Annals of Plant and Soil Research 24(2):331-337 (2022)
https://doi.org/10.47815/apsr.2022.10171

Impact of low molecular weight organic acids on soil phosphorus release in Inceptisol and Alfisol

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Received: October, 2021; Revised accepted: November, 2021

ABSTRACT

Secretion of LMWOAs by plants is one of the important mechanisms to make fixed soil phosphorus (P) bioavailable to plant. But the effectiveness of different LMWOAs in enhancing the soil available P varies significantly with the pH of the soil. Therefore the present study was undertaken at ICAR-IARI, New Delhi during 2018-19 to assess the effect of oxalic and citric acid in increasing the soil available phosphorus in two soil orders i.e. Inceptisol and Alfisol, during different intervals of incubation (i.e. 0, 15, 30, 45, 60 and 90 days). The results showed that there was an increasing trend in soil available P release pattern under both the LMWOAs treatments up to 60 and 45 days of incubation in Inceptisol and Alfisol, respectively and after reaching this threshold value, it attained declining trend. Citric acid was found to be most effective than oxalic acid in mobilizing soil phosphorus in the acidic soil (Alfisol), whereas oxalic acid was superior in neutral soil (Inceptisol). With increasing rates of both LMWOAs, the soil available P increased significantly. Thus, the application of LMWOAs will reduce the excess application of phosphorus and its build-up in soils and causing eutrophication of water bodies.

Key words: Low molecular weight organic acids, oxalic acid, citric acid, phosphorus release

INTRODUCTION

Phosphorus is vital nutrient for plant growth and development and plays a key role in photosynthesis, energy transfer, sugars and starches transformation and nutrient movement within the plant system. It is also involved in transfer of genetic characteristics of plants. However, phosphorus deficiency is a universal constraint for the crop production (Bhattacharyya *et al.* 2015). In India, about 98% of soils were found be low to medium in phosphorus availability status (Dey*et al.* 2017). Because most of the applied P fertilizers gets fixed (non-bioavailable form) with Al and Fe in acidic and Ca in calcareous/normal soils, decreasing its use efficiency (Chang *et al.* 2014). Due to which, farmers need to apply excess P fertilizers to supply adequate P nutrient to the crop, which leads to excess soil P build-up in agricultural soils and its runoff leading to eutrophication of water resources (Chang *et al.* 2014). To overcome P deficiency of the soil, there are various mechanisms adopted by the crop and exudation of LMWOAs (Low molecular weight organic acid) is one of the important mechanisms among them (Oral and Uygur 2018). Low-molecular-weight organic-acids are carbon compound with at least one carboxyl group in their structure eg. oxalic, citric, succinic, tartaric, acetic, maleic acids etc. (Chen *et al.* 2018). There are number of evidences for soil solution P enhancement by application of LMWOAs (Nwoke*et al.* 2008) and P enhancement occurs mainly by three major mechanisms i.e. acidification, chelation and exchange reactions (Adeleke*et al.* 2012). Citrate was most effective in mobilizing soil phosphorus through its chelation with Al in acidic soils, whereas oxalate dominates in neutral or calcareous soils. (Clarholm*et al.* 2015; Menezes-Blackburn *et al.* 2016). So the application LMWOAs results in significant increase in soil solution P concentration thereby, reduces excess P fertilizer usage. Till now, there are limited number of works has been done by researchers to study the P release pattern by LMWOAs application in different types of soil under incubation. So, the present research aimed to know the impact of LMWOAs on releasing the soil bioavailable phosphorus in Inceptisol (neutral reaction) and Alfisol (acidic reaction) during different intervals of incubation periods.

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MATERIALS AND METHODS

A laboratory incubation experiment was conducted at ICAR-IARI, New Delhi during 2018-19 using Inceptisol (Alluvial soil) and Alfisol (Red soil). For this purpose, Inceptisol was collected from research farm of Indian Agricultural Research Institute (IARI), New Delhi and Alfisol from Konkan region of Maharashtra. The collected soils were air dried in shade under room temperature then it was ground and passed through 2-mm sieve (<2-mm fraction). The pH of Inceptisol and Alfisolwas 7.94 and 6.03 respectively. Five gram of Inceptisol and Alfisol were taken separately in 150 mL plastic bottles and phosphorus was applied at the rate of 0 and 10 mg $kg^{-1}$and the low molecular weight organic acids (LMWOAs) were applied @ 0, 5 and 10 mg/kgfor oxalic acid and 0, 10 and 20 mg kg^{-1} for citric acid. Such six sets of treatments with three replications each were kept under incubation study for 0, 15, 30, 45, 60 and 90 days at 25°C and field capacity moisture content was maintained throughout the incubation periods. The incubated soils were analysed for available P at the respective levels of incubation period. The P from soil samples was extracted by Olsen's reagent as an extractant for Inceptisol and Bray's reagent for Alfisol. Phosphorus content in the extracts was estimated using blue color method (Olsen *et al.* 1954 and Bray and Kurtz 1945).

RESULTS AND DISCUSSION

Phosphorus release pattern

The soil P released by different levels of LMWOAs along with phosphorus rates under Inceptisol and Alfisol was best fitted in polynomial equation with higher regression coefficient (R^2 value) ranging from 0.432 to 0.913 and from 0.65 to 0.85 respectively, (Table 1).

Table 1: Polynomial equation on soil available P release

Soil Type	Treatments	Polynomial equation	R^2
Inceptisol (Olsen P)	T_1	$y = -5E\text{-}05x^2 + 0.0144x + 6.2637$	0.9132
	T_2	$y = -0.0002x^2 + 0.0224x + 7.0898$	0.8756
	T_3	$y = -0.0001x^2 + 0.0244x + 7.2497$	0.6723
	T_4	$y = -0.0002x^2 + 0.0302x + 6.9089$	0.8533
	T_5	$y = -0.0001x^2 + 0.0227x + 7.3393$	0.696
	T_6	$y = 0.0002x^2 - 0.0364x + 11.595$	0.9136
	T_7	$y = -0.0002x^2 + 0.025x + 11.773$	0.5885
	T_8	$y = -0.0002x^2 + 0.0279x + 12.494$	0.6033
	T_9	$y = -0.0002x^2 + 0.0254x + 11.609$	0.5567
	T_{10}	$y = -0.0003x^2 + 0.0403x + 12.112$	0.4328
Alfisol (Bray P)	T_1	$y = -0.0005x^2 + 0.0503x + 28.147$	0.719
	T_2	$y = -0.0009x^2 + 0.1035x + 27.972$	0.7401
	T_3	$y = -0.0004x^2 + 0.0458x + 29.543$	0.7633
	T_4	$y = -0.0005x^2 + 0.0586x + 30.078$	0.8448
	T_5	$y = -0.0002x^2 + 0.0268x + 30.981$	0.7317
	T_6	$y = 0.0009x^2 - 0.1142x + 34.263$	0.8553
	T_7	$y = -0.0009x^2 + 0.1036x + 35.324$	0.6526
	T_8	$y = -0.0011x^2 + 0.1103x + 35.744$	0.7004
	T_9	$y = -0.0011x^2 + 0.1286x + 35.914$	0.7596
	T_{10}	$y = -0.0017x^2 + 0.1701x + 35.669$	0.848

T_1 : 0 mg P kg^{-1} (Control), T_2 : 0 mg P kg^{-1} + 5 mg OA kg^{-1} , T_3 : 0 mg P kg^{-1} + 10 mg OA kg^{-1}, T_4 : 0 mg P kg^{-1} + 10 mg CA kg^{-1}, T_5 : 0 mg P kg^{-1} + 20 mg OA kg^{-1}, T_6 : 10 mg P kg^{-1}, T_7 : 10 mg P kg^{-1} + 5 mg OA kg^{-1}, T_8 : 10 mg P kg^{-1} + 10 mg OA kg^{-1}, T_9 : 10 mg P kg^{-1} + 10 mg CA kg^{-1}, T_{10} : 10 mg P kg^{-1} + 20 mg CA kg^{-1}. (P- phosphorus; OA- oxalic acid; CA- citric acid)

Phosphorus release trend of both soils under different treatments which received LMWOAs increased gradually with days of incubation (DAI) up to certain maximum threshold and then it got decreased (Fig 1). But in both the soils, the treatment which received only external application of phosphorus i.e. T6 (10 mg P kg^{-1}) showed decreasing trend in soil available phosphorus release from 0 to 90 days of incubation. This may be attributed to the fixation of applied phosphorus in the soil. During the incubation time from 15 to 60 days with the applied P fertilizer, the extractable P decreased sharply in the acidic soil, while it decreased gradually in the alkaline soil due to fixation of phosphorus with Ca, Fe and Al in the soil (Ara *et al.* 2018). Most of the applied P gets fixed with aluminiumand iron in acidic soil and with calcium in calcareous/normal soils conditions (Chang *et al.* 2014). Application of both the LMWOAs (OA and CA) increased the soil available P concentration under Inceptisol and Alfisol. Similar findings were reported by Clarholm *et al.*(2015) and Menezes-Blackburn *et al.*(2016). The release of soil available P under LMWOAs treatments increased upto 60 and 45 DAI in Inceptisol and Alfisol respectively and after reaching this threshold value, it showed declined trend. Similarly Datta and Agarwal (1998)also reported that the soil treated with LMWOAs initially showed increased P release and later it attained maximum and thereafter the P release was decreased which may be due to exceeding threshold level of P fixation. There is also possibility of inactivation of LMWOAs by microorganism's decomposition in due course of incubation which might have decreased the LMWOAs efficiency in releasing the soil available P (Adeleke*et al.* 2017).

Effect of phosphorus and LMWOAs on soil available P

Under different LMWOAs, the effect of OA (10.07 mg kg^{-1}) was significantly superior over CA (9.66 mg kg^{-1}) in enhancing the soil available P in case of Inceptisol. Whereas, effect of CA (33.38 mg kg^{-1}) was significantly better over OA (32.62 mg kg^{-1}) under Alfisol (Table 2). Oxalic acid was found to be the most effective in enhancing the mobilization of inorganic phosphorus in neutral and calcareous soil due to its strong chelation ability with Ca leading to preferential formation and precipitation of Ca-oxalate. Whereas, citric acid application was most effective in acidic soil due to its higher affinity to Fe and/or Al and leading to formation of Fe- citrate and Al-citrate (Andrade *et al.* 2013). Wang *et al.* (2015) also reported that citric acid was most effective in enhancing P_i release from the NaOH-P_i (Fe/Al-P_i) fraction of the acidic-neutral soils and oxalic acid was most effective in releasing P_i from the HCl-P_i (Ca-P_i) fraction of the calcareous soil.

Table 2: Effect of LMWOAs and applied phosphorus on soil available P (mg kg^{-1})

Treatments	Inceptisol	Alfisol
LMWOAs (a)		
OA	10.07	32.62
CA	9.66	33.38
SEm(±)	0.07	0.09
CD (5%)	0.22	0.26
LMWOAs levels (l) (mg kg^{-1})		
0	8.72	30.41
O5 OA	10.16	33.5
10 OA	11.31	34.03
10CA	9.87	34.69
20CA	10.40	35.05
SEm(±)	0.09	0.11
CD (5%)	0.27	0.32
P levels (p) (mg kg^{-1})		
0	7.57	30.17
10	12.16	35.84
SEm(±)	0.07	0.09
CD (5%)	0.22	0.26
Interaction CD (5%)		
p*a	N/A	N/A
p*l	0.38	0.46
a*l	0.38	0.46
a*l*p	N/A	N/A

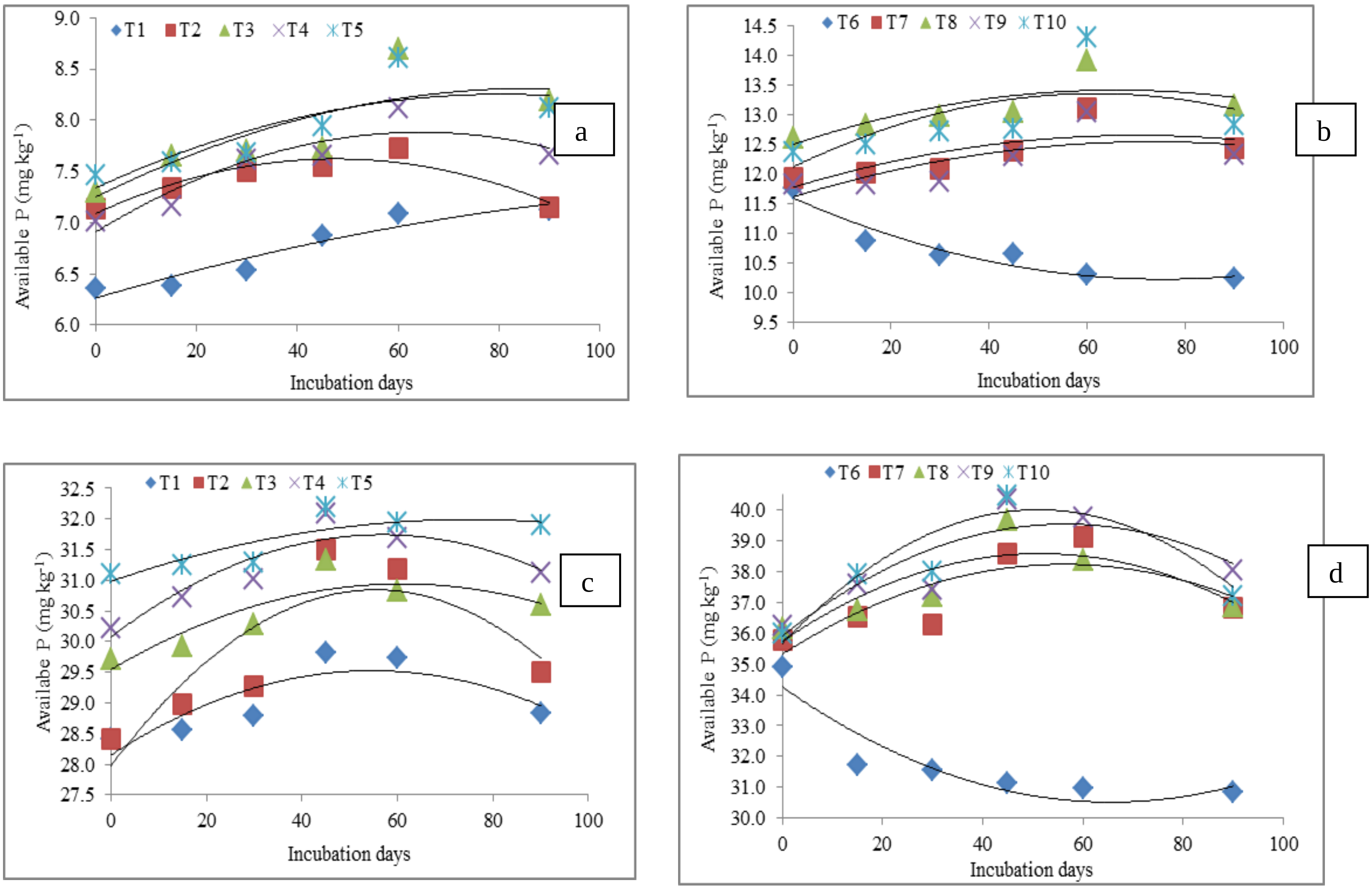

Figure 1. Release pattern of applied and native phosphorus as affected by LMWOAs in Inceptisol (a and b) and Alfisol (c and d)

In case of LMWOAs rates, all the levels of applied both LMWOAs (OA and CA) effectively enhanced the soil available P concentration over control in both the soils. In Inceptisol, the applied oxalic acid @ 10 mg kg^{-1} had significantly higher soil available P over other levels of LMWOAs and recorded 29.7% higher soil available P over control followed by applied 20 mg CA kg^{-1}with 19.2% higher soil available P over control. Whereas applied 20 mg CA kg^{-1} showed 15.2% higher soil available P over control in Alfisol and found significantly superior over all the other levels of applied LMWOAs. In Alfisol, all the applied levels of LMWOAs were found significantly different with each other with respect to available P. LMWOAs increased soil inorganic P mobilization by either releasing inorganic P or decreasing P adsorption (Wei *et al.* 2009). Among different LMWOAs, Oxalic ($C_2H_2O_4$), citric ($C_6H_8O_7$) and malic acids ($C_4H_6O_5$) are most effective in mobilization of soil nutrients (Moradi*et al.* 2012). The mobilization of inorganic P induced by LMWOAs was attributed to the following processes: replacement of phosphate ions on ligand exchange surfaces, chelating Fe, Al compounds in acidic and Ca compound in neutral/calcareous soils, altering pH of the rhizosphere, dissolving P containing soil minerals through shifting chemical their equilibrium status and changing surface characteristics of soil minerals (Chen *et al.* 2008).

With increase in concentration of oxalic and citric acid the available P under both the soil increased (Table 2). It is obvious that higher concentration of LMWOAs will offer higher surface for chelation with Ca, Fe and/or Al and releases bound phosphorus. The efficiency of LMWOAs to detoxify Al and to mobilize soil phosphorus depends on concentration and valency of the carboxyl group of the LMWOAs (Adeleke *et al.* 2017).

Application of phosphorus fertilizer showed increased soil available P under both the soils over control (without P). With application of 10 mg P kg^{-1}, Inceptisol recorded 60.6% higher soil available P over control, it was 18.7% higher soil available P in Alfisol. The water soluble and Olsen P content of the soil increased with application of different P fertilizers (Baharehet *al.* 2010) and a significant linear correlation between soil available P and the rates of P fertilizer application was recorded by Cao *et al.*(2012). Sucunza *et al.* (2018) also reported a significant and linear increase in Bray-P concentration in the soils fertilized with P.

It may be concluded that there was an increasing trend in soil P release pattern with application of oxalic and citric acids up to 60 and 45 days of incubation in Inceptisol and Alfisol, respectively and after reaching this threshold value, it showed declined trend. Applied phosphorus without any LMWOAs showed decreasing trend with days of incubation, which was due to the fixation of phosphorus in the soil. Applied citric acid was found to be most effective in mobilizing soil phosphorus in the acid soil (Alfisol), whereas oxalic acid was superior in neutral soil (Inceptisol). Thus the application of LMWOAs will reduce the excess application of phosphorus and its build-up in soils.

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