Comparative Efficiency of Different Organic Acids Spraying in Groundnut on Available Nutrient Status of Calcareous Soils

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A B S T R A C T

A pot culture experiment was conducted in Agricultural College, Bapatla, Andhra Pradesh to study the “comparative efficiency of different organic acids spraying in groundnut on available nutrient status of calcareous soils” during kharif season of 2015-16. The experimental soil was Calcareous (collected from Vertisol profile), low in available nitrogen, medium in available phosphorus and high in available potassium. All the micronutrients except iron were sufficient in the soil with values above their critical limits. The treatments comprised of control (T₁); FeSO₄.7H₂O @ 0.25% (T₂); citric acid @ 0.25% (T₃); acetic acid @ 0.25% (T₄); oxalic acid @ 0.125% (T₅); ascorbic acid @ 0.25% (T₆); hydroxyl amine hydrochloride (T₇) were replicated thrice in completely randomized design (CRD) with three replications. Foliar application of organic acids was applied to the respective pots at peak flowering, peg penetration and pod formation stage of the crop growth. Similarly, Foliar application of organic acids showed non-significant difference in N, P, K and significantly increased the S and Fe contents in soil. Availability of N, K nutrients was maximum in treatments treated with ascorbic acid @ 0.25%, P was higher in treatments received oxalic acid @ 0.125% and S, Fe contents in soil were higher in treatment supplied with FeSO₄.7H₂O @ 0.25% were found significantly superior to rest of the treatments.

Keywords
Available nutrient status, Groundnut, Calcareous soils, Organic acids

Article Info
Accepted: 30 February 2018
Available Online: 10 April 2018

Introduction

Nutrient management in calcareous soils differ from that in non-calcareous soils because of the effect of soil pH on soil nutrient availability and chemical reactions that affect the loss or fixation of almost all nutrients. Root exudation of organic acid anions (e.g. citrate, malate, oxalate) is thought to represent one of the main strategies used by plants to enhance nutrient mobilization and acquisition under phosphorus and micronutrient limiting conditions. Organic acids have been shown to induce the dissolution of insoluble ferric oxyhydroxides in soil in the absence of plants, their ability to mobilize iron in a complex rhizosphere environment remains largely unknown. Oxalic acid has the largest ability to chelate many metal ions (K⁺, Mn²⁺, Zn²⁺, and Cu²⁺), preventing their precipitation with P. Many studies have also confirmed that oxalic acid can efficiently remove phosphate from Ca-P in calcareous soils and from Fe-P and Al-P in acidic soils (Jones, 1998; Hinsinger,
2001). Gerke et al., (2000) also showed that oxalate can be almost as effective as citrate in increasing the solubility of soil P. Iron deficiency is common in soils that have a high CaCO$_3$ due to reduced solubility at alkaline pH values.

**Materials and Methods**

The representative soil samples up to 15 cm depth were collected during the month of August 2015. The nitrogen was analysed by alkaline potassium permanganate method (Subbiah and Asija, 1956). The phosphorus was analysed by Olsen’s method (Watanabe and Olsen, 1965). Potassium in soil was estimated by neutral normal ammonium acetate (Muhr et al., 1965). Available sulphur in soil was extracted with 0.15% CaCl$_2$ extractant and turbidity was developed with barium chloride followed by measuring intensity of turbidity with spectrophotometer at 420 nm as outlined by Hesse (1971). Available iron, manganese, zinc and copper in soil was determined by DTPA (Diethylene Triamine Penta Acetic Acid) was used as extractant and AAS was used for estimation as described by Tandon (1998).

**Results and Discussion**

**Available nutrient status**

Nitrogen content in treatments supplied with foliar application of organic acids treated pots showed non-significant difference among the treatments (Table 1) at all the stages of the crop growth. The data indicated that the higher available nitrogen was observed in ascorbic acid @ 0.25% treated pots at all stages of the crop growth. However marginal increment in nitrogen content was observed in ascorbic acid @ 0.25% treatment than to control at all stages of crop growth. The lowest values observed were 183.89, 203.37 and 195.48 (recommended dose of fertilizers only), while the highest values were 206.25, 229.47 and 219.17 kg ha$^{-1}$ (ascorbic acid @ 0.25%) at flowering, peg penetration and harvest stages of crop growth respectively. At flowering, peg penetration stage available nitrogen in soil observed increasing trend, then decreasing trend at harvest stage of crop growth. The increase in the available nitrogen content with the foliar application of organic acids might be due to the mineralization and release of nitrogen.

Phosphorus content in treatments supplied with foliar application of organic acids treated pots showed non-significant trend among the treatments (Table 1) at all the stages of the crop growth. Highest (19.91 kg ha$^{-1}$) available Phosphorus (P$_2$O$_5$) at flowering stage was observed in T$_5$ i.e., oxalic acid @ 0.125% and the lowest (15.38 kg ha$^{-1}$) in T$_1$ (recommended dose of fertilizers only). The range was in between 23.72 kg ha$^{-1}$ in T$_5$ (oxalic acid @ 0.125%) and 19.31 kg ha$^{-1}$ in T$_1$ (recommended dose of fertilizers only) at peg penetration stage of the crop growth. At harvest the range was in between 22.43 and 18.46 kg ha$^{-1}$ in T$_1$ (recommended dose of fertilizers only) treatments, respectively. However increased in the phosphorus content in the organic acids treated pots i.e., T$_2$ to T$_7$ as compared to control was discernible. Available phosphorus content was increased on foliar application of organic acids might be due to organic acids has been suggested to increase P availability in calcareous soils (Kpomblekou and Tabatabai 2003), Gerke et al., (2000) showed that oxalate can be almost as effective as citrate in increasing the solubility of soil P. Available potassium (K$_2$O) contents in soil was not significantly influenced by the imposed treatments (Table 1) at all stages of the crop growth. At flowering stage, the highest (540.72 kg ha$^{-1}$) value was recorded by T$_6$ (ascorbic acid @ 0.25%) followed by T$_2$ i.e., FeSO$_4$.7H$_2$O @ 0.25% (534.55).
Table 1: Influence of organic acids on soil available N, P₂O₅ and K₂O (kg ha⁻¹) at different growth stages of groundnut

| Treatments                                      | Nitrogen   |          | P₂O₅     |          | K₂O     |          |
|------------------------------------------------|------------|----------|----------|----------|---------|----------|
|                                                | Flowering  | Peg penetration | Harvesting | Flowering | Peg penetration | Harvesting | Flowering | Peg penetration | Harvesting |
| T₁: Control                                    | 183.89     | 203.37   | 195.48   | 15.38    | 19.31   | 18.46    | 509.64    | 554.16    | 521.59    |
| T₂: FeSO₄·7H₂O @ 0.25%                         | 202.62     | 220.32   | 214.11   | 17.51    | 22.15   | 21.24    | 534.55    | 567.35    | 541.36    |
| T₃: Citric acid @ 0.25%                        | 197.66     | 214.25   | 209.35   | 19.58    | 22.73   | 21.69    | 525.97    | 585.54    | 549.04    |
| T₄: Acetic acid @ 0.25%                        | 194.79     | 217.27   | 203.29   | 18.68    | 21.95   | 20.70    | 533.51    | 581.34    | 543.27    |
| T₅: Oxalic acid @ 0.125%                       | 199.72     | 223.10   | 209.17   | 19.91    | 23.72   | 22.43    | 524.69    | 566.49    | 538.09    |
| T₆: Ascorbic acid @ 0.25%                      | 206.25     | 229.47   | 219.17   | 18.92    | 22.61   | 21.58    | 540.72    | 593.04    | 557.34    |
| T₇: Hydroxyl amine hydrochloride @ 0.25%       | 191.84     | 212.05   | 198.62   | 18.85    | 21.98   | 20.76    | 529.17    | 574.74    | 539.83    |
| SEm±                                           | 6.20       | 7.03     | 6.66     | 0.94     | 1.40    | 0.87     | 17.88     | 19.19     | 18.67     |
| CD @ 0.05                                      | NS         | NS       | NS       | NS       | NS      | NS       | NS        | NS        | NS        |
| CV (%)                                         | 5.46       | 5.61     | 5.57     | 6.07     | 6.51    | 5.94     | 5.86      | 5.78      | 5.97      |
| Initial                                        | 196.0      | 14.49    | 520.01   |          |         |          |           |           |           |

Table 2: Influence of organic acids on available sulphur (ppm) in soil at different growth stages of groundnut

| Treatments                                      | Flowering | Peg penetration | Harvesting |
|------------------------------------------------|-----------|-----------------|------------|
| T₁: Control                                    | 33.50     | 34.78           | 33.08      |
| T₂: FeSO₄·7H₂O @ 0.25%                         | 39.48     | 41.14           | 40.63      |
| T₃: Citric acid @ 0.25%                        | 39.36     | 40.38           | 40.27      |
| T₄: Acetic acid @ 0.25%                        | 38.75     | 39.43           | 38.43      |
| T₅: Oxalic acid @ 0.125%                       | 38.45     | 39.51           | 39.11      |
| T₆: Ascorbic acid @ 0.25%                      | 38.98     | 39.03           | 38.27      |
| T₇: Hydroxyl amine hydrochloride @ 0.25%       | 37.65     | 38.96           | 38.12      |
| SEm±                                           | 1.11      | 1.17            | 1.19       |
| CD @ 0.05                                      | 3.38      | 3.54            | 3.61       |
| CV (%)                                         | 5.07      | 5.18            | 5.39       |
| Initial                                        |          | 34.59           |            |
Table 3: Influence of organic acids on available iron (ppm) in soil at different growth stages of groundnut

| Treatments                                  | Flowering | Peg penetration | Harvesting |
|---------------------------------------------|-----------|-----------------|------------|
| $T_1$: Control                              | 2.56      | 2.61            | 2.48       |
| $T_2$: FeSO$_4$.7H$_2$O @ 0.25%             | 3.47      | 3.59            | 3.51       |
| $T_3$: Citric acid @ 0.25%                  | 3.79      | 4.09            | 3.81       |
| $T_4$: Acetic acid @ 0.25%                  | 3.56      | 3.86            | 3.56       |
| $T_5$: Oxalic acid @ 0.125%                 | 3.81      | 4.11            | 3.85       |
| $T_6$: Ascorbic acid @ 0.25%                | 3.53      | 3.80            | 3.57       |
| $T_7$: Hydroxyl amine hydrochloride @ 0.25% | 3.76      | 3.83            | 3.79       |
| SEM±                                        | 0.10      | 0.11            | 0.10       |
| CD @ 0.05                                   | 0.30      | 0.33            | 0.30       |
| CV (%)                                      | 4.59      | 4.87            | 4.71       |
| Initial                                     | 2.70      |                 |            |

Table 4: Influence of organic acids on available micronutrients (ppm) in soil at harvest stage of groundnut

| Treatments                                    | Iron    | Manganese | Zinc  | Copper |
|------------------------------------------------|---------|-----------|-------|--------|
| $T_1$: Control                                | 2.48    | 12.11     | 0.95  | 15.29  |
| $T_2$: FeSO$_4$.7H$_2$O @ 0.25%               | 3.51    | 12.36     | 0.97  | 15.73  |
| $T_3$: Citric acid @ 0.25%                    | 3.81    | 12.72     | 1.02  | 19.15  |
| $T_4$: Acetic acid @ 0.25%                    | 3.56    | 12.64     | 1.01  | 17.67  |
| $T_5$: Oxalic acid @ 0.125%                   | 3.85    | 12.87     | 1.05  | 20.10  |
| $T_6$: Ascorbic acid @ 0.25%                  | 3.79    | 12.56     | 0.99  | 17.63  |
| $T_7$: Hydroxyl amine hydrochloride @ 0.25%   | 3.57    | 12.22     | 0.98  | 17.49  |
| SEM±                                          | 0.10    | 0.38      | 0.03  | 0.57   |
| CD @ 0.05                                     | 0.30    | NS        | NS    | 1.73   |
| CV (%)                                        | 4.71    | 5.30      | 5.88  | 5.61   |
| Initial                                       | 2.70    | 12.13     | 0.92  | 4.04   |
At peg penetration stage of crop growth the highest values (593.04 and 585.54 kg ha⁻¹) were recorded in the treatment received ascorbic acid @ 0.25% (T₆) followed by citric acid @ 0.25% (585.54 kg ha⁻¹). At harvest the highest value (557.34 kg ha⁻¹) was recorded in ascorbic acid @ 0.25%. The lowest available potassium contents of 509.64, 554.16 and 521.59 at flowering, peg penetration and harvest, respectively were recorded in T₁ (control i.e. recommended dose of fertilizers only).

Available manganese (Table 4) contents in soil were not significantly influenced by the imposed treatments at harvest stage of crop growth. At harvesting stage, the highest (12.87 ppm) value was recorded by T₃ (citric acid @ 0.25%) followed by T₆ i.e., ascorbic acid @ 0.25% (12.72 ppm). The lowest available manganese content of 12.11 was recorded in T₁ (control). Najafi and Jalali (2015) reported that on foliar application of organic acids, there was no significance influence of soil available manganese content.

Available zinc (Table 4) contents were influenced by the treatments (Table 2) at all the stages of the crop growth. Among the treatments, FeSO₄·7H₂O @ 0.25% (T₃) recorded higher available zinc concentration of 20.10 ppm and is on par with citric acid @ 0.25% (1.02 ppm) and acetic acid @ 0.25% (1.01) at harvesting stage of the crop growth. However slight increment in zinc content was discernible in foliar spray treatments than to control (0.95) at harvest stage of crop growth. Available Zn content was increased on foliar application of organic acids might be due to mineralization process and ability to chelate metal ions (Mn²⁺, Zn²⁺, and Cu²⁺). The results were confirmed with the findings of Jones (1998) and Hinsinger (2001).

Available copper (Table 4) contents were not significantly influenced by the treatments at harvest stage of crop growth. Among the treatments, the treatment receiving oxalic acid @ 0.125% recorded higher available copper concentration of 20.10 ppm and is on par with the treatment receiving citric acid @ 0.25% (T₃) which recorded available copper concentration of 19.15 ppm followed by acetic acid @ 0.25% (T₄-17.67 ppm), ascorbic acid @ 0.125% (T₆-17.63 ppm) and hydroxyl amine hydrochloride @ 0.25% (T₇-17.49 ppm). This might be due to organic acids mainly exist in soil as natural products of root exudates, microbial secretions, and decomposition of plant and animal residues. Due to their chelation and complexion characteristics, organic acids are important products in controlling mobility and transport of metals (Jiang et al., 2012). Najafi and Jalali (2015) reported that Organic acids affected the

Sulphur content in treatments supplied with foliar application of organic acids treated pots showed significance influence (Table 2) at all the stages of the crop growth. Among the treatments, FeSO₄·7H₂O @ 0.25% recorded higher sulphur content (39.48, 41.14 and 40.63 ppm). The treatments FeSO₄·7H₂O @ 0.25%, citric acid @ 0.25% (T₃-39.36, 40.38 and 40.27 ppm), ascorbic acid @ 0.25% (T₆-38.98, 39.03 and 38.27 ppm), acetic acid @ 0.25% (T₄-38.75, 39.43 and 38.43 ppm), oxalic acid @ 0.125% (T₅-38.45, 39.51 and 39.11 ppm) and hydroxyl amine hydrochloride (T₇-37.65, 38.96 and 38.12 ppm) were on par with each other and significantly superior over control (33.50, 34.78 and 33.08 ppm).

The data indicated that (Table 3) the higher available iron was observed in all the treatments when compared to control at all stages of the crop growth. Among the treatments, the treatment receiving oxalic acid @ 0.125% was recorded highest available iron concentration of 3.81, 4.11, 3.85 ppm at flowering, peg penetration and harvesting respectively, which was on par with the treatment receiving citric acid @ 0.25% which recorded available iron concentration of 3.79, 4.09, 3.81 ppm. This may be due to high CaCO₃ (17.5%) per cent. However, the foliar spray of oxalic acid significantly increased iron, here it was difficult to attribute the reason behind the increase in concentration of iron after spraying of oxalic acid. These were in accordance with findings of Pierre et al., (2002) and Ramireddy and Basavaraj (2012).

The data (Table 4) indicated that the higher (1.05 ppm) available zinc was observed in oxalic acid @ 0.125% treated pots followed by citric acid @ 0.25% (1.02 ppm) and acetic acid @ 0.25% (1.01) at harvesting stage of the crop growth. However slight increment in zinc content was discernible in foliar spray treatments than to control (0.95) at harvest stage of crop growth. Available Zn content was increased on foliar application of organic acids might be due to mineralization process and ability to chelate metal ions (Mn²⁺, Zn²⁺, and Cu²⁺). The results were confirmed with the findings of Jones (1998) and Hinsinger (2001).
behavior of Cu in soils. This result can be attributed to higher stability constants of Cu-organic acids complexes.

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How to cite this article:

Jagga Rao, I., P. Ravindra Babu, P.R.K. Prasad and Venkata Lakshmi, N. 2018. Comparative Efficiency of Different Organic Acids Spraying in Groundnut on Available Nutrient Status of Calcareous Soils. Int.J.Curr.Microbiol.App.Sci. 7(04): 3784-3789. doi: https://doi.org/10.20546/ijcemas.2018.704.426