PHOSPHORUS LEACHING IN AN ACID TROPICAL SOIL “RECAPITALIZED” WITH PHOSPHATE ROCK AND TRIPLE SUPERPHOSPHATE


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ABSTRACT
Repeated P fertilizer applications result in accumulation of phosphorus in soils. A lysimeter study was conducted in the field to evaluate P leached from soils treated with triple super phosphate (TSP) and Gafsa Phosphate Rock (GPR) at 300, 600 and 900 kg P ha\(^{-1}\) with and without integration with cattle manure. The lysimeter, made from PVC tubes of 30 cm length were inserted into the soil up to 25 cm depth. The tubes were then retrieved from the soil and a resin bag containing a mixture of cation and anion exchange resin in a 50:50 weight ratio were placed at the lower end of the tube and reinserted into the soil. The tubes arranged in a completely randomized design were sampled randomly at 10 weeks intervals for 12 months. The P remaining in the top and bottom 5 cm soil at the end of experiment and in the resins were determined. Generally, more P was found to be leached out from TSP (3 folds) as compared to GPR and the amount of P leached increased with increasing rates of P fertilizer applied. Application of manure intensified the amounts of P leached from TSP, particularly at 6 months sampling time. There was hardly any substantial P leached from the soil treated with GPR. Thus for effective and efficient long term P fertilizer management strategies, choosing the right P fertilizer source and monitoring P losses through leaching has to be done for enhanced fertilizer use efficiency thus reducing P pollution of ground waters.

Keywords: Acid Soil, Phosphorus leaching, Recapitalized

INTRODUCTION
Repeated fertilizer P applications result in high accumulations of P in the soils. The P reacts with soil components, mainly hydrous oxides of Fe and Al in the acid soils of the tropics, forming relatively less soluble compounds. As fixation of the negatively charged phosphate ion continues, there is a ‘semi-permanent’ increase in negative charge and therefore a decrease in the electric potential of the reacting soil particle (Barrow et al., 1998), which will result in decrease in sorption of phosphate anions.

Although phosphorus reacts readily with soil components, the capacity of a soil to bind P is limited. Therefore, upper soil layers become saturated with P if systematically applied in excess of plant needs. Then substantial amounts of P can be leached to deeper soil and/or ground waters. The degree of phosphorus saturation (DPS), which is a ratio of extractable P relative to the P sorption capacity of a soil, has been widely used in describing the soil P status of soils (Lookman et al., 1995; Leinwerber et al., 1997). The
DPS has been found to be correlated with P release from soils to runoff and leaching (Breeusma, 1995). Consequently, DPS is widely used in Europe for predicting P loss for environmental purposes (Breeusma, 1995 and Lookman, 1995). In Netherlands, environmental thresholds has been set at 25% DPS. The P threshold is a critical point beyond which the potential for P release from soils increases dramatically (Hecrath et al., 1995; Kleiman et al., 2000). The objectives of this study were:

(i) To evaluate the magnitude of P leaching in soils treated with two P sources, with and without manure addition and,
(ii) To evaluate the relationship between extractable Mehlich-3 P (Mehlich, 1984) in the soil and P leached.

MATERIALS AND METHODS
Experimental Site: The experiment was conducted at Puchong Research Farm, Universiti Putra Malaysia (UPM). The soil is classified as Bungor soil series, a sandy clay loam Ultisol (Typic Paleudult, clayey, kaolinitic, isohyperthermic). Top soil air dried and sieved to pass 2 mm sieve was characterized by standard methods (Page et al, 1982). The soil pH water (1:2.5 w/v) was 4.5; total carbon 3%; total P 280 mg P kg$^{-1}$; P sorption maximum 769 mg P kg$^{-1}$; Bray 1, Olsen and Iron oxide impregnated paper strip P of 4.9, 5.2 and 0.6 mg P kg$^{-1}$, respectively; Citrate dithionite extractable Al$_2$O$_3$ and Fe$_2$O$_3$ of 1.52 and 3.08%, respectively; cation exchange capacity 5.4 cmol (+) kg$^{-1}$. Characterization of the fertilizers and manure revealed that: Triple super phosphate (TSP) had total P 20.4%; CaO 19.2; CaO/ P$_2$O$_5$ 0.4; Al$_2$O$_3$ 0.6; Fe$_2$O$_3$ 1.6; solubility in water and 2% citric acid was 38 and 43%, respectively. Gafsa phosphate rock (GPR) had total P 12.5%; CaO 46%; CaO/ P$_2$O$_5$ 1.5; Al$_2$O$_3$ 0.4; Fe$_2$O$_3$ 0.9; solubility in water and 0.02%; citric acid 10%. Thus, based on the citric acid solubility (Diamond, 1978) it was considered a reactive PR that has been extensively used for direct application. The manure had total P 1% which is considered high possibly associated with a high phosphate feed given to the cattle; CaO 5%; Fe$_2$O$_3$ 0.3; Al$_2$O$_3$ 0.04 and magnesium 1.1%. Additional characterization of manure revealed that the manure had a high DOC level (21 g kg$^{-1}$) compared to 4 g kg$^{-1}$ of stabilized or mature composts (Zmora-Nahum et al., 2005). The C/N ratio was also high (27) compared to 10-15 of mature composts (Zmora-Nahum et al., 2005) while humic and fulvic acids were low indicating that the manure used was not decomposed.

The rainfall pattern in the duration of the experiment (July 2003 to July 2004) is presented in Fig. 1. Amount of rainfall received monthly was relatively uniform (ranging from 150 – 200 mm) in eight out of the 12 months the experiment was conducted. However, in 3 months the rainfall received each month was more than double the monthly amount received in the eight months. The lowest amount of rainfall received (June, 2004) was about 50% of that received in each of the eight months. Considering the sampling frequency of 10 weeks (approximately 2.5 months), the total amounts of rainfall received during the different sampling cycles would not vary greatly. Nevertheless, the third sampling covering the period between 19 November 2003 and 22 January 2004 seems to have received the highest rainfall.
Experimental Treatments and Design

Experimental treatments consisted of two P sources namely TSP and GPR at three application rates (300, 600 and 900 kg P ha⁻¹) plus control with and without cattle manure (20 Mg ha⁻¹). The experimental design was (2x4x2) factorial arranged in a randomized complete block with three replications.

The intact leaching columns were constructed using polyvinyl chloride (PVC) tubes of 9 cm internal diameter and 30 cm long (Fig. 2). With the aid of a hammer, the PVC tubes were vertically inserted into the soil to a depth of about 25 cm. Care was taken not to disrupt the soil structure. A shovel was then used to remove the soil around the exterior of the tube. Next the soil column was removed by breaking off the core from the main soil body. The PVC containing the soil column was lifted off the pit and the bottom 1.5 cm soil within the PVC tube was removed with a sharp knife to give room for the resin bag.

The resin bags were made from a nylon netting fabric (Monyl 58-70 HDX brand, Swiss silk Safar Inc. Printing Division, Switzerland) with mesh opening of about 0.9 µm. The resin bag diameter was approximately equal to the PVC internal diameter of 9 cm. They were sealed using an electric plastic sealer leaving a small perforation through which the cation-anion mixed exchange resin was placed into the bag before finally sealing it.

The cations and anions resins were purchased separately and were hand-mixed prior to use. The cation resin (Amberlite IR – 120; Fluka Chemie AG, Buchs, Switzerland) is strongly acid with close-linked polystyrene matrix and –SO₂H as functional group, mesh size 14-52. The cations had an exchange capacity of 1.95 Cmol·dm⁻³. The anion resin (Amberrlite IRA-93; Fluka Chemie AG, Buchs, Switzerland) was macro-reticular, weakly basic resin with tertiary amine groups attached to the cross-linked polystyrene matrix, mesh size 20-50 (BDH, 1981). They had a capacity of 1.40 Cmol·dm⁻³. Cations and anions resins were weighed in equal weights of 12.5 g each, mixed and placed into the bags. A mixed cation-anion exchange resin was used rather than an anion exchange resin because the former, extracts more P than the anion exchange resin alone (Fernandes and Coutino, 1997).

A resin bag (25 g) was then placed flat at the bottom of the soil column covering the whole area. The whole system of soil column and resin bag was re-inserted into the pit and the excavated soil carefully repacked around each PVC tube.

The tubes were installed 0.5 m x 2 m apart within plots and a total of 42 PVC tubes were installed at the experimental site. Treatments were applied at the top of each soil column and mixed to about 5 cm depth with a knife.
Non-destructive sampling (NDS) method was used and sampling was done at 10 weeks intervals for a total of 50 weeks. At sampling, the PVC tubes were dug out of the soil by removing soil adjacent to tube and the resin bag resting at the bottom of the tube was removed and placed in a labeled polythene bag. Freshly prepared resin bags were placed at the bottom of the PVC tubes and placed in-situ until the next sampling time. The process was repeated at every sampling. At the end of the experiment, top and sub-soil sampling was done at the top (5 cm) and bottom (5 cm), respectively.

\textit{(Insert Figure 3 here)}

The resin bags removed from the field were air-dried and adhering soil brushed off using a dry brush. Each resin bag was then opened and the cation-anion exchange resins were transferred into a 250 ml centrifuge tubes. For P elution, 100 ml of 0.1M H\textsubscript{2}SO\textsubscript{4} was added and the mixture shaken on an oscillatory shaker at 200 rpm for 2 hours. The suspension was then filtered through filter paper No. 5C and the extract analyzed for P by the ICP (Thermal Elemental IRIS Advantage model).

Amount of P leached was calculated using the following formula:

\[
P \text{ leached} (\text{kg P ha}^{-1}\text{yr}^{-1}) = \frac{500[\text{leachate P (mg P L}^{-1}) \times \text{Vol. of extractant (L)}]}{\text{Cross sectional area of tube (cm}^2)} \ 
\]  

[1]

Where, 500 is a factor to convert the 5 leachates in one year multiplied by 100 resulting from conversion of units in the equation.

The air-dried soil samples taken at the end of the experiment were extracted with Mehlich 3 extractant (0.2 M CH\textsubscript{3}COOH + 0.25 M NH\textsubscript{4}NO\textsubscript{3} + 0.015 M NH\textsubscript{4}F + 0.013 M HNO\textsubscript{3} + 0.001 M EDTA) at 1:20, soil/solution ratio with 5 minutes shaking (Mehlich, 1984). After filtration, the supernatant was read on the ICP for P.

Analysis of treatments effects on P leached over time were evaluated by combined analysis using proc mixed model procedure.

RESULTS

\textit{Effects of Different Treatments on P Leached from the Leaching Columns}

The P leached was significantly influenced by P source (P = 0.0001) and P rate (P = 0.0051) but not influenced significantly by manure addition (P = 0.06). The P leached ranged from 0.01 in the control to 3.88 kg P ha\textsuperscript{-1}yr\textsuperscript{-1} in the TSP/manure combination treatment. Generally, more P was leached from TSP than GPR treatments notably due to the higher solubility of TSP compared to GPR. On average, amounts of P leached from TSP treatments were three folds the P leached from GPR treatments and besides, the amounts of P leached increased with increasing P rates. Application of phosphate as TSP
at 300 kg P ha\(^{-1}\) led to 61% P leached compared to the control, while increasing the P rate to 600 and 900 kg P ha\(^{-1}\) resulted in elevated P leached, by about 158% and 289% of the control, respectively. Phosphorus leached from the different P sources was dependent on the P rates as indicated by a significant P source x P rate interaction. Over time, P leached was highly significant (P= 0.0001) and the three factors; P source, P rate and manure interacted significantly with time. Thus over time, the total amount of P leached was dependent on an interaction of P source x P rate x manure x time, presented in Fig. 4.

Phosphorus leached increased with increasing P rates (Fig. 4a to 4d). Manure alone did not increase P leached significantly (Fig. 4a). However, when manure was integrated with TSP, the magnitude of P leached was significant, particularly, at the sixth month sampling at all the P rates (Fig. 4b to 4d). However, at the initial sampling after 10 weeks, more P was leached from TSP alone than the combination of manure and TSP, while the trend reversed in the next sampling (20 weeks). After the 20 weeks, P leached declined at a high rate with an exception of the 600 kg P ha\(^{-1}\) rate for the manure and TSP combination which gave relatively high P leached throughout the experimental period. The P leached in TSP alone was reasonably high at the 600 and 900 kg P ha\(^{-1}\) rate at the first 10 weeks sampling, but declined more rapidly to low levels at 20 weeks (Fig. 4c-4d). On the other hand, the 20 weeks sampling coincided with the highest P leached sampling in the TSP-manure combination. No significant P was leached from the GPR treated soils with an exception of the 600 kg P ha\(^{-1}\) rate, where significantly low amounts of leached P were recorded at the sixth month (Fig 4c).

Mehlich-3 Extractable P and Ca from the Top Soil Samples at the End of Experiment

Extracted Mehlich-3 P in solution was determined using the ICP for both the top and subsoil samples. In both samples, extractable P was related to P application in a quadratic relationship in GPR and linear relationship in TSP (Fig. 6). Mehlich-3 P levels in the top soil were significantly influenced by P source and P rate (P = 0.0001 for both) and their interactions (P = 0.0005), while the P source x manure was not significant with P = 0.08 (Fig. 6). Even after 12 months, Mehlich-3 P levels were still high ranging from 19 to 302 mg P kg\(^{-1}\) in control and TSP, respectively.

Between the two P sources used, TSP exhibited the highest P levels as reported in all other experiments in this study. On average, the magnitude of P in TSP was more than 200% of GPR. Extractable P in TSP and TSP-manure combination increased linearly with increasing P rates. Equations describing increase in Mehlich-3 P in TSP and TSP-manure combinations are: \(y = 41.16 + 0.33x\) and \(y = 38.7 + 0.27x\), respectively. Alternatively, in GPR treatments, Mehlich-3 P increased in a quadratic fashion from 0 to a maximum at 600 kg P ha\(^{-1}\) and then declined slightly at P rate 900 kg P ha\(^{-1}\). Equations describing Mehlich-3 P in GPR and GPR-manure combinations are \(y =24.37 + 0.51x - 0.0005x^2\) and \(y = 15.26 + 0.25x – 0.00002x^2\), respectively. There was a significant correlation between

(Insert Figure 4 here)
Mehlich-3 P in the top soil and average leached P when three outliers were removed from the correlation \( (r = 0.86, P=0.0001) \) as shown in Fig. 5b. Additionally, Mehlich-3 P extracted at the top soil was also significantly correlated to the P levels in the sub-soil \( (r = 0.95, P=0.0001) \) as shown in Fig. 5c.

Manure effect on the TSP and GPR, P sources was striking; they exhibited opposite effects as shown on Fig. 6. Thus, TSP and manure combination exhibited lower extractable P levels than sole TSP treatment. Alternatively, GPR and manure combination resulted in higher P levels than the sole GPR treatment (Fig. 6).

On the other hand, Ca levels in the top soil were influenced significantly by P source \( (P = 0.048) \), while the effect of P rate was not significant \( (P = 0.073) \). The Ca levels ranged from 428 to 900 mg Ca kg\(^{-1}\) in control and GPR at highest rate of application \( (900 \text{ kg P ha}^{-1}) \). Gafsa PR gave significantly higher Ca levels than TSP whereby the magnitude was 30% more Ca in GPR than TSP. The rate of application influenced Ca levels in a trend similar to P where \( 600 = 900 > 300 > 0 \text{ kg P ha}^{-1} \) but 600 and 900 were not statistically different. Manure did not increase Ca levels significantly.

**Mehlich 3 Extractable P and Ca in the sub-soil samples at end of experiment**

Extractable Mehlich-3 P in the sub-soil was significantly influenced by the treatments which includes; fertilizer type, rate of application and manure addition \( (P = 0.004) \). Partitioning the treatment effects indicated that P application rate and manure addition significantly influenced subsoil P \( (P = 0.009 \text{ and } 0.031, \text{ respectively}) \). Contrary to the finding for the top soil, in the subsoil, P source effects were not significant on Mehlich-3 P. However, the subsoil P levels were determined by P source x P rate x manure interaction \( (P = 0.017) \). The P levels ranged between 10.7 and 45.7 mg P kg\(^{-1}\) in the control and TSP \( (600 \text{ kg P ha}^{-1}) \) with manure treatments, respectively.

On average, addition of manure increased the subsoil P by 40%. Mehlich-3 P levels increased with increasing P rates from the control \( (2.2 \text{ mg P kg}^{-1}) \) to a maximum at 600 kg P ha\(^{-1}\) \( (\text{P level four folds of the control}) \) and tended to decrease at 900 kg P ha\(^{-1}\) (Fig 7). However, only P level at 600 kg P ha\(^{-1}\) was significantly different from the control.

*(Insert Figure 5 here)*

The results indicated a distinct difference between TSP + manure combination and other treatments (Fig. 7). The P levels increased linearly \( y = 15.3 + 0.016x \) with increasing P rate, while the increase in other treatments were not significant. This implies that the highest P leaching occurred in the TSP + manure treatment and hence explains the earlier observation in the top soil, where P level in TSP + manure combination was lower than TSP alone (Fig 6). Consequently, this is evident of downward movement of P from the top to the subsoil.

*(Insert Figure 6 here)*
Alternatively, Ca was only influenced significantly by the rate of fertilizer application. Similar to P, Ca increased with increasing fertilizer rate to a maximum of 600 kg P ha\(^{-1}\) and then declined slightly at 900 kg P ha\(^{-1}\) (Quadratic relationship). The equation showing the relationship was as follows: \(y = 443 + 0.81x - 0.0006x^2\). Calcium increased by about 80% between control and 600 kg P ha\(^{-1}\).

**DISCUSSION**

*Phosphorus Leached in Relation to P Sources, P Rates and Manure from the Leaching Columns*

More P was leached from the TSP treatments than GPR owing to the higher solubility of TSP relative to GPR. The super-phosphate was 2000 folds as soluble as GPR in water while it was four folds as soluble in both 2% citric and 2% formic acids. In the absence of manure, P leached in TSP increased with increasing P rates and declined rapidly particularly at the 900 kg P ha\(^{-1}\). The highly soluble TSP may have led to higher P saturation of the soil sorption complex as evidenced by the higher Mehlich-3 P levels in the top soil compared to GPR (Figure 6). From, previous findings, increasing P saturation is associated with decreasing bonding strength between soil adsorbents and P, resulting to continued weakening P retention and hence high P leached (Borggaard, 2002). The high and rapid decline of P leached at 900 kg P ha\(^{-1}\) rate could probably be ascribed to very high P saturation most likely above the critical threshold point (Kleiman et al., 2000). For GPR, P leaching was only recorded at the 600 kg P ha\(^{-1}\) but not at 300 or 900 kg P ha\(^{-1}\) rates probably due to very low available P at the lower rate of 300 kg P ha\(^{-1}\) and also low available P at 900 kg P ha\(^{-1}\) despite the high rate of application due to lower GPR solubility at the higher application rate. The quadratic relationship between extractable Mehlich-3 P and P application rate is evident of the decreasing GPR dissolution with P rate.

A combination of manure with GPR resulted in insignificant P leached despite the P increase in the top soil Mehlich-3 P (Fig. 7). Nevertheless, the magnitudes of P levels were still lower than those of TSP and consequently, the P saturation was still lower than TSP, hence no significant P leached. Alternatively, manure addition to TSP, led to distinctly higher leached P particularly at the six months sampling but declined at a fast rate to lower levels at the nine months sampling (Fig. 4). The low P leached at the first sampling (three months) was probably due to P immobilization by the micro-organisms associated with increased organic matter. The increase afterwards could be explained probably by additional P from manure mineralization, reduced P fixation of the soil (Iymuremye et al., 1996), all resulting in higher P saturation coupled with the fact that organic P has higher mobility relative to inorganic P (Chardon et al., 1997). Similar findings of higher P leaching in treatments with manure than without were also reported by Chardon et al. (1997).
Phosphorus Leached Based on Extractable Mehlich-3 P in the Top and Sub-Soil Samples

The soil P levels in TSP treatments increased linearly with increasing P rates but the TSP and manure combination exhibited lower P than TSP alone. Alternatively, Mehlich-3 P in the sub-soil indicated that TSP plus manure gave higher Mehlich-3 P than TSP alone and the two were related as shown by the regression coefficient ($R^2=0.89$), which most probably is an indication of higher P leaching from the top soil, subsequently accumulating in the sub-soil (Fig 7). Thus, increase in sub-soil P must have been the result of a downward movement of fertilizer P. This was further affirmed by the relationship between P in the top soil and P leached ($R^2=0.73$). Comparable results of fertilizer P leaching downwards from the top to the sub-soil have been previously reported (Zhang et al., 1995; Eghball, 1996). McDowell (2004) reported highest P losses above soil Mehlich-3 P concentrations of more than 100-130 mg P kg$^{-1}$. In this experiment, Mehlich-3 P was above 100 mg P kg$^{-1}$ in TSP but below for GPR, which explains why P loss was higher in the TSP than GPR treated soils.

In sole TSP treated soils, there was no difference in Mehlich-3 P in the subsoil and control treatment due to lower amounts of P leached down the soil profile probably due to high fixation of P by the soil in absence of manure thus limiting the P leached. Some P leaching was observed from the sole TSP treatments for the first 20 weeks in the columns. The inconsistency may be explained from some observations made by Djodjic (2000). He reported one situation of P leaching that is dominated by preferential flow transport P, that is, water transport occurring rapidly through cracks, wall flow and bio-pores hence only a small part of the sub-soil interacts with the P. Thus, the leachate bypasses most of the sorbing area of sub-soil. Probably, in the current experiment, preferential flow may have been dominant as deduced from the high coefficients of variation ranging from 84 to 176% for the different sampling times thus resulting in significant P leached without P accumulating in the subsoil. However, in TSP-manure integration the higher amount of P due to additional P from manure mineralization coupled with reduced P fixation, some P may still have been lost through the matrix and hence the P accumulation observed. Similar to the current findings, Bolland et al. (1996) reported highest P levels in soils treated with super-phosphates (SSP) and lowest for PR. He also observed P leaching downward the soil profile.

CONCLUSIONS

It is evident that P can be leached when applied at very high rates particularly the soluble TSP and leaching is much higher when TSP is integrated with manure. However, although, farmers do not apply such high P levels as used in this experiment, repeated P applications may result in the progressive saturation of adsorption sites hence leading to P leaching. No significant leaching occurred in GPR.

Levels of Mehlich-3 P in the top and sub soil could be used to predict the P leaching potential of the soil. However, the profile soil characteristics may fail to reveal the P leaching potential, where P is dominantly water translocated through preferential flow pathways. In such cases, leaching columns may be preferred or could complement the soil profile P leaching assessment.
Consequently, effective and efficient long term P management strategies ought to monitor P leaching for enhanced fertilizer use efficiency and reduced environmental pollution of ground water.

REFERENCES


Figure 1: Rainfall pattern during the experimental period (July 2003 to July 2004)
Fig. 2: Schematic diagram showing the intact leaching column modified with ion exchange resin.
Figure 3: Sampling procedure showing (a) A view of the PVC tubes as inserted and sampling bags, (b) Tubes after excavation of surrounding soil, (c) Old resin bags removal, and (d) Replacement of old resin bags with fresh ones.
Figure 4: Effect of P source, plus/minus manure at different P rates on P leached over time (a) at 0 kg P ha\(^{-1}\) (control + / -manure), (b) 300 kg P ha\(^{-1}\), (c) 600 kg P ha\(^{-1}\), and (d) 900 kg P ha\(^{-1}\). The bars denote standard error (S.E).
Figure 5: Relationship between (a) Mehlich-3 P vs. P leached and (b) Sub-soil P vs. Topsoil P. (**Denotes significance at 1%)
Figure 6: Mehlich-3 extractable P from the top soil samples.
Figure 7: Mehlich-3 extractable P from the subsoil samples.