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Research Article

Citric Acid Promotes the Mobilization of Phosphorus under the Lower Concentration of Low Molecular Weight Organic Acids in Acidic Forest Soil

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Low molecular weight organic acids (LMWOAs) secreted by plant roots enhanced the release of inorganic P (Pi) and organic P (Po) into the soil solution and thereby increased plant-available Pi in soils. Not the effect of LMWOAs on inducing organic P (Po) released into soil solution through soil microorganisms at different temperatures was poorly understood, but the transform mechanism for P fraction was also not well explained. This study used three experiments to determine the release of P and the transformation mechanism of P fractions induced by oxalic acid, citric acid, and malic acid in acidic forest soils. The results showed that LMWOAs, as carbon sources for microorganisms, mobilize Po more effectively than glucose. Inorganic P and organic P were released by LMWOAs followed by oxalic acid > citric acid > malic acid if the substrates of P and LMWOAs were enough. There may be a critical threshold for the concentration of citric acid and oxalic acid between 10 mM and 25 mM to require for the solution of adsorbed and precipitated P, respectively. In all, LMWOAs increased the concentration of labile P by decreasing the concentration of stable P. The results indicated that LMWOAs can significantly promote P availability in acidic forests soils, and the effect of microorganisms on soil available P was more inclined to use LMWOAs than glucose.

1. Introduction

Phosphorus (P), as an essential element for plant growth, often limits the primary productivity of global terrestrial ecosystems [1]. Although the content of total P (TP) in the soil is very high (usually between 50 and 1500 mg/kg), soil available forms of inorganic P, which is directly absorbed and utilized by plants, only account for a small part of the soil TP in most soils [2–4]. For example, although the average available form of inorganic P extracted by resin in global natural soil is 17.2 mg/kg (accounting for 4.12% of the TP), its proportion is not invariable [5, 6]. Therefore, it is essential to explore the variation of soil P solubility and its driving factors for further understanding the strategies of plants to cope with the spatial variations of P deficiency and P limitation of primary productivity in terrestrial ecosystems [7, 8].

When the content of P in soil is deficient, plants can release low molecular weight organic acids (LMWOAs)

through their physiological strategies to increase the amount of soil bioavailable P (Bio-P) in the soil [9]. Previous studies have shown that LMWOAs can effectively increase the release of inorganic P (Pi) in the soil, thus, increasing the concentration of Bio-P in the soil [10, 11]. It has been widely speculated that LMWOAs enhance the mobilization of soil inorganic P through (1) directly promoting the dissolution of sparingly soluble minerals containing Pi, (2) shifting pH and chemical equilibria in soil solution, (3) altering the surface characteristics of mineral particles or occupying ligand exchange surface, and (4) forming complexes with Fe^{2+}, Al^{2+}, and Ca^{2+}, thus, blocking P adsorption sites on soil particles [12–14]. Moreover, LMWOAs may enhance the release of organic P (Po) bound to soil minerals. However, the mechanism for Po release induced by LMWOAs is not well explained, especially for soils with contrasting physicchemical properties (e.g., pH, Fe-/Al-oxide, and Ca-carbonate) similar to inorganic P, which may affect Po release from

soil because Fe, Al, and Ca oxides are the main soil minerals that affect the solubility of soil P. Fe and Al oxides play a leading role in acidic soil, while Ca oxides play a leading role in alkaline soils [4]. Although organic P needs to be mineralized to be absorbed by plants, it is an important component of TP and a potential source of Bio-P [15, 16]. Coincidentally, LMWOAs are important carbon sources for microorganisms, which play an important role in the mineralization of organic P. Hence, the effectiveness of mobilization depends on the soil type and the chemical structures and concentrations of LMWOAs [17]. Consequently, knowledge of the different P fractions can be used to directly determine the P pools acted upon by LMWOAs and deduce the mechanisms of P transformation.

To address these issues, to better study the effect of LMWOAs on the variations of P fractions and the mobilization of soil bioavailable P in soil, this study set up three groups of experiments to study these phenomena. First, both LMWOAs and glucose affect the transformation mechanism of P fractions as carbon sources for microorganisms, considering whether microorganisms play a role of organic P in this mechanism at different temperatures. Second, to verify the ability of different concentrations of LMWOAs to activate inorganic P and the threshold affecting its ability between different LMWOAs. Lastly, the objective of this study was to study the impact of three common LMWOAs (oxalic acid, citric acid, and malic acid) on the kinetics of Pi and Po release in acidic soils. In all, we hypothesized that both LMWOAs and glucose can act as carbon sources to affect the transformation of P fractions through microbial mineralization. In addition, our hypothesis is that LMWOAs will increase the rate of the kinetics of both Pi and Po release than water, and citric acid will be the most effective reagent for increasing the rate of Pi and Po release into soil solution of acidic soils.

2. Materials and Methods

2.1. Soil and Organic Acids. Surface layers (0-20 cm, removing the litter layer) of the soil were collected at 3000 m a.s.l. in August 2018 in Gongga Mountain (29°20′-30°20′N, 101°30′-102°15′E), located in the southwest of China at the southwest edge of Tibetan Plateau with an elevation 7556 m a.s.l. The parent materials are dominated by granites, ordering feldspar (43.7%) > quartz (32.7%) > hornblende (17.9%) > chlorite (4.9%) > muscovite (0.8%) [18]. The specific types of soil and vegetation with altitude have been described by Bing et al. [19] and Zhou et al. [18], and the same vegetation type (Abies fabric) and bedrocks on the Mt. Gongga were found from 2700 m to 3600 m a.s.l. The collected soil samples were air-dried and passed through a 2 mm sieve before experimental design. The LMWOAs selected for this study were oxalic acid, citric acid, and malic acid because of their widespread natural occurrence in soils in Mt. Gongga [20].

2.2. Experimental Designs

2.2.1. The Effects of Temperature on the Mobilization of Bio-P in Soil by LMWOAs. Soil (2 g) was placed in 50 mL centri-fuge tubes and added deionized water (control), organic acids, and glucose solution was added to each tube (containing 10 mmol kg^{-1} soil of citric acid, malic acid, oxalic acid, or glucose). Combined with the concentrations of three kinds of LMWOAs in soil, the mobilization experiments of Bio-P by LMWOAs were carried out at different temperatures (4°C, 14°C, and 24°C). In this study, the experimental temperature gradient was set at 14°C at 3022 m in the growing season (August). The minimum temperature was set at 4°C in the progrowing season (May) to restrain the microbial metabolism activity, and the maximum temperature was set at 24°C to verify the mobilization effects of LMWOAs and microbial metabolism activity on the release of P. The soil moisture content was set at 70% of its maximum field capacity. Under the corresponding temperature conditions for 15 days, it was weighed every day to keep the soil moisture content unchanged. After incubation for 15 days, the soil was collected from the centrifuge tube and dried in an oven (40°C for 72 h) for subsequent P component analysis.

2.2.2. The Effects of Concentrations on the Mobilization of Bio-P by LMWOAs. According to the existing studies, the higher the concentration of LMWOAs, the stronger their ability to activate P in soil. Combined with the concentration of LMWOAs observed in situ, the concentration gradient of LMWOAs in this experiment was set to 6 gradients (0, 5, 10, 25, 50, and 100 mM) to study the amount of P mobilization at 1 hour. Hence, soils (2 g) were placed in 50 mL centrifuge tubes, and then 20 mL of deionized water (control) or 20 mL of organic acid solution was added to each tube. Meanwhile, two drops of toluene were added to inhibit microbial activity before capping the tubes. The suspensions were shaken on an end-to-end shaker (200-cycles min^{-1} at 24°C) for 1 hour, centrifuged at 12,000 g for 10 min, and filtered through Whatman filter paper (no. 42). The filtered suspensions were used to measure the release of Pi by LMWOAs.

2.2.3. The Effects of LMWOAs at a Different Time on the Mobilization of Bio-P. LMWOAs with 100 mM kg^{-1} concentration were selected for the experiment according to the experimental design 2.2.2. The reason was that, compared with other low concentrations of LMWOAs, the LMWOA concentration of more than 100 mM in the soil can better reflect the mobilization of LMWOAs from soil P. Soils (2 g) were placed in 50 mL centrifuge tubes, and then 20 mL of deionized water (control) or 20 mL of organic acids solution was added to each tube. Meanwhile, two drops of toluene were added to inhibit microbial activity before capping the tubes. The suspensions were shaken on an end-to-end shaker (200-cycles min^{-1} at 24°C) for 5, 10, 15, 30, 60, 120, 240, 480, 960, 1,440, or 2,880 min, centrifuged at 12,000 g for 10 min, and filtered through Whatman filter paper (no. 42). The residues were washed three times with deionized water to completely remove the residual low molecular weight organic acids. The suspensions were used to measure the release of Pi and Po by LMWOAs. The soil was collected into centrifuge tubes that were shaken for 2,880 min, rinsed, and dried (40°C for 72 h) for subsequent

P fractionation analysis. Three replicates were set for all experimental treatments in our study.

2.3. Soil P Fractions. The extractions of P fractions were performed by using the modified Hedley methods [21]. Briefly, approximately 0.5 g dry soils were successively extracted by the anion-exchange membrane, 0.5 M NaHCO₃ (pH = 8.5), 0.1 M NaOH, and 1 M HCl. The extracted P fraction was designated as a resin-Pi, NaHCO₃-P, NaOH-P, and HCl-P. For 0.5 M NaHCO₃ (pH = 8.5) and 0.1 M NaOH extract, the total P (NaHCO₃-Pt and NaOH-Pt) was measured by digesting the solution with 0.9 M H₂SO₄ and ammonium persulfate. NaHCO₃-Po and NaOH-Po were measured as the difference between undigested and digested. The concentrations of P were measured by the UV-vis spectrophotometer (SHIMADZU UV 2450) using the phosphomolybdate blue method [22]. The sum of resin-Pi, NaHCO₃-Pi, and NaHCO₃-Po was defined to be the fraction of bioavailable P (Bio-P). Finally, the remaining residual soil P was determined by digestion in boiling concentrated H₂SO₄ with repeated addition of 30% H₂O₂.

2.4. Statistical Analysis. Soil P fraction data were subjected to normality and homogeneity tests before analysis of variance (ANOVA) using SPSS. Significant differences ($P < 0.05$) in the concentration of each P fraction before and after shaking with each treatment solution (water, citric acid, oxalic acid, malic acid, and glucose) were evaluated with a one-way analysis of variance (ANOVA) for each soil studied. All statistical analysis in this study was performed by the software package SPSS 19.0 and Origin 2017 for Windows.

3. Results

3.1. The Effects of Temperature on the Mobilization of Phosphorus by LMWOAs. The results showed that different kinds of LMWOAs had different effects on P fractions at different temperatures. LMWOAs promoted, unchanged, or inhibited the process of P fractions at different temperatures (Figure S1). The results showed that LMWOAs changed the concentrations of other P fractions by reducing the residual P at 4°C (Figure 1(a)). For example, only oxalic acid significantly increased the concentration of resin-P compared with deionized water, glucose, and other two organic acids at 4°C. Oxalic acid increased the concentrations of NaHCO₃-Po and NaOH-Po, thus, increasing the concentration of NaHCO₃-Pt and NaOH-Pt. Citric acid increased the concentrations of Bio-P and reduced the concentrations of NaOH-Pt, HCl-P, and residual P. However, malic acid did not change the fractions of Bio-P and other P fractions compared with oxalic and citric acids. LMWOAs inhibited the concentration of resin-P in the soil at 14°C but increased the concentration of Bio-P by increasing the concentration of NaHCO₃-Pt (Figure 1(b)). Oxalic acid increased the concentration of NaHCO₃-Po and NaOH-Po, thus, increasing the concentration of NaHCO₃-Pt and NaOH-Pt. Citric acid mainly reduced the concentration of NaOH-Pt, HCl-P, and residual P at 14 °C. Malic acid reduces the concentrations of NaHCO₃-Po and HCl-P, thus, increasing the Bio-P frac-

tions. The three kinds of LMWOAs showed similar characteristics in changing P fractions at 24°C (Figure 1(c)). All three LMWOAs significantly increased the concentration of Bio-P and decreased the concentrations of NaOH-Po, NaOH-Pt, and HCl-P. In all, LMWOAs increased the concentration of Bio-P mainly through increasing the concentrations of NaHCO₃-Pi. And significant variations of organic P were observed in higher temperatures.

3.2. The Effects of Concentration of Soil Inorganic P by LMWOAs. The mobilization ability of inorganic P was different from the various concentrations of LMWOAs in soil, showing that the higher concentration of LMWOAs had the greater mobilization ability of inorganic P in soil (Figure 2). With the increasing concentrations of LMWOAs, the release of inorganic P showed a linear increasing trend (Figure 2). Oxalic acid has the strongest mobilization ability, followed by citric and malic acids. However, with different concentrations of LMWOAs, different kinds of LMWOAs have different abilities to liberate soil P at 1 hour. The results showed that when the concentration of LMWOAs was lower than 10 mM, the mobilization ability of citric acid and malic acid was greater than that of oxalic acid, while the mobilization ability of oxalic acid was significantly enhanced when the concentration of LMWOAs was higher than 25 mM compared with citric acid and malic acid (Figure 2).

3.3. Kinetics of Pi and Po Release and Variation of P Fractions by the Effects of LMWOAs. The results showed that soil inorganic P and organic P in soil were released by the influence of LMWOAs with the increase of time (Figure 3). Three kinds of LMWOAs rapidly released inorganic P and organic P in a short time, but the release rate slowed down with the increase of time. Specially, oxalic acid had the fastest mobilization rate, citric acid and malic acid had less mobilization rate for inorganic P than oxalic acid, and deionized water had no obvious mobilization rate for inorganic P. Inorganic P was released by deionized water and LMWOAs followed by oxalic acid (26.88 mg/kg) > citric acid (21.27 mg/kg) > malic acid (9.51 mg/kg) > deionized water (1.56 mg/kg) after 48 hours. Like the variation of LMWOAs mobilized inorganic P, the three LMWOAs also released Po rapidly in a short time, and then the release rate slowed down with the increase of time. Organic P was released by deionized water and LMWOAs followed by oxalic acid (23.69 mg/kg) > citric acid (23.03 mg/kg) > malic acid (14.73 mg/kg) > deionized water (6.19 mg/kg) after 48 hours.

The results showed that the order of NaHCO₃-Pi was followed by citric acid > oxalic acid > malic acid, while the order of NaHCO₃-Pt was oxalic acid > citric acid > malic acid (Figure 4). The concentrations of NaOH-Pi, NaOH-Pt, and HCl-P decreased in the samples with citric acid, but only HCl-P decreased in the samples with oxalic acid, while the concentrations of NaOH-Pi and HCl-P decreased in the samples with malic acid. Meanwhile, the variations of organic P were significantly observed than those of inorganic P. Therefore, we thought that the inorganic P mobilized by citric acid mainly comes from NaOH-Pt, i.e., P
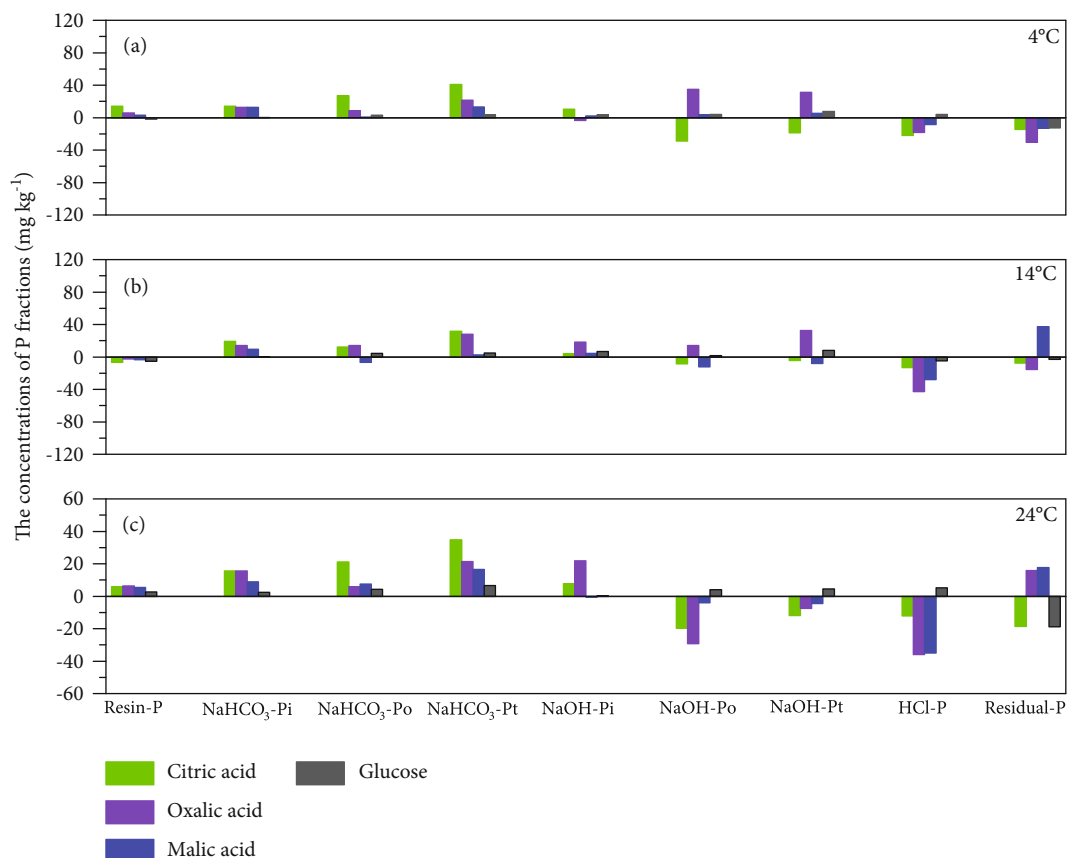
FIGURE 1: The variations of P fraction after addition of low molecular weight organic acids (oxalic acid, citric acid, and malic acid) and glucose compared with deionized water at different temperatures ((a) 4°C; (b) 14°C; (c) 24°C).
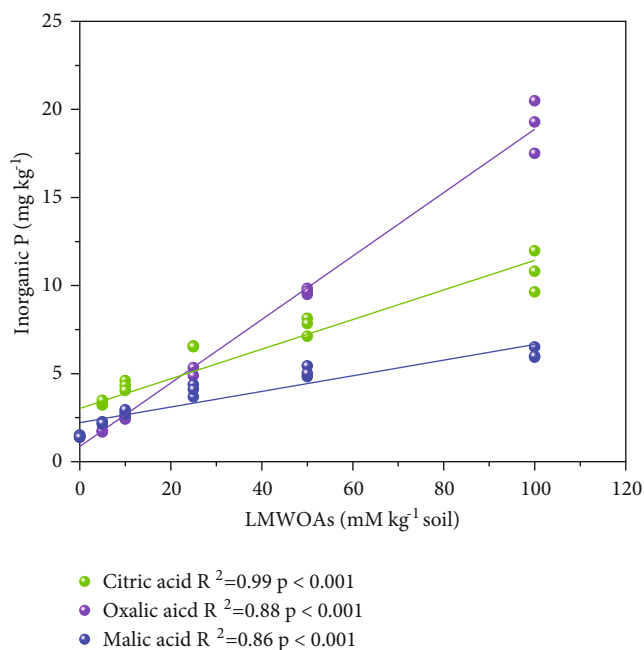

FIGURE 2: The release of inorganic P after the addition of different concentrations of low molecular weight organic acids (oxalic acid, citric acid, and malic acid) for one hour.

bound to Fe and Al, while the P mobilized by oxalic acid and citric acid mainly comes from HCl, i.e., P bound to Ca.

4. Discussion

Consistent with our first hypothesis, we found that LMWOAs had little effect on the fractions of organic P at lower temperatures when the role of microorganisms was ignored in our study (Figure 1(a)) and significantly changed the P fraction at higher temperatures (Figure 1(c)). Temperature played an important role in the change of P fraction by microorganisms. As we all know, LMWOAs can provide energy for microorganisms and affect bioavailable P through the mineralization of organic P. The results showed that the concentrations of organic P decreased with the increasing temperature in the process of LMWOAs changing P fraction, and $NaHCO_3$-Po and NaOH-Po decreased the most at 24°C than those at the other two temperatures. The main reason may be that LMWOAs promoted the activity of soil microorganisms at higher temperatures, and a part of organic P could be transformed into available inorganic P by microbial mineralization, leading to the increase of the fraction of inorganic P [23]. The transformation from organic P into inorganic P by mineralization was the main reason for the increasing concentrations of resin-P and $NaHCO_3$-Pi [24, 25], which was consistent with the transformation mechanism of P fractions in this study. Compared

(a)   (b)
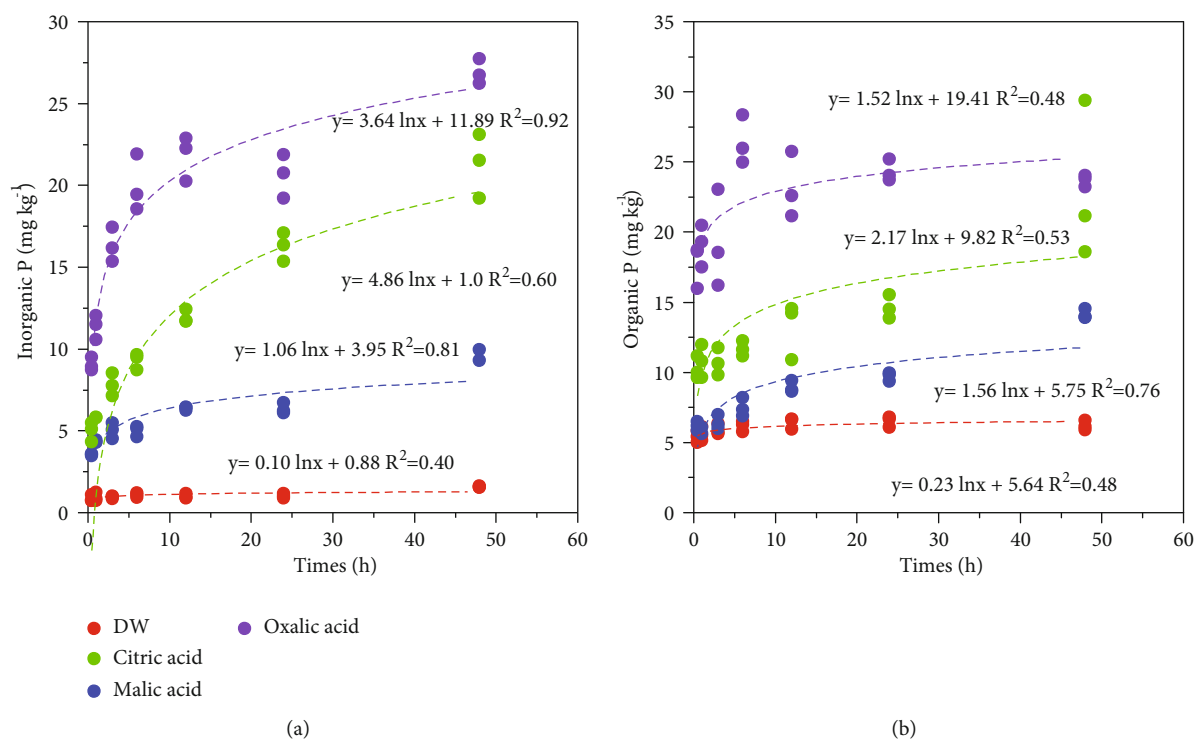
FIGURE 3: The kinetics of inorganic P (Pi, a) and organic P (Po, b) release by water, oxalic acid, citric acid, and malic acid at 100 mmol kg^{-1} soil from the acidic forest soils. DW: deionized water.
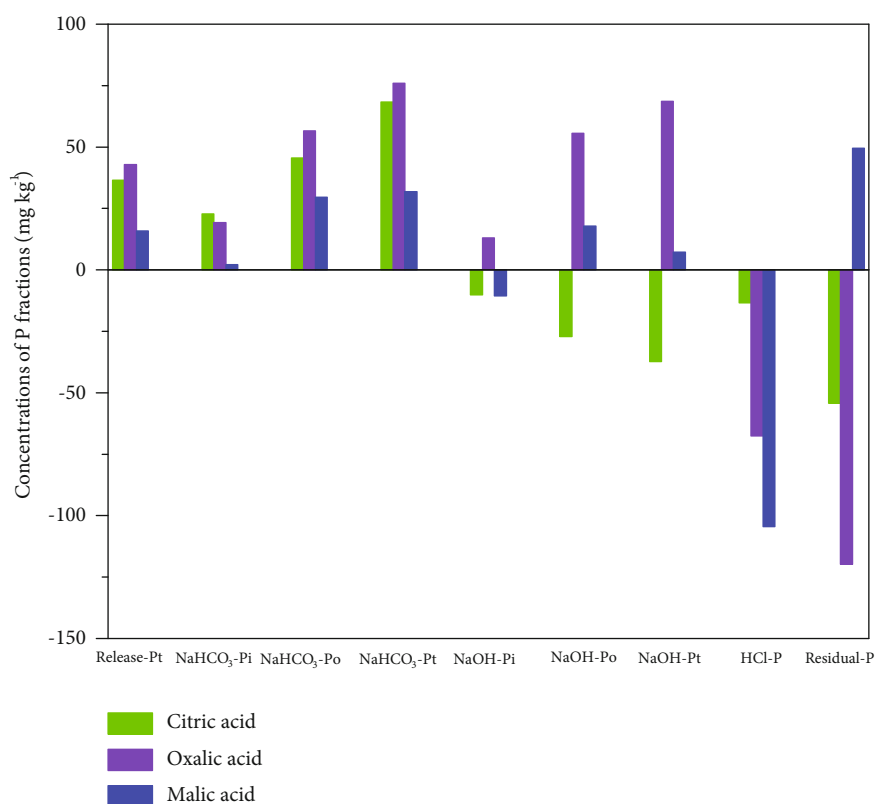

FIGURE 4: The variations of P fraction after addition of low molecular weight organic acids (oxalic acid, citric acid, and malic acid) compared with deionized water after 2880 minutes.

with the other two acids, malic acid had a weaker effect on the P fraction at the same temperature. Meanwhile, although glucose also could be used as a microbial carbon source, the varied mechanism of P fraction by glucose at three temperatures was consistent. Glucose did not significantly change the concentration of organic P in soil compared with citric and oxalic acids, meaning that oxalic and citric acids were more easily used by microorganisms than malic acid and glucose to affect the release of organic P [26].

Temperature affects the release of organic P not only through microorganisms. Our results showed that different kinds of LMWOAs had different effects on P fractions at lower temperatures through their own (Table 1; Figures 1(a) and 1(b)). For instance, the mechanism of oxalic acid was different from that of citric acid in our study. We found that oxalic acid reduced HCl-P (Ca-P) and residual P at 4°C and 14°C, while citric acid mainly reduced NaOH-P (Fe/Al-P) at two temperatures to increase the concentrations of Bio-P. Consequently, these results indicated that the effects of oxalic and citric acids on the change of P fraction were different in alkaline and acidic soils, respectively. Although some studies have shown that the dissolution mechanism of organic P is similar to that of inorganic P [25, 27], Wei et al. indicated that a concentration of 10 mM citric acid significantly increased the concentration of organic P in forest soils in subtropical and tropical Australia (Table 1), but did not show the effective mobilization of inorganic P [10]. By contrast, LMWOAs seem to be effective in the release of Po as Pi in our study. Different starting substrates of organic P may be the main reason for this phenomenon (Table 1) [24], and the change of temperature would affect the adsorption/desorption and precipitation/dissolution of P.

Consistent with our second hypothesis, LMWOAs would increase the rate of the kinetics of both Pi and Po release, which was supported by the higher Pi and Po kinetic parameters in LMWOAs than water in our study (Figures 2 and 3). Many studies have demonstrated the potential of LMWOAs to dissolve mineral P in soil [8, 9, 28], and LMWOAs significantly changed the P fractions and improved the Bio-P in acidic, neutral, and alkaline soils. The solubility of soil P was mainly controlled by adsorption/desorption and precipitation/dissolution [2], which were affected by soil physicochemical properties (such as soil pH) and biological activities (such as biological fixation, secretions of LMWOAs, and phosphatase) [4, 29–31]. Citric, malic, and oxalic acids could be obtained from plant roots and soil microorganisms to cope with P deficiency [9, 31, 32]. LMWOAs in the soil were the important substances to improve the soluble of P and the concentrations of Bio-P in soil.

The different types and concentrations of LMWOAs dominated the P released through carboxyl groups in most studies, and the different types of LMWOAs had different mobilizing abilities of P in soil (Table 1). LMWOAs may influence the solubility of P in soil through direct ligand exchange with phosphate, and ligand promotes mineral dissolution [10, 28, 32, 33]. Hence, the mobilization ability of LMWOAs was followed by ternary carboxylic acid > binary

carboxylic acid > monocarboxylic acid. Ternary carboxylic acids (such as citric acid) were generally more capable of dissolving inorganic P than binary carboxylic acids (such as oxalic acid) and monocarboxylic acids [33, 34]. Although the carboxyl number of oxalic acid (dicarboxylic acid) was less than that of citric acid (ternary carboxylic acid), the existing research showed that oxalic acid is stronger than citric acid in the process of P mobilization due to the buffering capacity of the forest soils. The mobilization ability of oxalic acid was also stronger than citric and malic acids in our study when the concentration of oxalic acid was enough high (Figures 2 and 3). Hence, the number of carboxyl groups in soil solution was the decisive factor to determine the transformation of P fractions. Consequently, the higher concentration of LMWOAs means that more carboxyl groups can be exchanged by metal cations. The concentrations of dissolved inorganic P fractions by LMWOAs usually increased with the increasing concentration of LMWOAs. However, there may be a critical threshold for the concentration of LMWOAs required for the solution of adsorbed and precipitated P [26, 35]. In our study, citric acid could mobilize more P at a lower concentration than oxalic acid. However, when the concentration of LMWOAs was more than 25 mM, oxalic acid could mobilize more Ca-P, while citric acid had a weak mobilize ability to Ca-P compared with oxalic acid. As in other studies, the mobilization of Ca-P by oxalic acid was more significant in alkaline soils or high apatite soils [35]. Therefore, the results showed the order of P mobilization was oxalic acid > citric acid > malic acid in our study when the concentration of LMWOAs was more than 25 mM. This result also explained why citric acid had a significant effect on Bio-P in the rhizosphere soil in Mt. Gongga, but oxalic acid was not significant in acidic soil [20]. In all, both the concentrations and types of LMWOAs affect the concentrations and transformation of inorganic P fractions.

As the mobilization capacity of LMWOAs increased with time, more stable P was mobilized to liable P fractions. Our results showed that LMWOAs tend to mobilize stable P fractions to liable P fractions (Figure 4). The concentrations of released Pi and Po from stable P fractions in soil increase rapidly during the first 5 to 240 min of the kinetic study and then plateaued as an apparent equilibrium was reached. This two-phase pattern of initially rapid P release followed by slower release was reported by other reports [36–38] and was attributed to a combination of dissolution and desorption process. In this study, the fraction of $NaHCO_3$-Pi tended to increase after releasing Pi into the soil solution with the addition of LMWOAs. There was a fast first and slow reaction process for the release of Bio-P by LMWOAs in nonlime soil [24, 27]. Consequently, the Bio-P in the soil was also released rapidly within one hour after LMWOAs were added to the soil, and then the release rate gradually slowed down in our study (Figure 2).

LMWOAs could make stable P fractions (Fe/Al-P and Ca-P) transformed to liable P ($NaHCO_3$-P and resin-P). Our results showed that the pH in the solution increases gradually with the increase of time and P release, which means that the H^+ in the solution decreases (Figure S2).

TABLE 1: The variations of P fractions induced by organic acids compared with other reports.

Soil type	Concentrations (mM)	Area	Organic acids	Soluble-Pi	Soluble-Po	NaHCO$_3$-Pi	NaHCO$_3$-Po	NaOH-Pi	NaOH-Po	HCl-P	Reference
Acid soil	100	Southwest China	Citric acid	↑	↑	↑	↑	↓	↓	↓	This study
			Oxalic acid	↑	↑	↑	↑	↑	↑	↓	
			Malic acid	↑	↑	↑	↑	↓	↑	↓	
Acid soil			Citric acid	ns	ns	—	↓	↓	—	—	
			Oxalic acid	ns	ns	—	—	—	—	—	
			Malic acid	ns	ns	—	—	—	—	—	
Neutral soil	10	Northeast China	Citric acid	ns	ns	—	↓	—	—	—	[24]
			Oxalic acid	ns	ns	—	—	—	—	—	
			Malic acid	ns	ns	—	—	—	—	—	
Alkaline soil			Citric acid	ns	ns	—	—	—	—	—	
			Oxalic acid	ns	ns	—	—	—	—	—	
			Malic acid	ns	ns	—	—	—	—	—	
Acid soil	10	Australia	Citric acid	—	↑	ns	ns	ns	ns	ns	[10]
			Oxalic acid	—	↑	ns	ns	ns	ns	ns	
			Malic acid	—	—	ns	ns	ns	ns	ns	
Alkaline soil	100	East China	Citric acid	↑	ns	↓	↓	↓	—	↓	[41]
			Oxalic acid	↑	ns	—	↑	↓	—	↓	
			Malic acid	↑	ns	↓	↑	—	—	↓	
Acid soil	1	South China	Citric acid	↑	ns	ns	ns	ns	ns	ns	[5]
			Oxalic acid	↑	↑	ns	ns	ns	ns	ns	
			Malic acid	—	—	ns	ns	ns	ns	ns	

Note: ns means no data; ↑ or ↓ means increase or decrease relative to control; - means no significant variation.

The reason was that H$^+$ in LMWOAs occupied the adsorption sites of the original Fe/Al or Ca by reacting with Fe/Al or Ca in the soil, which complexes with COOH$^-$ or chelates, thus, realizing the mineral-bound P fraction and increasing concentration of Bio-P. When pH = 4.0, citric acid can form stable compounds with Fe^{3+}, which promotes the release of P from Fe-P. When pH is less than 4.0, LMWOAs can mobilize Ca-P effectively. In this study, the pH after the LMWOAs was added is less than or equal to 4.0. Therefore, the soil in the Gongga Mountain could effectively liberate both Fe-P and Ca-P in the soil after 10 mM LMWOAs were added. The significant variations of pH value in oxalic acid during the initial rapid phase were further to confirm that the sources of Pi and Po in the solution were HCl-P (Ca-P) or NaOH-Pi (Fe/Al-Pi) by the end of the kinetic experiment, indicating the dissolution of mineral-bound P compounds occurred when the soil was treated with LMWOAs.

Although LMWOAs could make stable P fractions (Fe/Al-P and Ca-P) transformed to liable P (NaHCO$_3$-P and resin-P), we found that this rule is not completely consistent with the transformation process. The possible reason was that although LMWOAs can liberate part of the stable P, there was also adsorption on the particle surface, which made part of the P fixed again because of the high soil organic matter [24, 39]. In addition, we found that the concentration of resin-P increased significantly after LMWOAs were added, and resin-P was the most easily absorbed and utilized by plants in the soil. This also proved that LMWOAs secreted by roots increase Bio-P according to their growth requirements [31, 40]. Therefore, the production of LMWOAs by plants in the rhizosphere was an important mechanism to improve Bio-P in soil, mainly because LMWOAs significantly increase the concentration of resin-P and then increase the concentration of Bio-P absorbed by plants. In conclusion, the concentration of Bio-P in the soil was increased due to partial chelation and dissolution of phosphate in the main Fe/Al binding. The release of Bio-P by LMWOAs in acid soil was mainly through the reduction and dissolution of Fe/Al and Ca, or the subsequent release of P bound or enclosed in the Fe/Al and Ca [5, 39].

5. Conclusion

The addition of low molecular weight organic acids increased both the concentration and rate of the kinetics of inorganic P and organic P release in acidic forest soils. Low molecular weight organic acids were more easily used by microorganisms than glucose to affect the release of P through the mineralization of more organic P. However, removing the effects of microorganisms, the Po released upon treatment with low molecular weight organic acids represented half of the total P released, which promoted the understanding of the mechanisms of organic P release in the presence of low molecular weight organic acids, while the enhanced inorganic P release was likely due to the accelerated desorption and dissolution process. Fractions of inorganic P and organic P were greater when soils were treated with oxalic acid than those with the other organic acids when the concentrations of low molecular weight organic acids were greater than 25 mM. Future research should highlight the sources and consumption of low molecular weight organic acids effects on the availability and transformation of soil P to better understand the biogeochemical cycling of P and the underlying mechanisms in different ecosystems.

Data Availability

We provide our data in the Supplementary Information files to support the conclusions of our study.

Conflicts of Interest

All authors in this manuscript have directly participated in the planning, execution, and/or data analysis of this study, and we have no conflicts of interest in this work. We declare that the manuscript was not published or under review elsewhere. And we also declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Acknowledgments

Supplementary Materials

Figure S1: the concentrations of P fractions after addition with deionized water (ck), the organic acids, and glucose solution in acidic forest soils. Figure S2: the variations of suspensions pH after addition with deionized water (ck) and the organic acids with in acidic forest soils. (Supplementary Materials)

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