sulphate on goethite (α-FeOOH): A note. N. Z. J. Sci. 25:147–148.

Parfitt, R.L., R.J. Atkinson, and R.S.C. Smart. 1975. The mechanism of phosphate fixation by iron oxides. Soil Sci. Soc. Am. Proc. 39:837–841. doi:10.2136/sssaj1975.03615995003900050017x

Parfitt, R.L., and R.S.C. Smart. 1977. Infrared spectra from binuclear bridging complexes of sulphate adsorbed on goethite (α-FeOOH). J. Chem. Soc., Faraday Trans. 73:796–802. doi:10.1039/f19777300796

Parfitt, R.L., and R.S.C. Smart. 1978. The mechanism of sulfate adsorption on iron oxides. Soil Sci. Soc. Am. J. 42:48–50. doi:10.2136/sssaj1978.03615995004200010011x

Peak, D., E.J. Elzinga, and D.L. Sparks. 2001. Understanding sulfate adsorption mechanisms on iron (III) oxides and hydroxides: Results from ATR-FTIR spectroscopy. In: H.M. Selim and D.L. Sparks, editors, Heavy Metals Release in Soils. Lewis Publishers, Boca Raton, FL. p. 167–190.

Peak, D., R.G. Ford, and D.L. Sparks. 1999. An in situ ATR-FTIR investigation of sulfate bonding mechanisms on goethite. J. Colloid Interface Sci. 218:289–299. doi:10.1006/jcis.1999.6405

Rahnemaie, R., T. Hiemstra, and W.H. van Riemsdijk. 2007. Geometry, charge distribution, and surface speciation of phosphate on goethite. Langmuir 23:3680–3689. doi:10.1021/la062965n

SAS Institute. 2012. SAS 9.3 Language reference: Concepts. SAS Inst. Inc., Cary, NC.

Shuai, X., X. Li, R.S. Yost, and O. Wendroth. 2016. State-space estimation of the intrinsic soil phosphorus pools from the Mehlich-3 test. Commun. Soil Sci. Plant Anal. 47:1058–1068. doi:10.1080/00103624.2016.1166244

Shuai, X., R.S. Yost, and T.J. Smyth. 2011. Predicting soil phosphorus fertilizer rate using hierarchical segmented regression models. Soil Sci. 176:303–306. doi:10.1097/SS.0b013e318219db24

Shuai, X., R.S. Yost, and O. Wendroth. 2014. State-space estimation of the intrinsic soil phosphorus pools from soil phosphorus tests. Geoderma 214:239–245. doi:10.1016/j.geoderma.2013.09.006

Soil Survey Laboratory Staff. 1991. Soil survey laboratory methods manual. Soil Survey Invest. Rep. 42. USDA-SCS Natl. Soil Survey Center, Washington, DC.

Soil Survey Staff. 1994. Keys to soil taxonomy. Soil Manage. Support Serv. Tech. Monogr. 19. 6th ed. Pocahontas Press, Blacksburg, VA.

Sparks, D.L. 1988. Kinetics of soil chemical processes. Academic Press, San Diego, CA.

Sposito, G. 1984. The surface chemistry of soils. Oxford Univ. Press, New York.

Sverjensky, D.A., and K. Fukushi. 2006. Anion adsorption on oxide surfaces: Inclusion of the water dipole in modeling the electrostatics of ligand exchange. Environ. Sci. Technol. 40:263–271. doi:10.1021/es051521v

Taylor, J.C. 1991. Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile. Powder Diffr. 6:2–9. doi:10.1017/S0885715600016778

Truog, E. 1930. The determination of the readily available phosphorus in soils. J. Am. Soc. Agron. 22:874–882. doi:10.2134/agronj1930.00021962002200100008x

Uehara, G., and G. Gillman. 1981. The mineralogy, chemistry and physics of tropical soils with variable charge clays. Westview Press, Boulder, CO.

Wang, D., and D.W. Anderson. 1998. Direct measurement of organic carbon content in soils by the Leco CR-12 Carbon Analyzer. Commun. Soil Sci. Plant Anal. 29:15–21. doi:10.1080/00103629809369925

Wijnja, H., and C.P. Schulthess. 2000. Vibrational spectroscopy study of selenate and sulfate adsorption mechanisms on Fe and Al (Hydr) oxide surfaces. J. Colloid Interface Sci. 229:286–297. doi:10.1006/jcis.2000.6960

Wuenscher, R., H. Unterfrauner, R. Peticzka, and F. Zehetner. 2015. A comparison of 14 soil phosphorus extraction methods applied to 50 agricultural soils from Central Europe. Plant Soil Environ. 61:86–96. doi:10.17221/932/2014-PSE

Yao, W., and F.J. Millero. 1996. Adsorption of phosphate on manganese dioxide in seawater. Environ. Sci. Technol. 30:536–541. doi:10.1021/es950290x