Phosphorus release from the soils in the Yellow River Delta: dynamic factors and implications for eco-restoration

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ABSTRACT

Root-released organic acids are reported to increase phosphorus (P) availability in the soil. In this study a dynamic study of P release from soil was conducted to get more exact information of the organic acids role in P availability in soil. The results show that organic acids in different concentrations significantly affected P release. In a concentration of 10 mmol/L, no significant differences can be observed among citric acid, malic acid and acetic acid in terms of their effect on the release of soil P. However, when the concentration reduced to 1 mmol/L, both the total release amount and the maximum release amount of soil P significantly declined, and the decline degree were citric acid < malic acid < oxalic acid and acetic acid. When the concentration of organic acids was 0.1 mmol/L no P has been leached in the leaching solution of any of the four types of organic acids. The parabolic diffusion equation showed that organic acids can improve the migration rate of P in the soil, with the following order of citric acid > malic acid > acetic acid > oxalic acid. The higher the concentration of the organic acids was, the higher the migration rate of P would be. Given that the P needed by plants basically migrates by means of diffusion, under the condition of P deficiency of plants, improving the secretion amount of organic acids can effectively increase the biological utilization rate of P.

Keywords: macronutrient; dynamic leaching; fertilizer; plant-available

Phosphorus is a key nutrient element for the growth and development of crops (Gerke 1994, Lan et al. 1995, Wang et al. 2011). The phosphorus needed by crops is mainly supplied from the soil. However, the phosphorus in the soil can easily be fixed, and generally, the seasonal utilization rate of phosphorus fertilizer by crops is only 10~25% (Liu et al. 2012, Sun et al. 2012, Xu et al. 2012). Excessive application of phosphorus fertilizer will not only result in waste of existing phosphorus resources, but also may easily cause environmental problems like eutrophication of water bodies (Cheng et al. 2012, Bai et al. 2013, Chintala et al. 2013, Wang and Zheng 2013). The low molecular weight organic acids of the soil are thought to promote transformation of phosphorus (Jones 1998, Ding et al. 2011, Xu et al. 2013). It is held by many researchers that organic acids can exert a positive effect on the release and availability of phosphorus in the soil. For example, Fox and Comerford (1990) in his study found that organic acids could increase the phosphorus in soil solution by 10~1000 times. Qu et al. (1994) added citric acid, tartaric acid and oxalic acid of different concentrations into soil and found that the content

of available phosphorus increased. However, there are also researchers who believe that organic acids exert an inhibitory effect or no effect on the availability of phosphorus. For example, Iyamuremye and Dick (1996) found that only citric acid showed a significant effect. Therefore, the activation effect of organic acids needs to be further verified.

However, there are some drawbacks with the short-term extraction experiment. The present study employed the soil column leaching method to better promote the studies on the process and degrees of soil phosphorus release and to reflect the changes of soil phosphorus. In this study, the dynamic process of the activation of soil phosphorus by organic acids under the continuous leaching condition was studied using the soil column simulation experiment, and the effects of various organic acids in different concentrations on phosphorus activation were also studied.

MATERIAL AND METHODS

Experimental design. The surface soil (0~2 cm) collected from the Yellow River Delta in Dongying, Shandong province, China. This type of soil is alluvial loess parent material, which mainly consists of silts, and the plants growing on it are mainly saline-alkaline tolerant *Suaeda salsa* and *Tamarix chinensis*. The specific physical and chemical properties of the soil are listed in Table 1.

In the leaching experiment an organic glass tube (7 cm in length, 3 cm in inner diameter) was used, with two pieces of qualitative filter paper placed at the bottom. A layer of quartz sand (1.5 cm in thickness) was placed on the paper, and then covered by another filter paper. After that, three layers of soil (45 g in total) were added into the tube to form a soil column with a length of about 4 cm, and each layer was compacted to ensure a soil bulk density of around 1.5 g/cm^3. A piece of filter paper was place on the soil column, followed

by a layer of quartz sand (1.5 cm in thickness) that was soaked by salpeter solution.

Citric acid, malic acid, oxalic acid and acetic acid were prepared in a concentration of 10, 1 and 0.1 mmol/L, respectively. The leaching solution was then flowed out at a rate of 0.4 mL/min from the top and collected by an automatic collector. The concentration of phosphorus in the leaching solution was determined by molybdenum method (Murphy and Riley 1962).

Data processing. The parabolic diffusion equation was employed for the fitting of the experimental results:

$$Q_t = Q_e + Rt^{1/2}$$

Where: Q_t – release amount of phosphorus within time *t*; Q_e – release amount of phosphorus when reaching balance; *R* – diffusion rate constant of phosphorus.

The significance test of processing differences was conducted with the one-way ANOVA method of SPSS 17.0, showing a significance level of *P* < 0.05.

RESULTS AND DISCUSSION

The dynamics of soil phosphorus leaching by different types of low molecular weight organic acids. As shown in Table 2, at the beginning of leaching, none of the acids could leach out the soil phosphorus, which might be explained by the adsorption of these four organic acids by the soil. Xu et al. (2007) found that no aluminum was leached out at the beginning of leaching due to the adsorption of salicylic acid by the soil. When the adsorption became saturated, the organic acids manifested a strong facilitation for the migration of aluminum. For citric acid, the soil phosphorus began to be leached out when the volume of the leaching solution reached 310 mL (Table 2). The leached phosphorus increased rapidly to its maximum level (8.4 mg/kg). The leached phosphorus

Table 1. Characteristics of the soil samples

Soil	pH	Clay	Silt	Sand	TOC	TP	Fe-P	Al-P	Ca-P
		(%)			(mg/kg)		(%)		
Fluvo-aquic	8.1	4.7	83.5	11.8	6710	748	2.5	3.8	74.7

TOC – total organic carbon; TP – total phosphorus; Fe-P – mainly Fe bounded phosphorus; Al-P – mainly Al bounded phosphorus; Ca-P – mainly Ca bounded phosphorus

Table 2. The effects of four organic acids on the soil phosphorus (P) release with soft leaching

Acid	V_{min} (mL)	P_{maxi} (mg/kg)	P/T_{maxi} (%)	$P_{cumulative}$ (mg/kg)	$P/T_{cumulative}$ (%)
Citric	310	8.4	1.1	469.1	62.7
Malic	430	5.4	0.7	507.8	67.9
Oxalic	1030	4.5	0.6	267.5	35.8
Acetic	970	2.7	0.36	445.2	60.0

V_{min} – least organic acid for P release; P_{maxi}, P/T_{maxi} – maximum P and rate of total P released at leaching experiment; $P_{cumulative}$, $P/T_{cumulative}$ – cumulative P and cumulative rate of total P released at leaching experiment

began to decline when it reached 2710 mL, and the concentration of phosphorus became 0 at the point of 3550 mL. For malic acid, the starting leaching volume was 430 mL and then decreased when the volume was above 4150 mL. For oxalic acid, the soil phosphorus began to be leached out when the leaching volume reached 1030 mL. When the leaching volume was between 1030 and 3100 mL, the amount of phosphorus leached was maintained at a relatively low level, which might be explained by the fact that the oxalic acid is more easily adsorbed by the soil. When the leaching volume reached 3100 mL, the amount of phosphorus leached began to gradually increase to its peak (4.5 mg/kg) and then rapidly decreased to 0 after the point of 3550 mL. Affected by acetic acid, the released amount of phosphorus also showed a trend of increasing first and decreasing then; however, its maximum released amount of phosphorus (2.7 mg/kg) was lower than that of citric acid, malic acid and oxalic acid. In addition, the activation of soil phosphorus by acetic acid is a stable and slow process. After the leaching volume reached 12 000 mL, there was still phosphorus being leached out, but the concentration was already very low. The following order could be observed in terms of the maximum release amount of phosphorus: citric acid > malic acid > oxalic acid > acetic acid. For the accumulated release amount of phosphorus, the order was malic acid > citric acid > acetic acid > oxalic acid.

The dynamics of soil phosphorus leaching by low molecular weight organic acids in different concentrations. The leaching curves of phosphorus when citric acid and malic acid in different concentrations were used to leach the soil column. When oxalic acid and acetic acid with a concentration of 1 mmol/L were used to leach the soil, before the point of 12 000 mL the total amount of phosphorus leached was 0. For the citric acid and malic acid with a concentration of 0.1 mmol/L, before the point of 6000 mL the total amount of phosphorus leached was 0. The total amounts of phosphorus leached by citric acid and malic acid in a concentration of 1 mmol/L were 129.7 and 17.3 mg/kg, respectively (Table 3). The total amounts of phosphorus leached by citric acid and malic acid in a concentration of 10 mmol/L were, respectively, 3.5 and 32.6 times of the amounts leached when citric acid and malic acid were in a concentration of 1 mmol/L. Meanwhile, the start point and peak of phosphorus leaching

Table 3. The effects of different concentration of organic acids on the soil phosphorus (P) release with soft leaching

Acid	Concentration (mmol)	V_{min} (mL)	P_{maxi} (mg/kg)	P/T_{maxi} (%)	$P_{cumulative}$ (mg/kg)	$P/T_{cumulative}$ (%)
Citric	10	310	8.4	1.1	469.1	62.7
	1	1990	0.93	0.1	129.7	17.3
Malic	10	430	5.4	0.7	507.8	67.9
	1	2640	0.42	0.06	17.3	2.3

V_{min} – least organic acid for P release; P_{maxi}, P/T_{maxi} – maximum P and rate of total P released at leaching experiment; $P_{cumulative}$, $P/T_{cumulative}$ – cumulative P and cumulative rate of total P released at leaching experiment

were also affected by the concentrations of citric acid and malic acid. For citric acid and malic acid, when their concentrations declined from 10 to 1 mmol/L, the start point of phosphorus leaching was also delayed correspondingly, indicating that the lower the initial concentration of the low molecular weight organic acids, the longer the time it would take for the adsorption by the soil to become saturated.

Kinetic fitting of phosphorus release during soil leaching by low molecular weight organic acids. As known from Table 4, when the parabolic diffusion equation was employed for the fitting of the dynamic leaching curve of soil phosphorus release, a significant level was achieved in all cases ($P < 0.05$). The letter R in the parabolic diffusion equation represents the relative diffusion coefficient of phosphorus. Lu et al. (1998) reported that citric acid and oxalic acid could obviously improve the diffusion coefficient of phosphorus in the soil. Feng (2012) found that adding low molecular weight organic acids could improve the relative diffusion coefficient of phosphorus in the soil. Oxalic acid was found to form precipitate under the effect of calcium and thus lose its activation, which further affected the diffusion coefficient of phosphorus. In our experiment, the relative diffusion coefficients of phosphorus showed the following sequence: citric acid > malic acid > acetic acid. The diffusion coefficient of phosphorus was affected in the case of oxalic acid which was susceptible to form calcium oxalate precipitate with calcium (Table 4), which was consistent with the characteristics of the phosphorus release curve of the soil treated with oxalic acid. Meanwhile, the concentration of low molecular weight organic acids also significantly affected the relative diffusion coefficient of phosphorus, owing to the

fact that lower concentration of organic acids decreased concentration of phosphorus in the soil and thereby the decreased diffusion rate of phosphorus.

In conclusions, the release of soil phosphorus is a dynamic process under the effect of low molecular weight organic acids. Organic acids in different concentrations also significantly affected phosphorus release. When the concentration reduced to 1 mmol/L, both the total and maximum release amount of soil phosphorus significantly declined, and the order was citric acid < malic acid < oxalic acid and acetic acid. The parabolic diffusion equation showed that organic acids can improve the migration rate of phosphorus in the soil.

Table 4. The rate constants of diffusion (R) fitting by parabolic diffusion equation

Acid	Concentration (mmol)	R
Citric	10	8.02
	1	1.32
Malic	10	7.62
	1	0.33
Oxalic	10	3.95
Acetic	10	4.68

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