USE OF BRAY-2 TEST TO EVALUATE AVAILABLE PHOSPHORUS IN SOILS TREATED WITH PHOSPHATE ROCKS FOR OIL PALM: A REVIEW
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Abstract
Bray-2 test has been widely used to evaluate available P in acid soils treated with different phosphate rock (PR) sources for oil palm plantations in Malaysia and Indonesia. The review shows that Bray-2 test, which is a strong acid reagent, often overestimates available P in the soil compared with the actual P in soil solution from the dissolution of PR. Consequently, none or poor correlations between fresh fruit bunch (FFB) yield of oil palm and Bray-2 P have often been obtained. This problem occurs when comparing Bray-2 P from PR with that from water-soluble P (WSP) fertilizer such as TSP or comparing highly reactive PR with low-reactive PR. A new mixed cation-anion resin has been proven effective for evaluating available P from different types of P sources including PRs of varying reactivity and WSP for field crops. The resin method should be studied to test if it can be used to replace the current Bray-2 test to evaluate available P for oil palm.

1. Introduction
Soil testing for phosphorus (P) has been researched extensively over the past several decades. Numerous tests ranging from strong acids, alkaline solutions, organic and inorganic complexing agents have been used to estimate P bioavailability for different crops and soils. The most widely used soil P tests are Bray-1¹, Bray-2¹, Mehlich-1², and Olsen³. Other commonly used tests include Mehlich-2² and Mehlich-3². All these soil tests have been developed mainly for evaluating P availability of water-soluble P (WSP) fertilizers such as mono ammonium phosphate (MAP), diammonium phosphate (DAP), single superphosphate (SSP), and triple superphosphate (TSP) to various crops. Reports in literature have shown that these conventional acid or alkaline soil tests do not work well in soils fertilized with phosphate rock (PR) which have low water solubility⁴,⁵,⁶. Thus, there is a need to develop and use appropriate soil tests that closely reflect P uptake from PR sources varying in reactivity used on different soils for different crops. Furthermore, the soil tests must be suitable for both PR and WSP fertilizers.

Keywords
Bray-2 P, resin P, oil palm, phosphate rock, available P

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The use of Bray-2 P for P recommendations to oil palm in Malaysia and Indonesia might be attributed to historical events where Owen first demonstrated its use to distinguish soils that were P responsive in rubber in Malaya from those which were non-responsive to P applications. Subsequent researchers obtained a “satisfactory” relationship between soil Bray-2 P and P fertilizer responses in rubber. These researchers recognised the large variations in results and interpretation of the data and suggested further work on better soil analytical techniques to evaluate P availability. Despite this, agronomists in Malaysia and Indonesia adopted Bray-2 P as the de facto soil extraction method to determine the PR requirements of oil palm when oil palm planting expanded in the 1970s and beyond to new soils and environments. This situation did not change even when PRs from various countries with different reactivity and physical properties were widely used in oil palm cultivation. However, it is known that Bray-2 P was mainly employed to monitor build-up of P nutrient in the soils and to detect its application in the field to prevent fraudulent practices e.g. fertilizer theft.

Bray-2 test is the most widely used method in Malaysia and Indonesia to estimate soil P availability for oil palm. Besides, another available P soil test method using the cation-anion resin is popular in Brazil. This study is carried out to see the suitability of these two methods to estimate available P in the soils of tropical countries.

2. Soil phosphorus reaction and soil testing

When WSP fertilizers are applied to acid soils containing Fe-Al-oxides, reaction products in the form of Fe-Al-P become the main sources of available P for plant uptake through desorption/dissolution process. This reaction is rapid and, therefore, much of the WSP is readily transformed to the reaction products and is no longer present in soil solution shortly after application. If the amount of available P extracted by a soil test ($k_1$) is proportional (i.e. good correlation) to the amount of P uptake by plant or crop yield($k_1$), then this soil test is suitable to be calibrated for recommendation of fertilizer rate of WSP (Figure 1).

Figure 1: Relationship between plant P uptake and soil available P from TSP and PR applied to acid soil

Source: Chien.

[Diagram of soil phosphorus reaction and soil testing with labels and arrows indicating soil testing, plant P uptake, available P, and reaction products.]

Source: Chien.
When PR is applied to acid soil, dissolution of PR releases P to the soil solution. Part of the released P can be absorbed by the plant roots directly \((k_0)\) while the remainder reacts with Fe-Al-oxides to form Fe-Al-P, which may also provide available P \((k_0')\) later through the desorption process. However, unlike WSP, soil solution P concentration from PR dissolution is too low to precipitate Fe-Al-P compounds. Thus, both the reaction products and undissolved PR can provide available P to the plant\(^9\). The degree of relative P availability from undissolved PR \((k_0)\) versus Fe-Al-P \((k_0')\) depends on PR reactivity, soil P-fixing capacity and duration of PR reaction with soil. However, due to the nature of water-insoluble PR, available P in soil solution mainly comes from the continuous dissolution of undissolved PR instead of desorption from a small fraction of Fe-Al-P during the crop growth\(^9\). When a soil test for available P results in a good correlation between P uptake or crop yield \((k_0)\) and available P from PR \((k_0')\) in the soil, then this soil test is suitable to be calibrated for recommendation of fertilizer rate of PR fertilizers, provided all PR sources follow the same regression line.

Although the soil test for available P from the reaction products of PR dissolution \((k_0')\) may be assumed to be the same as that of TSP dissolution, i.e., \(k_0/k_0' = k_1/k_1'\), the P mineral in PR is Ca-P, which differs from the reaction products of TSP in the form of Fe-Al-P. If \(k_0/k_0' = k_1/k_1'\), then the soil test would be applicable to both PR and TSP. \(k_0/k_0' > k_1/k_1'\), the soil test would have underestimated the available P from PR with respect to TSP. Conversely, if \(k_0/k_0' < k_1/k_1'\), the soil test would have overestimated the available P from PR with respect to TSP.

3. **Bray-2 test for soils treated with PR and WSP**

Bray-2 \((0.03 M NH_4F + 0.1 M HCl)\) test\(^i\) is a strong acidic reagent that is used to extract available P in acid soils in USA. Later it was adopted for humid tropical acid soils (Ultisols and Oxisols) in Southeast Asia and South America because of their high P-fixing capacity by amorphous Fe-Al-oxides in the soils. This test is widely used in Malaysia, Indonesia, Colombia and other countries for oil palm grown on acid soils where PR is commonly used.

Being a strong acidic reagent, Bray-2 test can extract a substantial amount of undisolved PR in the soil. Menon et al.\(^5\) showed a relationship between dry-matter yield (DMY) of maize and Bray-2 P in an acid soil (pH 5.2) treated with TSP and a medium reactive central Florida PR. The linear regression of PR was below the regression line of TSP indicating Bray-2 overestimated available P from the PR with respect to that from TSP.

Bray-2, which can dissolve the PR in the soil during soil extraction, extracts much higher P than the actual dissolved P from PR in the soil used for plant growth resulting in \(k_0' > k_0\), whereas the reverse is true for TSP, i.e., \(k_1' < k_1\) (Figure 1). Consequently, \(k_0'/k_0 < k_1'/k_1\) which indicates that Bray-2 overestimates available P from PR. This overestimation may provide a misleading conclusion that PR can build up higher soil available P than TSP.

In a study on dissolution of PR in four Malaysian acid soils under rubber, Lau and Mahmud\(^10\) compared five PR sources with TSP at two P rates for DMY of *Pueraria javanica* after three consecutive cropping in the greenhouse. Although there was a significant correlation \((p < 0.001)\) between Bray-2 P and DMY, the R\(^2\) value of 0.39 was low and suggested that Bray-2 was not a sensitive test for available P in acid soils treated with PR and TSP for plant growth.

4. **Use of Bray-2 test on soils applied with PR for oil palm**

Zaharah et al.\(^1\) evaluated two PR sources at different rates of application on oil palm grown on peat soils in Sarawak, Malaysia for five consecutive years. The soluble P\(_2\)O\(_5\), as measured by 2% citric acid (CA) and 2% formic acid (FA), was higher for Morocco PR or MPR (2% CA = 10.6% and 2% FA = 17.9%) than that of Christmas Island phosphate rock or CIPR (2% CA = 9.3% and 2% FA = 11.6%). They used quadratic equations to predict accurately the FFB yields in every year with each PR source at a specific PR rate. From the second year onwards, a significant increase in FFB yield was observed with increasing rate of MPR and CIPR applied. However, FFB yields with MPR were lower than that of CIPR, especially at the highest rate (2,000 g/palm/year), even though MPR was more reactive than CIPR (Figure 2).
The FFB yields in Figure 2 show MPR-2000 < MPR-1000 ≈ CIPR-1000 < CIPR-2000. Zaharah et al.\textsuperscript{11} speculated that the lower FFB yields of MPR-1000 and MPR-2000 < CIPR-2000 was due to their excess Bray 2-P and other nutrient interactions that could influence oil palm growth. In contrast, they explained that the lower Bray-2 P with MPR-2000 than that of MPR-1000 was probably due to the decreased MPR solubility at the higher rate and, therefore, released less available soil P that resulted in FFB yield of MPR-2000 < MPR-1000 (Figure 2). These two explanations seemed to contradict each other regarding the role of Bray-2 P test in predicting FFB yield as influenced by PR solubility, rate and time. In short, they concluded the whole scenario was complex due to the many factors acting together.

Here, we propose another alternative and more logical explanation for the results of Zaharah et al.\textsuperscript{11} in terms of PR solubility and FFB yield. MPR and CIPR had about the same total P\textsubscript{2}O\textsubscript{5} (33.4%) but CaO content was higher in MPR (46.8%) compared with CIPR (31.1%). This suggests that MPR contains significantly higher amount of CaCO\textsubscript{3} equivalent of at least 
\[(46.8 – 31.1) \times (\text{CaCO}_3/\text{CaO}) \times 100 = 15.7 \times (100/40) \times 100 = 28.3\%\]. At MPR-2000 rate applied annually for five years, this was equivalent to 2000 x 0.283 x 5 = 2.83 kg of CaCO\textsubscript{3}/palm. The presence of CaCO\textsubscript{3} was identified by x-ray diffraction (XRD) method in MPR, but not in CIPR, by Zaharah et al.\textsuperscript{11}. Since CaCO\textsubscript{3} is more soluble than apatite, it can depress the dissolution of PR in acid soil solution by raising soil pH and increasing exchangeable Ca\textsuperscript{2+}. This decreases available P to oil palm.

This negative effect on the agronomic effectiveness of MPR increased with increasing P rate and time because more CaCO\textsubscript{3} would have been applied to the soil. At the highest rate (2,000 g PR/palm/year), FFB yield of MPR was significantly lower than CIPR (Figure 2) despite Bray-2 P being about the same for both. Since Bray-2 is much stronger than the acid soil solution, it suggests that Bray-2 may have overestimated available P from the undissolved CIPR in the soil compared to undissolved MPR, which contained a significant amount of CaCO\textsubscript{3} at
this P rate. However, Bray-2 P of MPR-2000 in the fifth year was very high (540 mg P/kg) as compared to MPR-1000 (350 mg P/kg) and CIPR-2000 (190 mg P/kg), yet FFB yield of MPR-2000 (19.4 t/ha) was lower compared to MPR-1000 (20.3 t/ha) and CIPR-2000 (21.2 t/ha) based on each regression equation. The data of Bray-2 P was inconsistent in relating to FFB yield in the study by Zaharah et al.\textsuperscript{11}. This might be partially attributed to the different time intervals between taking soil samples and PR application, which were not standardized in the experiment.

Zin et al.\textsuperscript{13} studied the relationship between FFB yield of oil palm and Bray-2 P in six inland and four coastal soils treated with CIPR. The relationship was not found to be significant as $R^2 = 0.32$ and suggested that Bray-2 test was not a good test for available P.

Ng et al.\textsuperscript{14} reported that an average FFB yield of 25.9 t/ha/year was obtained when 13.5 kg/ha/year of a highly reactive Bayovar PR from Peru was applied. This yield was higher than that obtained by applying 23.3 t/ha/year of a medium reactive Jordanian PR, in fourth and fifth year after planting. This difference was significant at $p = 0.10$. This difference was attributed to the high reactivity of Bayovar PR compared to Jordanian PR.

Bray-2 P extracted from the soil in the inter-rows treated with Jordanian PR was significantly higher than that of Bayovar PR (16 versus 6 mg P/kg respectively) in second year after planting. It suggests that Bray-2 may have overestimated available P from Jordanian PR. It is possible that more Jordanian PR than Bayovar PR remain in the soil due to Jordanian PR's lower reactivity. If so, Bray-2 could extract higher P from the soil where Jordanian RP has been applied. This explanation differs from Ng et al.\textsuperscript{13} who stated that Jordanian PR resulted in a higher build-up of soil available P. This statement would be true if the build-up of P referred to total instead of available P.

The use of Bray-2 test, which overestimates available P from lower-reactive PR, could be more problematic for soils with low pH buffering capacity such as light-textured or peat soils. This may partially explain why Bray-2 P was lower in the soil applied with the medium-reactive MPR-2000 than that with the low-reactive CIPR-2000 in the peat soils as reported by Zaharah et al.\textsuperscript{17}

In another study on soil nutrient changes on Ultisols under oil palm in Johor, Malaysia, Ng et al.\textsuperscript{15} collected paired soil samples from the inter-rows in two depths (0-15 and 15-45 cm) at two sites. After PR application over a period of 13 years, the % change of the same soil samples for total P content ranged from a minimum of 83% to a maximum of 402% and the corresponding % changes in Bray 2-P ranged from a minimum of 98% to a maximum of 1,595%. The huge % increase in Bray-2 P as compared to % increase in total P suggests that Bray-2 may have dissolved the remaining undecomposed PR left in the soils during Bray-2 extraction and thus may have overestimated available P from PR in the soils with respect to the actual dissolution of PR in soil solution.

Zin et al.\textsuperscript{16} evaluated six P sources, namely, TSP, North Carolina PR (NCRP), Gafsa PR (GRP), Jordan PR (JRP), Christmas Island PR (CIPR) and China PR (CRP) applied to oil palms grown on an inland sedimentary soil (Ultisol) and a coastal alluvial soil (Inceptisol) over a nine-year period. The results in the Ultisol showed a significant non-linear (power function) relationship between average FFB yield (3\textsuperscript{rd} to 8\textsuperscript{th} harvest) and Bray-2 P extracted from the soil samples (0-15 cm depth) collected after the last harvest. No significant correlation was found in the Inceptisol.

In the study of Zin et al.\textsuperscript{16}, there was no theoretical basis to relate Bray-2 P in the Ultisol treated with annual application of PR and TSP for 8 years to the average FFB yield/year obtained during the same years. There was a problem of the confounding effect on the available P in the soil because the amounts of undissolved PR and reaction product (Fe-Al-P) kept changing along with time. Thus Bray-2 P extracted from the soil after the 8\textsuperscript{th} harvest of FFB represented only from the freshly applied P after 7\textsuperscript{th} harvest and the residual P applied previously (1\textsuperscript{st} -6\textsuperscript{th} harvests). Since Bray-2 P extracted P from PR and Fe-Al-P in the soil will not provide the same in P availability to oil palm, the regression curve across all P sources will not have a significant agronomic implication.

In a study by Chien et al.\textsuperscript{17}, six PR sources, ranging from low to high reactivity, were applied as a singular application at 176 kg
P/ha on an acid Oxisol (pH 4.2) in Colombia. After 22 cuttings of Brachiaria grass in five years, the amount of P recovered from the least reactive PR (Pesca PR, Colombia) was 21% of the initial applied PR whereas only 2% was recovered from the highly reactive Bayovar PR (Peru). If Pesca PR had been applied annually, there would be a substantial amount of the undisolved Pesca PR left in the soil.

Since both CRP used by Zin et al.\textsuperscript{16} and Pesca PR used by Chien et al.\textsuperscript{17} had about the same low reactivity, it suggests that there could have been a substantial amount of yearly applied CRP left in the soil in the study of Zin et al.\textsuperscript{16}. Indeed, at the highest yearly applied P rate (4.5 kg of CRP equivalent) for eight years, Bray-2 P content in the soil (1,628 mg P/kg) was significantly higher than that of TSP (861 mg P/kg) while the FFB yields of both P sources were about the same (23.3 and 23.9 t/ha/year respectively). This indicated a possible overestimation of available P by Bray-2 from CRP. Likewise, Bray-2 also overestimated available P from GRP (2,176 mg P/kg) at the same highest P rate applied to the soil, although both PR sources were high in reactivity and FFB yields obtained for both were about 24 t/ha/year. It appeared that Bray-2 extracted the undisolved PR in the soil in the study of Zin et al.\textsuperscript{16} and, therefore, it should not be recommended as a soil P test for PR and TSP.

5. Mixed anion and cation exchange resins

A resin membrane strip containing a mixture of cation (Na) and anion (HCO\textsubscript{3}) was first introduced by Saggar et al.\textsuperscript{18} to evaluate available P in the soils treated with PR and WSP. The inclusion of Na\textsuperscript{+}-saturated resin will enhance P release from PR by removing Ca\textsuperscript{2+}-associated with P in the apatite structure. In other words, it results in \( \frac{k_2}{k'_2} = \frac{k_1}{k'_1} \) (Figure 1). The amount of P extracted by the mixed resin procedure correlated well with the solubility of P sources applied to the soils. Subsequently, Saggar et al.\textsuperscript{19} compared the method of mixed cation-anion resin membrane strip with seven other soil tests and found that the resin method was the best to assess the available P status of soils treated with PR sources varying in reactivity. A good relationship between crop yield and available P for both PR and monocalcium phosphate (MCP), which is the P compound of SSP/TSP\textsuperscript{20}, was obtained by this method (Figure 3).

Figure 3: Relationship between relative yield of ryegrass in glasshouse experiment and anion-cation exchange resin (AER + CER) test soil test for PR treatments (symbols) and monocalcium phosphate (MCP) treated or untreated soils (lines)

The relationship between P uptake (minus control) and strongly acidic Mehlich-1 P in soil treated with TSP1, TSP2, low-reactive Alvorada PR (Brazil) and calcined Al-P (Brazil) for soybean grown on a Brazilian acid soil was reported by Raji et al.\textsuperscript{21} and shown in Figure 4. All the P sources were applied at 75 days prior to seeding except TSP2 which was applied at seeding. It can be seen clearly that there was no significant correlation between P uptake and Mehlich-1. It also showed that Mehlich-1 extracted much higher available P from PR than TSP2 yet the P uptake was much lower. This indicates that Mehlich-1 extracted much more of the undisolved PR in the soil during soil extraction and did not reflect the actual PR dissolution in the soil solution during the soybean growth. Although Bray-2 was not used in the study, the same conclusion can be drawn from the study because Bray-2 is twice as strong as Mehlich-1 (0.05 M HCl + 0.0125 M H\textsubscript{2}SO\textsubscript{4}). Thus, it can be concluded that Bray-2 would also overestimate available P from PR with respect to TSP in the study of Raji et al.\textsuperscript{21}.
Figure 4: Relationship between P uptake (minus control) by soybean and Mehlich-1 P extracted from soil treated with TSP, low-reactive Alvorada PR and calcined Al-P in Brazil. All P sources were applied at 75 days prior to seeding except TSP2 at seeding.

Source: Raji et al. 21

When the Mehlich-1 P was replaced by resin P, a significant correlation was obtained; P uptake by soybean increased with increasing resin P (Figure 5). Furthermore, the relationship was found for all P sources, namely TSP, PR and Al-P and indicated that resin, unlike Bray 2, was a good soil test for P availability in soils treated with different types of P sources. A similar conclusion was found by Zulkifli et al. 22 based on the results obtained for 12-months old oil palm grown in the nursery when P uptake was significantly and linearly correlated to resin strip P but no correlation was obtained with Bray-2 P (Figure 6). Furthermore, Bray-2 P of PR sources were as high as that of TSP but the P uptakes by oil palm were very much lower for the former PR sources. This showed that Bray-2 overestimated available P from PR sources.

Figure 5: Relationship between P uptake (minus control) by soybean and resin P extracted from soil treated with TSP, low-reactive Alvorada PR and calcined Al-P in Brazil. All P sources were applied at 75 days prior to seeding except TSP2 at seeding.

Source: Raji et al. 21
One important application of the resin P test for oil palm production is that it can relate soil available P measured after the last FFB harvest to the average FFB yield per year during the whole period of oil palm production. Resin P can relate available P from undissolved PR and reaction products (Fe-Al-P) to FFB yield.

The resin method has been successfully used by over 100 laboratories in Brazil. Also, simple, time saving and inexpensive commercial-scale equipment for the resin test has been developed and marketed in the country.6

6. Conclusions

Bray-2 test is commonly used to evaluate P availability in the soil for oil palm. Since it is a strong acid reagent, it can extract much of the undissolved PR in the soil. As such, it can overestimate available P during oil palm growth. The cation-anion resin test has shown promise for use in estimating available P for plant growth on soils treated with WSP and different PR sources. It is recommended that the resin test be studied on tropical acid soils to gauge its utility as a better method to estimate P availability in the soil for oil palm growth.

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References