



Phosphorus Relationships in Water-logged Soils of Southern Nigeria as Influenced by Aluminum and Manganese Toxicity

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Authors' contributions

This work was carried out in collaboration between all authors. Authors WU and AUAI designed the study. Authors WU and GMU wrote the protocol and author WU wrote the first draft of the manuscript.

Authors ISE, WU and MNEO managed the literature searches. Authors WU, GMU and AUAI performed the analyses of the study. Authors WU, AUAI, GMU and MNEO managed the experimental process and author ISE determined the toxicity of samples. All authors read and approved the final manuscript.

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ABSTRACT

Aim: To determine the phosphorus relationships in mangrove swamp with particular reference to Al and Mn contents in acid sulphate soils.

Place and Duration of Study: The study was carried out in Mbiabet in Akwa Ibom State, Nigeria, in 2014 and 2015, respectively.

Methodology: Soil samples were collected in the order of 0-2, 2-4, 4-6, 6-8, 8-10, and 10-15 cm in depths. Treatments consisted of potassium di-hydrogen phosphate added to the swamp mud, cat-

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clay, and mud-clay in equal doses of 244 kg/ha P_2O_5 , fitted into Latin square of 36x5 m swamp, except for the control plot. Limestone ($CaCO_3$) was applied to both fertilized and unfertilized plots at the rate of 50 kg/ha to reduce the activity of aluminum.

Results: The results showed that phosphorus in the unfertilized local acid sulphate soils was largely in the organic and occluded forms. It is apparent that the bulk of the phosphate in the fresh mud was held within 2 cm of the mud surface, where 54-70% of the total phosphorus present was in organic and occluded forms, and remainder chiefly in association with Mn and Al. In spite of the fact that both organic and occluded phosphorus decreased in amount with soil profile depth, 94-97% of the total phosphorus present is in these forms at depths greater than 2 cm from surface mud. It was also found that the mud-clay had relatively high extractable manganese content of 7,501 cmolkg/ha and 8,591 cmolkg/ha of aluminum. Unlike the cat-clay, the exchange between aluminum-bound phosphorus and manganese and calcium – bound phosphorus was masked by the occlusion of inorganic forms on drying through the formation of manganese oxide films on the surface of the sulphate particles. Occluded phosphate increased in quantity and in the mud-clay the net loss to the occluded fraction amounted to 235 mg/kg. Difference between the behavior of the unfertilized and fertilized pond – mud on drying, suggests that the amount of phosphate occluded may be insufficient to mask the exchange reactions, if sufficiently large amounts of phosphate are present to combine with the extractable manganese. All the extractable aluminum and manganese were available to fix phosphorus. The precipitation of Al by excess P was quantitative at pH 5.0-5.5. The results are discussed in light of phosphorus relationships in mangrove swamp with particular reference to aluminum and manganese toxicity.

Conclusion: The addition of acidic phosphate in the soil aggravated manganese toxicity levels, and the use of non-aluminum phosphate showed greater effect on Mn toxicity. In screening plants for Al-toxicity, some important factors to consider include soil pH, Al, P, and Ca levels of the soil. Tolerance of plants to Al-toxicity, could be enhanced by high Ca than low Ca. Al-toxicity may probably be more important than Mn-toxicity but because some areas may contain toxic levels of both Al and Mn and rice plant tolerance to the two factors may not necessary coincide, it may be necessary to develop genotypes with high tolerance. Both Al and Mn toxicity are important growth limiting factors in plants.

Keywords: Bound aluminum; extractable manganese; organic phosphorus; occluded forms; cat-clay; pond mud.

1. INTRODUCTION

Acid sulphate soils are basically soils of marine flood plains, which upon drainage and aeration, show definite and severe acidification due to the oxidation of sulphides (chiefly pyrites, FeS_2) which leads to the formation of sulphuric acid [1].

Aluminum is the most abundant metal in the earth's crust, occurring in a number of forms in soils. Al toxicity could therefore be considered as a primary factor limiting plant growth in acid soils [2]. The effects of Al toxicity on plants have been attributed to several physiological pathways, although the precise mechanism has not yet been understood. Some of the mechanisms of Al toxicity include Al interactions with the root cell wall, Al disruption of plasma membrane and membrane transport processes and Al inhibition of mineral uptake and metabolism especially those of Ca and P [1-4]. The detrimental effects of high soil acidity are traceable largely to exchangeable aluminum levels, thus, hydrolysis

of Al^{3+} generates H^+ and buffers the increase in soil solution pH [4,5]. Soil pH will not increase until sufficient lime is added to decrease the soluble Al^{3+} . Al toxicity is among the widespread problems of ion toxicity stress in plants. Equally the deficiencies of P, Ca and Mg coupled with the presence of phytotoxicity substances (solution Al and Mn) are basic attributes for the fertility limitation to acid soils [6]. Poor performance of crops in acid soils could be related to Al toxicity [6,7]. Aluminum limits plants performance due basically to series of chemical factors and interactions, including toxicities of Al and Mn. This soil limitation to plant growth in the tropics has an average of 23% of soil used, is definitely constrained to Al toxicity [7,8]. The danger posed by available Al on root growth in acid soils has been reported by several scientists [8-10]. However, critical levels of toxic aluminum seem to be different for each crop species and soil type. In working with cotton (*Gossypium hirsutum*) for instance, [11] reported that the exchangeable Al percent, Al saturation and

toxicity threshold values for Al in the soil solution varied considerably, depending upon the soil. It was also reported essentially the same threshold activity value for all when calculating Al^{3+} activity, that the total soluble Al was present in solution as Al^{3+} species. In another study, [11,12] similarly demonstrated that Al^{3+} activity was a good index of Al toxicity for corn (*Zea-mays*) and sorghum (*Sorghum vulgare*).

A report by Clarkson [12] indicated that the differences in the behavior of the muds on drying are reflected in the differences between the fixation capacities of the fresh and dried mud. This relationship was however expected in view of the ability of the extractable aluminum and manganese to fix phosphorous. However, the problem of low pH leading to toxic levels of exchangeable Al and the deficiency of Ca and Mg in the soil (basically soils of marine flood plains upon which drainage and aeration show definite and severe acidification) on the performance of rice has been established [12,13]. Hence, the detrimental effect of high soil acidity is traceable largely to exchange aluminum levels [13].

The swamps support three known genera of mangrove trees such as *Rhizophora*, *Aricenmia* and *Laguncularia*. However, *Rhizophora* species predominate the coastal fringes of South-South, Nigeria. The area is characterized by mean annual rainfall of 4012 mm with a high temperature of diurnal range of 24°C. A maximum of 32°C on the average and a humidity range of 80-90%.

However, the problem of low pH leading to toxic levels of exchangeable Al and the deficiency of Ca and Mg in the soil can definitely be ameliorated by the use of calcium carbonate (limestone).

The term "Cat-clay" has been used to denote acid soil material in its oxidized form [13,14], showing straw yellow mottling and steaks of basic ferric sulphate. Equally, [14] have proposed the term "mud-clay" to denote the non-drained unoxidized soil with high potential acidity. Both forms of acid sulphate soils are of fairly widespread occurrence along the coastal and riverine regions of South-South Nigeria. The present study was undertaken to obtain information hitherto lacking on the distribution of phosphorus currently present in the soils, and how this was affected by drying, the phosphorous fixation capacity of soils, the

distribution of newly fixed phosphorous as affected by time drying and changes in forms of phosphorus during incubation of muds. Subsidiary trials investigated the aluminum and manganese content of the soils, the effect of drying and also phosphorus and lime. In view of the above consideration and because of dearth of information on phosphate relationships in mangrove swamp mud with particular reference to aluminum and manganese toxicity, it was considered appropriate to determine the influence of $CaCO_3$ (lime) on the toxicity of aluminum and manganese in acid sulphate mangrove swamp mud.

The objective of the study is investigate the phosphorus relationships in mangrove swamp mud with aluminum and manganese toxicity.

2. MATERIALS AND METHODS

The study was carried out in 2014/2015 at the mangrove swamp of Mbiabet, Akwa Ibom State, situated on 07°34' and 07°36' East and 05°29' and 05°31' North. The soils are acid sulphate soils and are basically soils of marine flood plains and show definite and severe acidification due to the oxidation of sulphates (chiefly pyrites, FeS_2) which leads to the formation of sulphuric acid. These type of soils as reported by Edelman and Van Staveren [15] are exclusive to marine flood plains alone, but other soils that bear iron sulphate deposits.

2.1 Field Studies

The soil samples used for the experiments were obtained from muds in three sites within the mangrove swamp. The mud-clay was obtained outside the actual pond area from bottom of the canal, cut through swamp land and used for bringing water to the ponds. The cat-clay was obtained from the spill-way very close to the water gage. The unfertilized pond mud was taken from the ponds of the Latin Square, which had received a surface limestone dressing, but no phosphorus. An amount of $244 \text{ kg ha}^{-1} P_2O_5$ of potassium di-hydrogen phosphate was added to dried-mud and cat-clay and the mixture was shaken for 1 h. After extracting saloid bound phosphorus, the aluminum phosphate contents were then evaluated. Fertilizer trial was carried out in a Latin square of 36x5 m which had received a surface limestone dressing of 50 kg ha^{-1} following the modified methods of Ubi et al. [16] lack number of reference.

The samples were obtained with the aid of a plastic tube fitted with a rubber – stoppered

position to facilitate the extraction of the cores at varying depths of 0-2, 2-4, 4-6, 6-8, 8-10, and 10-15 cm. In the three soil types examined, 36 soil samples were collected, 12 samples per each soil type, giving a good representative sample of the three soil types for the analytical work.

2.2 Laboratory Studies

Inorganic phosphorus was fractionated by the method of Enwezor and Moore [15]. Total phosphorus was determined after fusion with Na_2CO_3 and organic phosphorus was taken as a difference between the total phosphorus and the summation values of the inorganic forms obtained from the fractionation analysis. Aluminum was estimated by the aluminon method and any fluoride present being removed by repeated evaporation with nitric acid as recommended by Frink and Peech [17]. Extractable aluminum was removed with neutral normal potassium chloride as recommended by Havlin et al. [18]. As it may be expected, the aluminum was referred to as extractable rather than exchangeable because although in the swamp mud and mud-clay, the extraction was made under nearly neutral condition, with cat-clay the extracting solution was at a very low pH. The soil pH was measured with a pH meter, using a soil to water ratio of 1:1 but in case of incubated water logged muds, the electrodes were inserted directly into the swamp mud of the mangrove at the specified study area. The fractionation of soil phosphorus was done using the previous reported methods [19].

3. RESULTS

3.1 Phosphorus Fixation Capacity

The immobilization of added inorganic phosphorus as potassium dihydrogen phosphate, by the fresh and dried muds is shown in Fig 1. The fixation was fairly rapid; equilibrium being obtained within 50-60 h. The fresh mud (with the exception of the cat-clay absorbed more phosphate than did the dried mud and nearly 50% of the absorption took place in 5 h). The amount of phosphate expressed as tons of triple super phosphate per hectare required to saturate the fresh and dry mud to a depth of 10 cm is given in Table 2 below.

3.1.1 Absorption of inorganic phosphorus by fresh and dried muds

(MgP_2O_5 absorbed per g mud 0.d. basis) (Fig. 1).

3.2 Distribution of Phosphate in Unfertilized Muds in the top 15 cm of the soil

The distribution of phosphorus in the top 15 cm of the unfertilized fresh and dried muds is given in Table 1. From which it can be seen that the bulk of the total phosphorus was in the organic and occluded forms and the remainder in association mostly with Mg and Ca. As it may be expected dried muds with a drying period of 12 days became more acidic occluded phosphate occurred in the case of mud-clay and pond mud.

In the cat-clay however, occlusion of phosphate did not occur, but aluminum phosphate increased at the expense of Mn and Ca phosphates, but not to any great extent. There were no saloid-bound phosphorus present in the fresh or dried muds.

The amount of Mn and aluminum extracted from dried pond mud by the fractionating solutions are given in Table 3.

The Mn was removed from the dried mud by the sodium dithionite-citrate extractant ($\text{Na}_2\text{S}_2\text{O}_4$ -Citrate). The result showed that the highest concentration of aluminum was found in the sulphuric acid and dithionite-citrate extracts and the lowest in the sodium hydroxide extract. Both ammonium chloride and ammonium fluoride removed considerable amounts of aluminum from the dried mud (Table 3). The value of Mn obtained from the use of H_2SO_4 was more than four times the value obtained from the use of NH_4F and more than twenty-seven times the value when NaOH was used. Equally, there was 7.7% ($\frac{2550-1780}{1780} \times 100$) increase in aluminum extracted when H_2SO_4 was compared with NH_4F .

Table 4 gives the average distribution of the forms of immobilized phosphate down the profile for those ponds which had received 244 kg ha^{-1} P_2O_5 as triple super phosphate. The fractionation analysis was performed on the same cores as were used for the extractable aluminum and Mn determinations. Although the determinations were done on the dried mud 10 days later. The low pH values for the air dried mud, shown in Table 4 are therefore due to the slightly longer storage period. It is apparent that the bulk of the phosphate in the fresh mud was held within 2 cm of the mud surface, where 54-70% of the total phosphorus present was in organic and occluded forms, and remainder chiefly in association with

Mn and Al. In spite of the fact that both organic and occluded phosphates decreased in amount with soil profile depth, 94-97% of the total phosphate present is in these forms at depths greater than 2 cm from the mud surface [12,18]. Manganese phosphate was more abundant than aluminum or calcium phosphate throughout the soil profile and there was equally no aluminum phosphate present below a soil depth of 8 cm.

The effect of drying the top 2 cm of the mud was to decrease the amount of aluminum phosphate and increase the amount of Mn and calcium phosphate. Below this soil depth, aluminum, manganese and calcium phosphates decreased in value. The amount of occluded phosphate also increased down the soil profile which was partly at the expense of the organic and inorganic phosphate present. However, there was no saloid-bound phosphorous present in the fresh and dried muds.

Changes in the form of added phosphorus when muds were incubated under water logged conditions.

The immobilized phosphorus appeared in various forms in the water logged fresh pond mud, cat-clay and mud-clay after various periods of time

as given in Table 5. Shortly after the addition of 224 kg ha⁻¹ P₂O₅ triple-super phosphate, as potassium di-hydrogen phosphate to the mud the aluminum-bound and manganese – bound phosphorus decreased, whereas the Ca-bound phosphorus increased. Occluded phosphate increased in amount in the pond mud and cat-clay, but decreased slightly, in the mud-clay. Organic phosphate decreased earlier in the season and tended to be inconsistent later in the season, in the cat-clay and mud-clay. Saloid-bound phosphorus was only found in the cat-clay.

Over a period of 6 months, the aluminum phosphate decreased in quantity. During the same period, manganese phosphate increased in value in the pond mud and cat-clay, but decreased in the mud-clay. The content of calcium phosphate having dropped immediately after the addition of the potassium dihydrogen phosphate, rose again for about 2 months when it later decreased. At this time, when the pond was disturbed, air-bubbles and gas evolved suspected to sulphide. Occluded phosphate decreased in value in the pond mud, but increased in the cat-clay and mud-clay. Organic phosphate showed a little change in the pond-mud and mud-clay, but increased in the cat-clay over the incubation period.

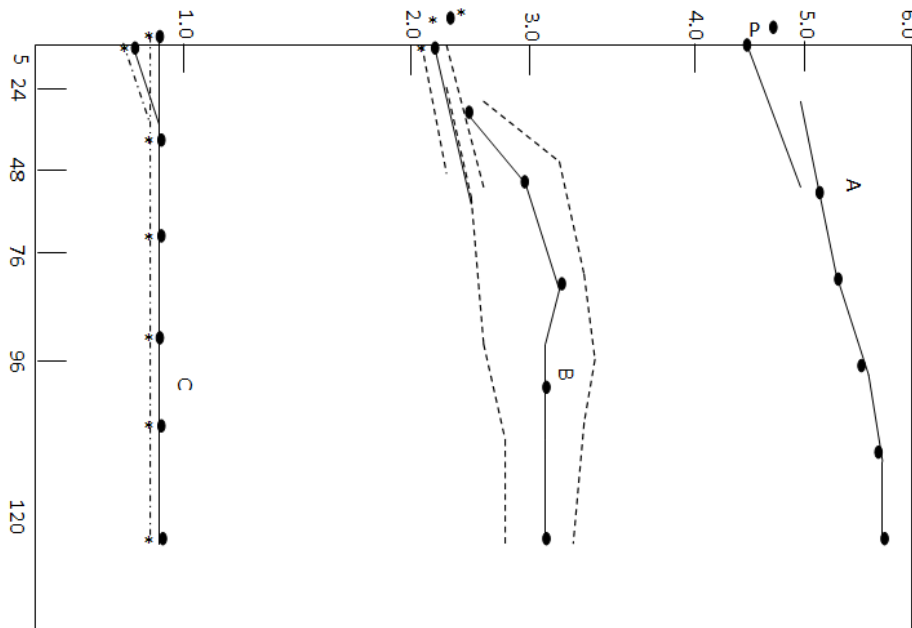


Fig. 1. Different forms of immobilize phosphorus absorption in the water-logged soils of southern Nigeria

Key: (Fresh mud 0.....0; dry mud x.....x) A = mud-clay, B = Cat-Clay C= Pond mud

Table 1. Amount of triple super phosphate (t/ha) required to saturate the fresh and dried muds to a depth of 5 cm

| Soil type | Fresh mud | pH | Dried mud (tons) | pH |
|-----------|-----------|------|------------------|------|
| Mud-clay | 8.12 | 6.8 | 4.92 | 5.7 |
| Cat-clay | 4.86 | 3.9 | 4.44 | 3.6 |
| Pond-clay | 2.42 | 6.3 | 1.28 | 5.5 |
| Total | 15.4 | 17.0 | 10.64 | 14.8 |

Table 2. Forms of phosphorus found in the top 15 cm of the unfertilized muds (Results of P₂O₅ oven dry mud and mean of 12 samples)

| Form of P | Mud-clay | Cat-clay | Pond mud |
|------------------|----------|----------|----------|
| Fresh mud | | | |
| Saloid-bound | 0 | 0 | 0 |
| Al-bound | 16 | 0 | 8 |
| Mn-bound | 136 | 25 | 18 |
| Ca-bound | 158 | 15 | 12 |
| Occluded | 278 | 108 | 74 |
| Organic | 419 | 125 | 87 |
| pH | 6.9 | 4.5 | 6.8 |
| Total | 1.008 | 273 | 199 |
| Dried mud | | | |
| Saloid-bound | 0 | 0 | 0 |
| Al-bound | 5 | 4 | 4 |
| Mn-bound | 65 | 21 | 15 |
| Ca-bound | 92 | 12 | 8 |
| Occluded | 376 | 105 | 85 |
| Organic | 415 | 116 | 88 |
| pH | 5.6 | 3.5 | 5.6 |
| Total | 953 | 258 | 388 |

Table 3. Manganese and aluminum extracted from dried pond mud by the phosphorus fractionating solutions

| Extracting solution | Form of p extracted | Mn extracted (cmol kg ha ⁻¹) | Al-extracted (cmol kg ha ⁻¹) |
|--|---------------------|--|--|
| NH ₄ Cl | Saloid-bound | 8 | 1055 |
| NH ₄ F | Al-bound | 185 | 1780 |
| NaOH | Mn-bound | 28 | 876 |
| H ₂ SO ₄ | Ca-bound | 780 | 2550 |
| Na ₂ S ₂ O ₄ -citrate | Occluded | 6500 | 2330 |
| Total | - | 7,501 | 8,591 |

Table 6 shows the effect of phosphate at the rate of 224 kg ha⁻¹ P₂O₅ as potassium dihydrogen phosphate added to the fresh muds, which were then dried and the dried muds incubated under water logged conditions.

The forms in which the immobilized phosphorus appeared in the water logged phosphate – treated dried mud showed that on drying, the value of aluminum phosphate decreased in the three mud types, whereas the values of calcium and manganese phosphates decreased in the

cat-clay and mud-clay, but increased in the pond-mud. The value of organic phosphate decreased in the pond-muds and mud-clay, but increased slightly in the cat-clay. Occluded phosphate increased in quantity and in the mud-clay the net loss to the occluded fraction amounted to 235 mg kg⁻¹. Saloid-bound phosphorus was present only in the cat-clay and decreased on drying. The results also showed that all the extractable aluminum and manganese were available to fix phosphorous.

Table 4. The average distribution of pH and KC1-extracted from Al and Mn with depth in ponds which had received 244 kg ha⁻¹ P₂O₅ (Results as mg/kg P₂O₅ over-dry mud)

| Fresh mud forms of phosphorus | | | | | | | | |
|-------------------------------------|------------|--------------|----------------|-------------|--------------|-------------|--------------|--------------|
| Depth (cm) | pH | Soloid-bound | Aluminum bound | Ca-bound | Mn-bound | Occluded | Organic | Total |
| 0-2 | 6.2±0.1 | 0 | 113±15.6 | 27±4.7 | 118±14.5 | 128±11.2 | 216±4.9 | 490.0±8.2 |
| 2-4 | 6.6±0.2 | 0 | 57±9.2 | 15±2.3 | 65±11.4 | 98±6.5 | 197±3.6 | 429.6±11.3 |
| 4-6 | 6.4±0.1 | 0 | 12±2.1 | 8±1.3 | 24±4.4 | 94±5.7 | 158±7.1 | 441.4±6.3 |
| 6-8 | 6.4±0.1 | 0 | 0±0 | 6±1.0 | 12±3.1 | 63±3.8 | 149±5.4 | 248.4±42.6 |
| 8-10 | 6.3±0.1 | 0 | 0±0 | 4±0.2 | 8±3.5 | 59±3.3 | 145±3.2 | 226.3±14.2 |
| 10-15 | 6.3±0.1 | 0 | 0±0 | 3±0.2 | 7±2.1 | 46±4.1 | 148±4.9 | 211.3±10.3 |
| Mean | 6.3 | - | 60.7 | 10.1 | 39.00 | 81.3 | 169.3 | 211.3 |
| Air-dried mud * forms of phosphorus | | | | | | | | |
| 0-2 | 5.4±0.2 | 0 | 85±6.9 | 38±3.2 | 136±12.6 | 138±11.3 | 218±4.2 | 620.4±43.2 |
| 2-4 | 5.1±0.1 | 0 | 36±2.6 | 29±1.0 | 84±4.4 | 116±8.9 | 179±7.3 | 449.1±18.6 |
| 4-6 | 5.0±0.1 | 0 | 9±0.4 | 10±0.2 | 18±2.1 | 109±5.4 | 148±5.5 | 299±14.9 |
| 6-8 | 5.1±0.1 | 0 | 0±0 | 6±0.3 | 9±0.5 | 89±2.2 | 137±12.1 | 246.1±21.7 |
| 8-10 | 4.9±0.1 | 0 | 0±0 | 0±0 | 6±0.3 | 71±2.5 | 131±9.4 | 212.9±11.8 |
| 10-15 | 4.6±0.2 | 0 | 0±0 | 0±0 | 4±0.2 | 62±1.9 | 133±7.7 | 203.6±13.4 |
| Mean | 5.0 | - | 43.3 | 20.8 | 42.8 | 97.5 | 157.7 | 2036 |

* based on drying period of 15 days

Table 5. Chronological changes in forms of immobilized phosphorus in phosphate treated fresh bond mud, cat-clay and mud-clay (Results are as mg kg⁻¹ P₂O₅ oven-dry mud)

| Time | Saloid (1) | Bound (2) | (3) | Al- (1) | Bound (2) | (3) | Mn- (1) | Bound (2) | (3) | Ca- (1) | Bound (2) | (3) | Occluded phosphate (1) | (2) | (3) | Organic (1) | Phosphate (2) | (3) |
|------------------------------|------------|-----------|-----|---------|-----------|-----|---------|-----------|-----|---------|-----------|-----|------------------------|-----|-----|-------------|---------------|-----|
| Before addition of phosphate | 0 | 0 | 0 | 6 | 2 | 4 | 18 | 3 | 97 | 10 | 8 | 145 | 125 | 106 | 195 | 57 | 94 | 228 |
| After addition of phosphate | 0 | 48 | 48 | 74 | 76 | 15 | 98 | 36 | 262 | 9 | 7 | 138 | 131 | 132 | 187 | 54 | 76 | 219 |
| 1 month | 0 | 6 | 6 | 57 | 66 | 0 | 94 | 65 | 268 | 19 | 9 | 125 | - | - | - | - | - | - |
| 2 months | 0 | 6 | 6 | 58 | 54 | 0 | 112 | 79 | 218 | 24 | 12 | 159 | - | - | - | - | - | - |
| 3 months | 0 | 8 | 8 | 45 | 49 | 0 | 120 | 68 | 208 | 26 | 13 | 168 | - | - | - | - | - | - |
| 4 months | 0 | 5 | 5 | 42 | 47 | 0 | 98 | 79 | 206 | 27 | 16 | 175 | - | - | - | - | - | - |
| 5 months | 0 | 4 | 0 | 46 | 47 | 0 | 127 | 74 | 196 | 18 | 10 | 138 | - | - | - | - | - | - |
| 6 months | 0 | 6 | 0 | 42 | 46 | 0 | 126 | 70 | 168 | 19 | 12 | 136 | 107 | 126 | 248 | 61 | 94 | 231 |

Key: (1) Pond mud (2) cat-clay (3) mud-clay

Table 6. Chronological changes in form of immobilized phosphorus in phosphate treated dried pond mud, cat-clay and mud-clay (Results as mg kg⁻¹ ha⁻¹ ¿check units? P₂O₅ oven-dry mud)

| Time | Saloid (1) | Bound (2) | (3) | Al- (1) | Bound (2) | (3) | Mn- (1) | Bound (2) | (3) | Ca- (1) | Bound (2) | (3) | Occluded phosphate (1) | (2) | (3) | Organic (1) | Phosphate (2) | (3) |
|------------------------------|------------|-----------|-----|---------|-----------|-----|---------|-----------|-----|---------|-----------|-----|------------------------|-----|-----|-------------|---------------|-----|
| Before addition of phosphate | 0 | 4 | 0 | 68 | 150 | 8 | 68 | 13 | 245 | 9 | 2 | 142 | 89 | 48 | 126 | 45 | 51 | 342 |
| After addition of phosphate | 0 | 35 | 0 | 72 | 145 | 6 | 76 | 9 | 162 | 7 | 1 | 138 | 101 | 61 | 360 | 30 | 56 | 250 |
| 1 month | 0 | 25 | 0 | 54 | 168 | 0 | 84 | 15 | 217 | 18 | 3 | 122 | 79 | 43 | 179 | 32 | 55 | 348 |
| 2 months | 0 | 15 | 0 | 76 | 163 | 0 | 179 | 14 | 240 | 24 | 4 | 158 | 78 | 50 | 150 | 44 | 56 | 325 |
| 3 months | 0 | 17 | 0 | 78 | 169 | 0 | 70 | 10 | 248 | 22 | 4 | 143 | 75 | 48 | 122 | 40 | 55 | 322 |
| 4 months | 0 | 16 | 0 | 74 | 149 | 0 | 69 | 12 | 253 | 20 | 4 | 138 | 76 | 50 | 130 | 41 | 62 | 343 |
| 5 months | 0 | 20 | 0 | 72 | 167 | 0 | 73 | 11 | 264 | 18 | 5 | 136 | 72 | 43 | 123 | 42 | 60 | 349 |
| 6 months | 0 | 20 | 0 | 72 | 163 | 0 | 65 | 13 | 276 | 16 | 4 | 134 | 76 | 45 | 120 | 49 | 57 | 356 |

Pond-mud (2) cat-clay (3) mud-clay

4. DISCUSSION

4.1 Field Studies

The field study results have revealed that the phosphorus in the unfertilized local acid sulphate soils was mostly in the organic and occluded forms as also observed and reported by [19]. Undoubtedly, organic phosphorus is the most important source of the element to crops, but in this study, no ready mineralization of organic phosphorus results when the phosphate – treated muds are incubated [16,20]. In this study, it was found that the mud-clay, which has a relatively high extractable manganese content, unlike the cat-clay, the exchange between aluminum-bound phosphorous was masked by the occlusion of inorganic forms on drying through the formation of manganese oxide films on the surface of the phosphate particles earlier reported [3,16,20]. The effect of liming definitely is to reduce the amount of extractable aluminum and manganese and when lime is combined with phosphate, the reduction effect of aluminum and manganese are enhanced [3,16,21]. [19,21] reported that the pH of the dried mud may continue to fall for as long as 2 months due to continuing oxidation of the sulphides present. However, the observed immobility in the amount of added fertilizer to the ponds was earlier reported [21,22]. The difference between the behavior of the unfertilized and fertilized pond-mud on drying suggests that the amount of phosphate occluded may be insufficient to mask the exchange reactions, if sufficiently large amounts of phosphate are present to combine with extractable manganese. Addition evidence on this aspect of phosphate fixation could be seen from the observation made on the distribution of immobilized phosphate in the limed and unlimed water logged muds. The results showed that the total phosphorus in combination with the inorganic forms and the amount of occluded phosphate present was indeed less in limed than unlimed muds and there was a corresponding decrease in the fixation capacity of the former mud [9,22,23].

It is apparent that more phosphorus could be fixed by the virgin pond mud and mud-clay than the pre-dried muds, but in the cat-clay the situation was reversed. The values obtained showed that the amount of fertilizer phosphate added to ponds during the fertilizer trials should

be totally immobilized. In either the fresh or dried mud, although immobilization is perhaps a misleading term to apply to the combination of phosphorus and manganese as under water logged conditions manganese can possibly be regarded as available phosphate.

4.2 Laboratory Studies

The laboratory studies results of the incubation experiment and presented in Table 6 using the pre-dried fertilized muds, shows that the changes in the forms of immobilized phosphate produced by drying may to some extent be reversed by prolong water logging. The occluded phosphate was converted to relatively more forms; a reaction which may possibly be associated with the presence of manganese reducing bacteria with which these soils (in particular, the mud-clay bound).

A similar exchange of phosphorus between the different inorganic forms of phosphate has been reported by [24,25], working on swamp muds from Sierra Leone. He reported that after adding 30 kg ha⁻¹ inorganic P₂O₅ to the mud, there was a net loss of 11 mg kg ha⁻¹ inorganic phosphorus at the end of a 6 months' incubation period, and concluded that this was loss to the organic fraction. Hesse [16], however, did not proceed with the fractionation analysis beyond the isolation of calcium-bound phosphorous, so it was uncertain whether the loss was due to the organic fraction or due to the occluded fraction as was observed in the mud-clay of this study. However, these soils have great potentials for rice production in the area, for greater economic benefit.

5. CONCLUSION

Addition of acidic phosphate in the soil aggravated manganese toxicity levels, and the use of non-aluminum phosphate showed greater effect on Mn toxicity. In screening plants for Al-toxicity, some important factors to consider should include soil pH, Al, P, and Ca levels of the soil. The precipitation of Al by excess P was quantitative at pH 5.0 to 5.5. Tolerance of plants to Al-toxicity, could be enhanced by high Ca than low Ca. Al-toxicity may probably be more important than Mn-toxicity but because some areas may contain toxic levels of both Al and Mn and rice plant tolerance to the two factors may

not necessary coincide, it may be necessary to develop genotypes with high tolerance. Since Al is a constituent of soil clay minerals, Al-toxicity is always possible at low pH, causing the mineral structure to decompose, especially below pH 5.5, some Al in mud-clay particles migrate to cation exchange sites on clay surfaces and into soil solutions with net loss. Both Al and Mn toxicity are important growth limiting factors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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