Role of Organic Acids on Phosphorus Fractions in Silty Clay Loam Soil

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Abstract

This study was conducted to evaluation the role of the organic acids in the phosphorus fractions in silty clay loam texture. The laboratory experiment was conducted by adding the organic acids (Humic acid, Citric acid, Oxalic acid, Malic acid, Acetic acid, and Lactic acid) to the fertilized soil with conc. super phosphate fertilizer with 100 kg h\textsuperscript{-1} level with concentrations (0, 15, 30, 45, and 60) mg L\textsuperscript{-1}, except Humic acid (500, 1000, 1500, and 2000) mg L\textsuperscript{-1}. The soil was incubated at 30\textdegree C for 14, 28, 42, 56, and 70 days period and the keep of field capacity about of incubation period during the daily weight. Amount of available, mineral, organic, and total phosphorus after each incubated period were measured. The results showed that the addition of organic acids of Humic acid, Citric acid, Oxalic acid, and Malic acid were caused to increase amount of available, mineral, organic, and constant of total phosphorus in fertilized soil with conc. super phosphate fertilizer and increased its amount with increasing of organic acid concentration and better of Humic acid 2000 mg L\textsuperscript{-1} significantly on all the treatments. The results of the study that the addition of organic acids were caused to increase amount of available and mineral phosphorus with increasing of incubation period and constant amount of total phosphorus and decreasing of organic phosphorus amount and available for only soil and only fertilizer treatment during increasing of incubation period. The organic acids can be arranged according to its ability to increase the availability of the phosphorus as follow:

Humic acid > Citric acid > Oxalic acid > Malic acid > Acetic acid > Lactic acid > control.

Introduction

Phosphorus is one of the necessary nutrient elements of plant growth, especially in arid and semi-arid soils. Amount of P in soil is depended on operations of weathering, quality and quantity of clay minerals, oxides, organic matter and calcium carbonate (1). Phosphorus can be found in the soil with multi forms as soluble, adsorption by clay minerals, CaCO\textsubscript{3}, Fe and Al oxides, and sedimentor as calcium and Fe and Al phosphate, combined with organic matter, degree combined of P with colloids of organic and mineral soil were by physiochemical properties (2). The availability and forms of P in soil are changed according to operation fertilization and soil management. The phosphate fertilization led to increase the available phosphorus from (3 -20) mg kg\textsuperscript{-1} at addition 26 kg Ph\textsuperscript{-1} (3). type and the level of adding phosphate fertilizer has an effect in its different forms and respond of production for its (5). Many of researchers (6)(7)(8)(9) were found on relation significant positive and negative between forms of P and singular of growth to different crops depending on nature and environment of soils. The organic acids are affected in forms of P in the soils during the ranges of reactions such as: soluble of compound the sedimentation phosphate,
mineralization of organic phosphorus, decreasing of soil pH and attention ions of 
$Ca^{++}, Fe^{++}, AL^{+++}$ (10) then increasing of phosphorus availability in soil .this research was conducted to evaluation role of Organic acids in the availability of the phosphorus in the silty clay loam texture.

**Materials and Methods.**

Soil studied

Soil texture was salty clay loam it was took from surface layer (0-30) cm from the fields in agriculture college/Wassit university and air dried was sieved by 2mm, then conducted on its of general analysis which show in the table below (1).

| Property           | Unit    | Range  |
|--------------------|---------|--------|
| Ec                 | dis m$^{-1}$ | 3.25   |
| pH                 |         | 7.80   |
| CaCO$_3$           | mg kg$^{-1}$ | 415.00 |
| CEC                | cmol kg$^{-1}$ | 15.18  |
| Organic matter     | gm kg$^{-1}$ | 2.25   |
| Ca$^{++}$          | mmol l$^{-1}$ | 9.63   |
| Mg$^{++}$          | mmol l$^{-1}$ | 6.04   |
| Na$^{+}$           | mmol l$^{-1}$ | 14.40  |
| K$^+$              | mmol l$^{-1}$ | 2.17   |
| Cl$^-$             | mmol l$^{-1}$ | 14.85  |
| CO$_3^{2-}$        | mmol l$^{-1}$ | ---    |
| HCO$_3^-$          | mmol l$^{-1}$ | 4.10   |
| SO$_4^{2-}$        | mmol l$^{-1}$ | 13.85  |
| Soluble-P          | mg l$^{-1}$ | 0.12   |
| Available-P        | mg kg$^{-1}$ | 6.17   |
| Mineral-P          | mg kg$^{-1}$ | 177.00 |
| Organic-P          | mg kg$^{-1}$ | 76.00  |
| Total-P            | mg kg$^{-1}$ | 253.00 |
| Silt               | gm kg$^{-1}$ | 560.00 |
| Clay               |         | 390.00 |
| Sand               |         | 50.00  |
| Texture            |         | Silty Clay Loam |

Role of organic acidsof Phosphorus fractions in soil.

75 gm of soil was air dried and put in plastic pots with 100cm$^3$ capacity .Five organic acids with low molecular weightwere added they were included Citric acid ,Oxalic acid ,Malic acid ,Acetic acid and Lactic acid with levels( 0.15 ,30,45,and 60) mg L$^{-1}$ . Humic acid with high molecular weightwas used with levels( 0.50,100,1500 and 2000) mg L$^{-1}$for soil of treatment with 100 kg h$^{-1}$. Moisture of pot was completed to field capacity limit .samples were incubated on 30 c at 70 day .the keep on moisture of pot in field capacity by weighting daily for its .samples were took each 14 day for five time period . available-P was determined by (12) ,mineral-P by (11),Organic-P from the difference between the total phosphorus and mineral phosphorus (11),total phosphorus by (13). In this study the experiment was designed as CRD design with three replications ,the properties were analysed with Gen Stat Discover ,average of treatments by L.S.D ,italysanalised with that factorial experiment with three factors :type of acid *concentration of acid *time of incubation(13).

**Results and Discussion**

Available phosphorus in soil.

Table (2) shows that the average amount of available phosphorus in soil was increased significant (P<0.01,0.05) follow to the...
concentration and type of acid. Addition concentrations of organic acids with levels (15, 30, 45 and 60) mgL⁻¹ except Humic acid with levels (500, 1000, 1500 and 2000) mg L⁻¹ were caused to increase amount of P-available in soil for all the treatments. Treatment of Humic acid was surpassed in amount of available-P significant (P<0.01,0.05) compared with all acids with average (45.64, 54.66, 60.17 and 65.41) mg P kg⁻¹ soil for the remember concentrations respectively compared with control treatment which gave 7.88 mg P kg⁻¹ soil ,and Citric acid was surpassed in amount of available-P significantly compared with low molecular weight acids in this study as Oxalic, Malic and Acetic acids for all the study concentrations (15, 30, 45 and 60) mg L⁻¹ were gave (35.15, 37.85, 40.70 and 45.67) mg P kg⁻¹ soil respectively while Lactic acid was gave less range in available-P which gave (16.90, 19.10, 21.52, and 25.37) mg P kg⁻¹ soil for the remember concentrations respectively. Humic acid was surpassed compared with all the treatments return to the added high concentration and its from the humus organic acids with high molecular weight and content many of carboxylic groups compared with no humus organic acids with low molecular weight and content on less number of carboxylic groups in this study. was showed the organic acids with high molecular weight such Humic and Folvic acids were caused prevent sedimentation of hydroxy apatite as result coatis particulars and prevent formation complete crystals which cant the organic acids with low molecular weight such Citric, Oxalic and Malic acids then increasing amount of available-P. Number and type of activity groups and decreasing of acidity cause important role in increase of phosphorus availability in soil as Citric acid which contain three carboxylic groups therefore affected in increasing amount of available -P compared with other acids especially Acetic and Lactic acids are contain one carboxylic group there for gave less amount of available phosphorus compared with other organic acids in this study. (14) were showed quality and quantity of carboxylic groups in organic acids are responsible about of different interaction with mineral elements or adsorption or formation of complexes , the organic acids which contain on one carboxylic group such acetic acid its effect limit by competition with phosphate ions on adsorption location ,while organic acids which contain two carboxylic group such Malic or Oxalic acids or the contain three carboxylic groups such Citric acid are strong competition on adsorption locations then increase from availability of phosphorus in soil, agree that with (15).

Table (2) Effect type and concentration of organic acid and conc. super phosphate fertilizer in amount of available phosphorus in soil (mg P kg⁻¹ soil) during different time incubation.

| type of acid | concentration of acid | (Day) incubation time | type of acid * concentration of acid (compound treatment) | L.S.D 0.01,0.05 |
|-------------|-----------------------|-----------------------|----------------------------------------------------------|----------------|
|             | 14   | 28   | 42   | 56   | 70   |                                  |                |
| Humic acid  | 0    | 9.18 | 8.52 | 7.93 | 7.00 | 6.75 | 7.88                          |                |
|             | 500  | 40.91| 42.74| 45.62| 47.97| 50.94| 45.64                          | 2.13,1.96      |
|             | 1000 | 47.01| 49.95| 55.74| 58.59| 62.03| 54.66                          |                |
|             | 1500 | 53.97| 56.08| 60.53| 63.41| 66.84| 60.17                          |                |
|             | 2000 | 58.80| 61.58| 66.47| 69.84| 70.34| 65.41                          |                |
| Citric acid | 0    | 9.18 | 8.52 | 7.93 | 7.00 | 6.75 | 7.88                          |                |
|             | 15   | 28.57| 31.10| 36.14| 38.60| 41.33| 35.15                          |                |
|             | 30   | 30.16| 33.38| 40.05| 41.61| 44.04| 37.85                          |                |
|             | 45   | 31.30| 35.78| 5.26 | 45.62| 47.52| 40.70                          |                |
| Time | Oxalic acid | Malic acid | Acetic acid | Lactic acid |
|------|-------------|------------|-------------|-------------|
| 0    | 9.18        | 9.18       | 9.18        | 9.18        |
| 15   | 26.42       | 20.43      | 11.73       | 11.36       |
| 30   | 27.31       | 23.04      | 14.17       | 13.93       |
| 45   | 29.70       | 24.95      | 15.30       | 15.94       |
| 60   | 31.20       | 26.14      | 16.71       | 17.38       |

The effect of time incubation on available phosphorus with different organic acids.

| L.S.D 0.01,0.05 | 0.87 , 0.75 |

Although Oxalic and Malic acids are Di of carboxylic groups, but the amount of available phosphorus by Oxalic acid is more than Malic acid. This is due to the structure of acid, degree of acidity, arrangement of ligands of acid and type of interactions each acid, this insured by (16) (17), such Acetic and Lactic acids are mono carboxylic group but amount of available phosphorus with Acetic acid is more than Lactic acid. This difference return to variety of carbonic series (18). Amount of available phosphorus in soil was differed with significant difference (P<0.01,0.05) between concentrations of organic acids, because increasing concentration of organic acids cause solubility of mineral compounds of phosphorus then increase its release and availability in soil (19)(20). Foundation of organic compounds (ligands) in region of plants root also organic acids with low molecular weight and amino acids are consider soluble to more of minerals which contain nutrient elements in soil because its formation stable complexes with mineral ions then increase availability of nutrient elements of plant. (21) were showed the roots product and high concentrations of organic acids are decrease of soil pH then make phosphorus more available in calcareous soil. In study to (22) were showed the organic acids with low molecular weight can arrangement according to amount of carboxylic group and ability on increase of availability phosphorus.
as follow: Tri-carboxylic (tri-carboxylate ) > di-carboxylic (di-carboxylate ) > mono-carboxylic acid (mono-carboxylate ). This result agree with Xu, Gang et al. (2012). We can be arrangement of organic acids in this study according to ability of phosphorus availability as follow:

Humic acid > Citric acid > Oxalic acid > Malic acid > Acetic acid > Lactic acid > only fertilizer.

The results of the table (2) shows that significant increasing (P<0.01,0.05) was found in amount of available phosphorus with increasing of time of incubation, increasing from 23.52 mg P kg⁻¹ soil after 14 days of incubation to 33.17 mg P kg⁻¹ soil at time of incubation 70 days. The amount of available phosphorus is about (25.78,29.69 and 31.06) mg P kg⁻¹ soil for periods of incubation 28, 42 and 56 days respectively. Returning to the organic acids cause decreasing of pH soil then increase from operations of soluble compounds of mineral phosphorus with continuous time also its competitive of phosphate ions on adsorption locations then increase from amount of available phosphorus with continuous time, this ensure by (18) that the organic acids with low molecular weight such Citric, Lactic and Malic acid have their ability on soluble of phosphorus form of natural phosphate rock. Citric acid was surpassed with soluble max amount of phosphorus from natural phosphate rock compared with lactic and Malic acid. While soil of control treatment amount of available phosphorus was significant decreased with increasing of incubation period where decreased from 9.18 mg P kg⁻¹ soil after 14 days from incubation to 6.7518 mg P kg⁻¹ soil at 70 days time incubation, this return to the addition phosphorus to calcareous soil with mineral fertilizers is suffer from operations of fixation by calcium carbonate and change from available form to sedimentation form with calcium phosphate form with continuous time (23).

Mineral phosphorus in soil. Table (3) shows that the amount of mineral phosphorus in soil was increased significant (P<0.01,0.05) according to concentration and type of acid. Increasing concentration of addition organic acids with levels (15,30,45 and 60) mg L⁻¹ except Humic acid with concentrations (500,100,1500 and 2000) mg L⁻¹ were lead to increase amount of mineral phosphorus in soil for all treatments compared with (0) level (only fertilizer). Treatment of Humic acid was surpassed in amount of mineral phosphorus significant (P<0.01,0.05) compared with all acids with average (256.59,259.48,262.58 and 265.78) mg P kg⁻¹ soil for remember concentration respectively, and Citric acid was surpassed in amount of mineral phosphorus significant compared with acids low molecular weight in this study such Oxalic, Malic, Acetic and Lactic acid for all study concentration (15,30,45 and 60) mg L⁻¹ gave (243.78,248.41,250.57 and 253.63) mg P kg⁻¹ soil, while achieved less range in amount of mineral phosphorus by lactic acid, was gave (222.81,225.34,228.09 and 229.84) mg P kg⁻¹ soil, this return to ability of organic acids on soluble and destroy part of phosphorus minerals then release from soil with mineral phosphorus form especial Humic acid with high molecular weight which achieved max amount of mineral phosphorus compared with other acids in this study, this ensure by (18) was showed each type of organic acids deferent interactions with soil phase of soil. Table (3) shows that significant increasing (P<0.01,0.05) in amount of mineral phosphorus in soil with increasing of time incubation, where increased from 230.39 mg P kg⁻¹ soil after 14 days of incubation to 243.23 mg P kg⁻¹ soil at time incubation 70 days, amount of mineral phosphorus (233.32,238.02 and 240.56) mg P kg⁻¹ soil for time incubation 28, 42 and 56 days respectively increasing amount of mineral phosphorus in soil with continuous time return to speed mineral for organic.
Table (3) Effect type and concentration of organic acid and conc. super phosphate fertilizer in amount of mineral phosphorus in soil (mg P kg\(^{-1}\) soil) during different time incubation.

| type of acid | concentration of acid | day) (incubation time | type of acid * concentration of acid(compound treatment) | L.S.D 0.01,0.05 |
|-------------|----------------------|-----------------------|---------------------------------------------------------|----------------|
| Humic acid  | 0                    | 212.33 215.36 222.81 225.86 228.22 220.92 |                                                         |                |
|             | 500                  | 248.53 253.00 258.00 260.23 263.17 256.59 |                                                         |                |
|             | 1000                 | 251.49 256.33 259.22 263.44 266.92 259.48 |                                                         |                |
|             | 1500                 | 255.16 259.47 262.13 266.70 269.46 262.58 |                                                         |                |
|             | 2000                 | 258.40 262.40 265.23 270.65 272.23 265.78 |                                                         |                |
| Citric acid | 0                    | 212.33 215.36 222.81 225.86 228.22 220.92 |                                                         |                |
|             | 15                   | 238.69 240.16 244.26 246.23 249.55 243.78 |                                                         |                |
|             | 30                   | 242.23 245.63 249.26 251.33 253.61 248.41 |                                                         |                |
|             | 45                   | 244.12 247.80 251.30 253.39 256.23 250.57 |                                                         |                |
|             | 60                   | 247.50 250.13 254.12 256.23 260.11 253.63 |                                                         |                |
| Oxalic acid | 0                    | 212.33 215.36 222.81 225.86 228.22 220.92 |                                                         |                |
|             | 15                   | 233.61 236.50 238.26 239.14 240.66 237.63 |                                                         |                |
|             | 30                   | 236.20 239.66 241.00 242.00 244.52 240.68 |                                                         |                |
|             | 45                   | 238.14 242.62 245.39 246.00 248.69 244.17 |                                                         |                |
|             | 60                   | 241.17 244.50 247.39 249.50 250.20 246.55 |                                                         | 3.61, 2.56     |
| Malic acid  | 0                    | 212.33 215.36 222.81 225.86 228.22 220.92 |                                                         |                |
|             | 15                   | 230.56 232.40 234.31 235.23 237.42 233.98 |                                                         |                |
|             | 30                   | 233.59 235.00 236.55 237.15 239.76 236.41 |                                                         |                |
|             | 45                   | 235.46 238.11 239.46 240.23 243.69 239.39 |                                                         |                |
|             | 60                   | 238.00 240.60 242.69 244.23 245.39 242.18 |                                                         |                |
| Acetic acid | 0                    | 212.33 215.36 222.81 225.86 228.22 220.92 |                                                         |                |
|             | 15                   | 217.55 219.25 227.88 229.64 232.34 225.33 |                                                         |                |
|             | 30                   | 221.00 223.18 229.13 233.53 236.47 228.66 |                                                         |                |
|             | 45                   | 225.00 227.33 231.46 234.60 238.47 231.37 |                                                         |                |
|             | 60                   | 227.13 229.66 235.51 237.83 241.56 234.34 |                                                         |                |
| Lactic acid | 0                    | 212.33 215.36 222.81 225.86 228.22 220.92 |                                                         |                |
|             | 15                   | 214.20 216.63 224.15 227.53 231.56 222.81 |                                                         |                |
|             | 30                   | 217.51 219.89 226.72 230.17 232.42 225.34 |                                                         |                |
|             | 45                   | 220.31 223.17 229.19 232.17 235.60 228.09 |                                                         |                |
|             | 60                   | 222.19 224.00 231.00 234.55 237.45 229.84 |                                                         |                |
| effect of time incubation | 230.39 233.32 238.02 240.56 243.23 | L.S.D 0.01,0.05 | 1.47, 1.25 |
Phosphorus also suitable heat and wet for activity of microorganisms which cause increasing speed analysis of organic phosphorus and change its from organic form to mineral form with continuous time then was caused to increase amount of mineral phosphorus and decreasing of organic phosphorus with continuous time also increasing soluble compounds of mineral phosphorus with continuous time incubation ,this agree with (18) was found to liner relation between soluble of phosphorus and time of incubation (day).

Generally the organic acids in this study can be arranged for all concentrations and time of incubation according to their ability on release of mineral phosphorus as follow:
Humic acid > Citric acid > Oxalic acid > Malic acid > Acetic acid > Lactic acid > only fertilizer.

Organic phosphorus in soil.
Table (4) shows that amount of organic phosphorus in soil was decreased significant (P<0.01,0.05) according to concentration and type of acid .Increasing concentration of addition organic acids(15,30,45 and 60)mg L⁻¹ except Humic acid with concentrations (50,1000,1500 and 2000)mg L⁻¹ were caused to decrease amount of organic phosphorus and increasing amount of mineral phosphorus in soil for all treatments compared with control treatment which increased amount of organic phosphorus ,also Humic acid was decreased in amount of organic phosphorus significant (P<0.01,0.05) compared with all acids and control treatment with average( 47.69,44.80,41.69 and 38.51) mg P kg⁻¹ soil for remember concentrations respectively ,and decreased amount of organic phosphorus by citric acid significant compared with acid low molecular weight in this study such Oxalic , Malic , Acetic and Lactic acid for all the study concentrations in this study(15,30,45 and 60)mg L⁻¹ were give (60,50,55.87,53.71 and 50.65) mg P kg⁻¹ soil respectively ,max amount of organic phosphorus was achieved by Lactic acid where gave 81.46,78.94,76.19 and 74.44) mg P kg⁻¹ soil ,decreasing amount of organic phosphorus in soil for first acids return to these acids are increase from activity of microorganisms the analysis of organic matter then increase from desorption of phosphorus from organic matter in finally decrease amount of organic phosphorus in soil ,this insure by Pavinato et al(2008),less ability of Lactic and Acetic acids on the soluble of phosphorus minerals were the cause in increasing amount of organic phosphorus in soil compared with study organic acids.

| type of acid | concentration of acid (compound treatment) | L.S.D 0.01,0.05 |
|-------------|------------------------------------------|-----------------|
| Humic acid  | 0                                        | 83.36           |
|             | 500                                      | 47.69           |
|             | 1000                                     | 44.80           |
|             | 1500                                     | 41.69           |
|             | 2000                                     | 38.51           |
| Citric acid | 0                                        | 83.36           |
|             | 15                                       | 60.50           |
|             | 30                                       | 55.87           |
|             | 45                                       | 50.65           |
|             | 60                                       | 1.10.0.98       |
we can be arrangement type of organic acids in this study for all concentrations and time of incubation according to ability decreasing amount of organic phosphorus and increasing amount of mineral phosphorus as follow: Humic acid > Citric acid > Oxalic acid > Malic acid > Acetic acid > Lactic acid > only fertilizer. Table (4) shows that to increasing significant (P<0.01,0.05) in amount of organic acid in soil with increasing of incubation time, where decreased from 72.94 mg P kg\(^{-1}\) soil after 14 days from incubation to 61.06 mg P kg\(^{-1}\) soil at time incubation 70 days. The amount of organic phosphorus 70.01, 67.20 and 64.68 mg P kg\(^{-1}\) soil for time incubation 28, 42 and 56 days respectively decreasing amount of organic phosphorus in the soil with continuous time return to speed mineralization of organic phosphorus also suitable heat and wet for activity of microorganisms were caused to increase speed analysis of organic phosphorus and change its from organic form to mineral form with continuous time then caused increasing amount of mineral phosphorus and decreasing of organic phosphorus with continuous time.

Total phosphorus in soil
The results of the study were showed that the addition of organic acids (Humic, Citric, Oxalic, Malic, Acetic and Lactic acid) with different concentrations (15, 30, 45 and 60) mg L\(^{-1}\) except Humic acid (500, 1000, 1500, 2000) mg L\(^{-1}\) not cause any increasing in amount of total phosphorus which gave average 304.28 mg P kg\(^{-1}\) soil compared with control treatment (only fertilizer) which gave 304.28 mg P kg\(^{-1}\) soil.
return to these acids in this study are pure chemical acids not contain any amount of phosphorus therefore gave results same to control treatment (only fertilizer). The results of the study also showed that the increasing time of incubation not cause any increasing in amount of total phosphorus were gave 303.33, 305.22 and 304.29 mg P kg$^{-1}$ soil for incubation time 14, 42 and 70 days respectively. return to element of phosphorus during incubation time not volatilization or addition, but the increasing or decreasing with other forms (mineral and organic) return to the total phosphorus which act sum of mineral and organic phosphorus, this amount remain constant of total phosphorus for the incubation time in this study (14, 42 and 70) days.

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