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

Xiufu Shuai,* Liwang Ma, and Ole Wendroth

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; Rahnenmaie 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; Wueensch 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 the P adsorption reaction kinetics to form different pairs of the two P pools over time and to measure the time series of soil P sorption site density.

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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 \([Ca(H_2PO_4)_2]\) 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\(\cdot\)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\(\cdot\)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).

\[
x_1 + SOH \xrightarrow{k_{d}} x_2
\]

where SOH is the sorption site at soil surface, and \(k_{d}\) 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
the dynamics of intrinsic P pools behave as linear differential equations (Sparks, 1988). The P adsorption kinetics are

\[
\frac{dx_1(t)}{dt} = -k_1[\text{SOH}]x_1 + k_2x_2 + u(t) \tag{2}
\]

\[
\frac{dx_2(t)}{dt} = k_3[\text{SOH}]x_1 - k_4x_2 \tag{3}
\]

where \(x_1\) and \(x_2\) are the amounts of the weakly adsorbed and tightly adsorbed P pools, respectively. 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 (Wuenchser et al., 2015) and it was denoted as \(\gamma_{\text{Olsen}}\) (Shuai et al., 2014). The relationship between weakly adsorbed P pool and the Olsen extractable P is

\[
\gamma_{\text{Olsen}}(t) = c_{1,\text{Olsen}}x_1(t) \tag{4}
\]

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 \(\gamma_{\text{Truog}}\) contains portions of both the weakly adsorbed P pool \(x_1\) and the tightly adsorbed P pool \(x_2\)

\[
\gamma_{\text{Truog}}(t) = c_{1,\text{Truog}}x_1(t) + c_{2,\text{Truog}}x_2(t) \tag{5}
\]

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 Schulteis, 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 weakly 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 \(\gamma_{\text{Olsen}}(t)\) and the modified Truog extractable P \(\gamma_{\text{Truog}}(t)\) 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

\[
u(t) = u(0)d_\delta(t) \tag{6}
\]

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):

\[
x_1(t) = \frac{k_1[x_1(0) + x_2(0) + u(0)]}{k_3[\text{SOH}]+k_{ad}} + \frac{k_2[\text{SOH}]x_1(0) - k_4x_2(0) + k_3[\text{SOH}]u(0)}{k_3[\text{SOH}]+k_{ad}}e^{-\frac{(k_3[\text{SOH}]+k_{ad})t}{2}} \tag{7}
\]

and

\[
x_2(t) = \frac{k_1[x_1(0) + x_2(0) + u(0)]}{k_3[\text{SOH}]+k_{ad}} - \frac{k_2[\text{SOH}]x_1(0) + k_3[\text{SOH}]u(0)}{k_3[\text{SOH}]+k_{ad}}e^{-\frac{(k_3[\text{SOH}]+k_{ad})t}{2}} - \frac{k_4x_2(0)}{k_3[\text{SOH}]+k_{ad}} \tag{8}
\]
Combining the Eq. [5, 7, 8] gives

\[
\begin{align*}
\gamma_{\text{tr}}(t) &= \left( \frac{c_{1,\text{Truog}}k_l + c_{2,\text{Truog}}k_\text{SOH}}{k_\text{SOH} + k_d} \right) x_i(0) + \frac{c_{1,\text{Truog}}k_l + c_{2,\text{Truog}}k_\text{SOH}}{k_\text{SOH} + k_d} x_1(0) \\
&+ \frac{1}{k_\text{SOH} + k_d} \left( \frac{c_{1,\text{Truog}}k_l - c_{2,\text{Truog}}k_\text{SOH}}{k_\text{SOH} + k_d} \right) e^{-(k_\text{SOH} + k_d)v} + \\
&+ \frac{1}{k_\text{SOH} + k_d} \left( \frac{c_{1,\text{Truog}}k_l + c_{2,\text{Truog}}k_\text{SOH}}{k_\text{SOH} + k_d} \right) e^{-(k_\text{SOH} + k_d)v} \\
&+ \frac{1}{k_\text{SOH} + k_d} \frac{1}{k_\text{SOH} + k_d} e^{-(k_\text{SOH} + k_d)v} \right) + \\
&+ \frac{1}{k_\text{SOH} + k_d} \frac{1}{k_\text{SOH} + k_d} e^{-(k_\text{SOH} + k_d)v} \right)
\end{align*}
\]

In Eq. [9], there is a linear relationship between the modified Truog extractable P (\(y_{\text{tr}}\)) as output and the external P input and output are all valid. 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 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 \(x_i(0) > k_d\). 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 \((x_1, x_2)\) and output \((y_{\text{tr}})\), denoted as \(g_1, g_2, \) and \(g_{\text{tr}}\) respectively, and they are

\[
g_1(t) = \frac{k_d}{k_\text{SOH} + k_d} + \frac{k_\text{SOH}}{k_\text{SOH} + k_d} e^{-(k_\text{SOH} + k_d)v} \] \quad (10)
\]

\[
g_2(t) = 1 - g_1(t) \] \quad (11)
\]

and

\[
g_{\text{tr}}(t) = \left( \frac{c_{1,\text{Truog}}k_l + c_{2,\text{Truog}}k_\text{SOH}}{k_\text{SOH} + k_d} \right) \left( \frac{c_{1,\text{Truog}}k_l - c_{2,\text{Truog}}k_\text{SOH}}{k_\text{SOH} + k_d} \right) e^{-(k_\text{SOH} + k_d)v} \] \quad (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.

**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 \(c_{2,\text{Truog}}\), \(k_1\), and \(k_1\) 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, \(g_{\text{tr}}(t)\). At each sampling time for each soil, Eq. [9] can be rewritten as a linear function of \(u(0)\)

\[
y_{\text{tr}}(t) = \beta_0(t) + u(0)g_{\text{tr}}(t) \] \quad (13)
\]

where \(\beta_0(t)\) was the effect of initial condition of soil P pools in the P adsorption experiments. The impulse response of modified Truog extractable P, \(g_{\text{tr}}(t)\), 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 \(g_{\text{tr}}(t)\) 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, \(g_1(t)\). The values of the adsorption rate \(k_1\text{SOH}\) 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 \(t\) as

\[
g_1(t) = \frac{k_d}{k_\text{SOH} + k_d} + \frac{k_\text{SOH}}{k_\text{SOH} + k_d} e^{-(k_\text{SOH} + k_d)v} \] \quad (14)
\]

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

\[
g_{\text{tr}}(t) = \left( c_{1,\text{Truog}} - c_{2,\text{Truog}} \right) g_1(t) + c_{2,\text{Truog}} \] \quad (15)
\]

The coefficients \(c_{1,\text{Truog}}\) and \(c_{2,\text{Truog}}\) in Eq. [15] was obtained using linear regressions of the results of \(g_{\text{tr}}(t)\) and \(g_1(t)\) 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 \(P_{\text{weak}}\), contains a portion of the weakly adsorbed P pool

\[
P_{\text{weak}} = c_{1,\text{weak}}x_i \] \quad (16)
Table 2. Adsorption and desorption rates in P adsorption experiments and extraction efficiency of the weakly adsorbed P pools based on the Olsen method (Shuai et al., 2014).

<table>
<thead>
<tr>
<th>Soil</th>
<th>Adsorption rates ($k_1$[SOH], $d^{-1}$)</th>
<th>Desorption rates ($k_2$ d$^{-1}$)</th>
<th>Extraction efficiency ($c_{1,Olsen}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hali</td>
<td>0.0271</td>
<td>0.0186</td>
<td>0.224</td>
</tr>
<tr>
<td>Kapaa</td>
<td>0.0566</td>
<td>0.0330</td>
<td>0.195</td>
</tr>
<tr>
<td>Maile</td>
<td>0.0280</td>
<td>0.0172</td>
<td>0.162</td>
</tr>
<tr>
<td>Makapili</td>
<td>0.0330</td>
<td>0.0152</td>
<td>0.121</td>
</tr>
<tr>
<td>Molokai</td>
<td>0.0184</td>
<td>0.0220</td>
<td>0.464</td>
</tr>
<tr>
<td>Pulehu</td>
<td>0.0319</td>
<td>0.0321</td>
<td>0.405</td>
</tr>
<tr>
<td>Wahiawa</td>
<td>0.0435</td>
<td>0.0313</td>
<td>0.353</td>
</tr>
</tbody>
</table>

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

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

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

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

and

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

RESULTS AND DISCUSSIONS

Modified Truong Extractable Phosphorus

The modified Truong 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 Truong 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 Truong Extractable Phosphorus and the Weakly Adsorbed Phosphorus Pool

The impulse response of the modified Truong extractable P of each soil shown in Fig. 2 was obtained from the linear regression of measured Truong 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 Truong Method

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

The extraction efficiencies $c_{1,Truong}$ of the weakly adsorbed P pools ranged from 22 to 62% for the seven soils. The extraction efficiencies $c_{2,Truong}$ 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 $c_{2,Truong}$ were below 2.1%.

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

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

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

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

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

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

The modified Truong 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

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

The modified Truong 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

$$x_2 = \frac{1}{-0.108\ln(PSSD) - 0.135}\left(P_{strong} - 1.288P_{weak}\right).$$  \[24\]
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 Wahaiawa 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. 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]).
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]).
The extractable P by the strong modified Truong method contained portions of the weakly adsorbed P pool and the tightly adsorbed P pool. The coefficients of the linear relationship between the modified Truong extractable P and the two intrinsic P pools, i.e., extraction efficiencies, were estimated based on the dynamics of the modified Truong 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 Truong 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 Truong extractable P as long as the extraction efficiencies by the strong modified Truong 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**


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**Table 3.** Estimates of the extraction efficiencies, $c_{1,\text{Truong}}$ and $c_{2,\text{Truong}}$, of the weakly and tightly adsorbed P pools by the modified Truong method.

<table>
<thead>
<tr>
<th>Soil</th>
<th>$c_{1,\text{Truong}}$</th>
<th>$c_{2,\text{Truong}}$</th>
<th>$R^2$</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halii</td>
<td>0.329</td>
<td>0.000</td>
<td>0.97</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Kapaa</td>
<td>0.223</td>
<td>0.021</td>
<td>0.76</td>
<td>0.002</td>
</tr>
<tr>
<td>Maile</td>
<td>0.247</td>
<td>0.000</td>
<td>0.92</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Makapili</td>
<td>0.239</td>
<td>0.011</td>
<td>0.92</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Molokai</td>
<td>0.622</td>
<td>0.361</td>
<td>0.56</td>
<td>0.021</td>
</tr>
<tr>
<td>Pulehu</td>
<td>0.505</td>
<td>0.186</td>
<td>0.54</td>
<td>0.024</td>
</tr>
<tr>
<td>Wahiawa</td>
<td>0.386</td>
<td>0.140</td>
<td>0.90</td>
<td>&lt; 0.001</td>
</tr>
</tbody>
</table>

**Fig. 4.** Change of the extraction efficiency of the weakly adsorbed P pool ($c_{1,\text{Truong}}$) by the modified Truong 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 ($c_{2,\text{Truong}}$) by the modified Truong method with soil P sorption site density (PSSD) and the fitted curve for the seven soils.