Study on the Effects of Low Molecular Organic Acids on the Availability and Morphology of Phosphorus in Calcite Soils

Wenjie Fu, Yazhen Wan*
School of Chemical Engineering, Zhengzhou University, China
*Email: 2725028109@qq.com

Abstract. Improving the availability of phosphate fertilizer in the soil can significantly improve the yield and quality of crops, which is related to China's food security. In the present study, malonic acid, a low molecular weight organic acid, was used as a synergist and monoammonium phosphate. The results showed that the availability of phosphorus increased by 12.02% compared with monophosphate. By analyzing the morphology and correlation of inorganic phosphorus in the soil, it was found that the conversion rate of Ca$^{2+}$-P to Ca$^{8+}$-P slowed down. Therefore, the addition of malonic acid can improve the availability of phosphate fertilizer in calcareous soil.

1. Introduction
Phosphorus is one of the most important elements of life [1]. The application of phosphate fertilizer greatly increased the yield of grain. However, the phosphate fertilizer entering the soil is easy to be adsorbed and fixed by calcium carbonate and iron and aluminum oxide, leading to a significant reduction in the availability of phosphate fertilizer [2]. Therefore, improving the effectiveness of phosphate fertilizer is a hot issue at present.

At present, studies on the synergies of phosphate fertilizers mainly focus on high molecular organic acids and low molecular organic acids [3]. Most low molecular organic acids are plant secretions. Therefore, the research on low molecular organic acids should be more in-depth. The previous studies have suggested that the low molecular organic acids of malonic acid, citric acid and oxalic acid [4] can activate phosphorus in soil and increased the physical and chemical properties of soil. Three kinds of low molecular organic acids can improve the efficiency of phosphate fertilizer. In this study, the effect of β-polyglutamic acid-enhanced phosphate fertilizer on the morphological transformation of available phosphate and phosphate in soil was detected by using malonic acid as the research object and mono ammonium phosphate as the source of phosphate. The purpose of this study was to provide a scheme for rational fertilization and improving the availability of phosphate fertilizer.

2. Materials and methods
Synergist malonic acid and monoammonium phosphate were provided by Henan production enterprises. Calcareous clay was used as the test material in the soil. The soil type is tidal soil. The soil was collected in the western suburb of Zhengzhou High-tech Zone according to Lu Rukun's soil Agrochemical Analysis. Collect all the test soil at one time, air dry, and store in a 100-mesh sieve for reserve. The basic physical and chemical properties of the tested soil were shown in table 1.
Table 1. Basic physical and chemical properties of soil.

| SOM (g/kg) | pH   | Total-P (g/kg) | Olsen-P (mg/kg) | CEC (cmol/kg) | CaCO₃ (mg/kg) |
|-----------|------|----------------|-----------------|---------------|---------------|
| 6.8       | 8.16 | 0.8            | 7.52            | 6.77          | 39.91         |

2.1. Test Methods
Cultivate the steps as shown below: dried soil through 100 mesh sieve, take 500 g soil samples in plastic containers, phosphate fertilizer synergist and monoammonium phosphate after mixing into the soil, in the constant temperature box, the temperature setting is 25 ℃, regular watering, keep soil moisture for around 70% of field capacity, calculate according to the 450 mgp2o5 per kilogram of soil p levels. In this experiment, three treatments were set up, including a blank control group (CK), single phosphate fertilizer group (0.5g), malonic acid (0.5g) and monoammonium phosphate (0.5g) mixed group, and each treatment was repeated for three times.

2.2. Analytical Methods
The soil pH and organic matter were determined by electrode potentiometric method and potassium dichromate oxidation bulk density method, respectively. The total phosphorus and available phosphorus was determined by H₂SO₄-HClO₄ molybdenum-antimony anticolorimetric method and NaHCO₃ daemon-antimony resistance assay, respectively. The inorganic phosphorus forms in calcareous soil were graded by Gu Yizhi and Jiang Baifan.

2.3. Data processing
All data in this study were processed by SPSS19 and DPS software. Graph the data using the origin 2016 software.

3. Results and analysis

3.1. Effects of malonic acid on soil available phosphorus
With the additional amount of malonic acid and monoammonium phosphate equal to 1:1, the effects of the malonic acid on the available phosphorus in the soil were shown in Figure 1. Under certain temperature and humidity, there were little changes in the available phosphorus in CK. Within 90 days of culture, the available phosphorus in the malonic acid group was higher than that in the monophosphate group. On the 90th day of culture, the available phosphorus was 94.19mg/kg and 84.08mg/kg in the malonic acid group and monophosphate group, respectively. The available phosphorus in the malonic acid group was 10.11mg/kg higher than that in the monophosphate treatment group, and the availability of phosphate fertilizer increased by 12.02%. Based on the above results, it was concluded that the addition of malonic acid improved the availability of phosphate fertilizer.

Figure 1. The effect of malonic acid treatment on the effective phosphorus content.
3.2. Effects of malonic acid on soil inorganic phosphorus forms

The forms of inorganic phosphorus in malonic acid-treated soil were classified. Table 2 showed that the content of Ca$_2$P in the phosphate fertilizer group and malonic acid group decreased with time, while the content of Ca$_8$P increased with time. These results indicated that the available phosphorus in the soil was transformed into the invalid phosphorus. The content of Ca$_2$P in the malonic acid group was higher than that in the phosphate fertilizer group, suggesting that malonic acid could inhibit the rapid transformation of Ca$_2$P to Ca$_8$P. The content of Ca$_{10}$P was increased in a malonic acid group and phosphate fertilizer group, indicating that part of Ca$_2$P was transformed into Ca$_8$P and then into Ca$_{10}$P with low conversion. Relevant studies showed that O-P was stable phosphorus, which was a reduced ferric aluminum phosphate coated by an iron oxide film. Part of O-P is bound in the lattice of silicic acid, which will not be decomposed and participated in the cycle of soil phosphorus in a short time under the condition of non-strong reduction.

Table 2. Effect of malonic acid on soil inorganic phosphorus forms.

| Day | Treatment       | Inorganic phosphorus content (mg/kg) |
|-----|-----------------|--------------------------------------|
|     |                 | Ca$_2$P    | Ca$_8$P    | Al-P       | Fe-P     | O-P       | Ca$_{10}$P |
| CK0 |                 | 3.56±0.47c | 19.06±0.73c | 10.37±0.71c | 22.87±1.08b | 10.77±0.81 | 652.53±3.24a |
| 1   | NH$_4$H$_2$P$_4$ | 169.31±0.65b | 102.69±1.81b | 27.48±1.59b | 37.45±1.48a | 143.32±0.56a | 552.05±0.64c |
|     | Malonic acid    | 173.86±2.89a | 92.28±3.86a | 31.55±1.79a | 38.57±0.66a | 137.3±1.68A | 573.4±3.89b |
| CK0 |                 | 5.99±0.3c   | 18.33±1.48c | 18.17±1.7b  | 19.09±2.0b  | 14.27±0.75c | 655.12±2.31a |
| 30  | NH$_4$H$_2$P$_4$ | 48.96±0.13b | 186.97±0.56a | 27.86±1.87a | 38.21±1.47a | 113.15±2.0b | 553.5±3.29c |
|     | Malonic acid    | 64.49±1.98a | 178.42±1.89b | 29.26±2.25a | 36.89±1.91a | 136±1.25a  | 587.36±3.58b |
| CK0 |                 | 6.05±0.41b  | 18.28±1.32c | 12.91±1.87b | 21.21±0.31c | 12.17±1.2c  | 628.05±4.15a |
| 60  | NH$_4$H$_2$P$_4$ | 62.88±1.56a | 190.48±1.28a | 28.2±1.88a  | 42.56±3.17a | 99.98±3.39b | 609.96±1.36ab|
|     | Malonic acid    | 77.23±2.84a | 182.79±3.21b | 30.57±4.31a | 45.64±2.98a | 119.27±2.78a | 596.68±3.25b |
| CK0 |                 | 4.19±0.17c  | 18.9±0.59c  | 10.75±2.25b | 22.24±1.91b | 10.82±0.91  | 616.66±5.49a |
| 90  | NH$_4$H$_2$P$_4$ | 41.03±0.46b | 187.88±0.99a | 34.13±0.86a | 47.89±1.88a | 91.69±1.21b | 604.73±4.79b |
|     | Malonic acid    | 58.7±3.78a  | 182.5±4.76b | 35.28±0.86a | 46.21±1.68a | 105.7±3.53a | 608.64±4.56b |

3.3. Correlation analysis between available phosphorus content in the malonic acid treatment group and different forms of inorganic phosphorus content

To further explore the effect of polyglutamic acid on the forms of available phosphorus and inorganic phosphorus, the correlation and path between the forms of available phosphorus and inorganic phosphorus in malonic acid-treated soil were analyzed. Table 3 shows that the correlation coefficients of Ca$_2$P, Ca$_8$P, Al-P, Fe-P, O-P and Ca$_{10}$P with available phosphorus in the malonic acid treatment group are 0.843, -0.892, 0.165, -0.12, 0.150 and -0.178 respectively. These results showed that the order of correlation between inorganic phosphorus components and available phosphorus was Ca$_8$P > Ca$_2$P > Ca$_{10}$P > Al-P > O-P > Fe-P. The results showed that only Ca$_2$P was positively correlated with available phosphorus. Ca$_8$P and Ca$_{10}$P were negatively correlated with available phosphorus. There was no significant correlation between Al-P, Fe-P and O-P and available phosphorus. Therefore, the results of the present study show that the content of available phosphorus can be increased by
increasing the content of Ca$_2$-P in soil, thus limiting the transformation of Ca$_2$-P to Ca$_8$-P and Ca$_{10}$-P in soil.

Table 3. Correlation analysis between available phosphorus content in the malonic acid treatment group and different forms of inorganic phosphorus content.

|        | Ca$_2$-P | Ca$_8$-P | Al-P   | Fe-P   | O-P   | Ca$_{10}$-P | Olsen-P |
|--------|----------|----------|--------|--------|--------|-------------|---------|
| Ca$_2$-P | 1        | -0.878** | -0.172 | -0.221 | -0.117 | -0.137      | 0.843** |
| Ca$_8$-P | 1        | 0.115    | 0.225  | 0.167  | 0.163  | -0.892**    |         |
| Al-P   | 1        | -0.187   | 0.864** | -0.550 | 0.165  |             |         |
| Fe-P   | 1        | -0.329   | 0.497  | -0.120 |        |             |         |
| O-P    | 1        | -0.441   | 0.150  |        |        |             |         |
| Ca$_{10}$-P | 1 | -0.178 |        |        |        |             |         |

4. Discussion
Malonic acid is a kind of low molecular organic acid with two carboxylic acid groups secreted by plants. When malonic acid was applied to the soil, these carboxylic acid groups combined with alkaline earth metals such as Ca, Mg, Al and Fe in calcareous soil, thus reducing the possibility of the combination of these metal ions with available phosphorus, and finally increased the available phosphorus in soil. Through the analysis of soil inorganic phosphorus form, malonic acid can better reduce the conversion of Ca$_2$-P to Ca$_8$-P and Ca$_{10}$-P. Besides, malonic acid, as a natural product, is non-toxic and harmless to the soil. Therefore, malonic acid can be used in agricultural production as a phosphate fertilizer synergist with excellent performance.

5. Conclusion
Malonic acid has the advantages of non-toxicity, biodegradability, etc., and has great application value in agricultural production. Our results suggested that malonic acid can reduce the fixation of phosphorus fertilizer in the soil and improve the availability of phosphorus. The present study provides a reliable scheme for crop yield and alleviating the crisis of phosphate resources.

Acknowledgements
This research is an Outstanding Talent Project of Henan Province (Project No. 184200510022), which the School of Chemical Engineering of Zhengzhou University. Thanks to Professor WAN and Professor ZHANG and all colleagues for their support.

Reference
[1] Wyngaard N, Cabrera M L, Jarosch K A and Bunemann E K 2016 Phosphorus in the coarse soil fraction is related to soil organic phosphorus mineralization measured by isotopic dilution Soil Biology & Biochemistry 96: 107-118
[2] Quesada C A, Lloyd J, Anderson L O, Fyllas N M, Schwarz M and Czimczik C I 2011 Soil of Amazonia with particular reference to the rainfor sites Biogeosciences 8: 3851–3921
[3] Teng Z, Zhu J, Shao W, Zhang K, Li M and Whelan M J 2019 Increasing plant availability of legacy phosphorus in calcareous soils using some phosphorus activators Journal of Environmental Management 256: 109952
[4] Jie X L, Li Y T and Pang R L Effect of Low Molecular Weight Organic Acids on Transformation and Availability of Phosphates in Calcareous Soil Chinese Journal of Soil Science 36(6) 856-860