Low-molecular-weight Organic Acids As a Phosphorus Fertilizer Alternative for Vegetable Production in Calcareous Soil Regions

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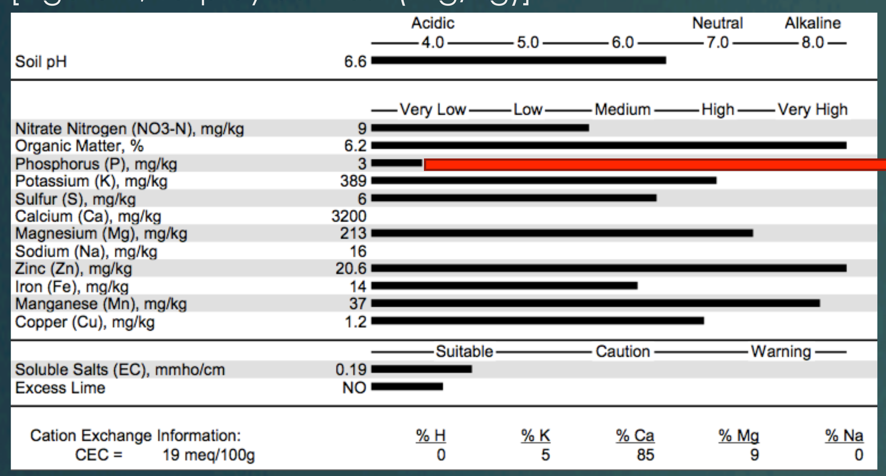
The rising STAR of Texas

Introduction

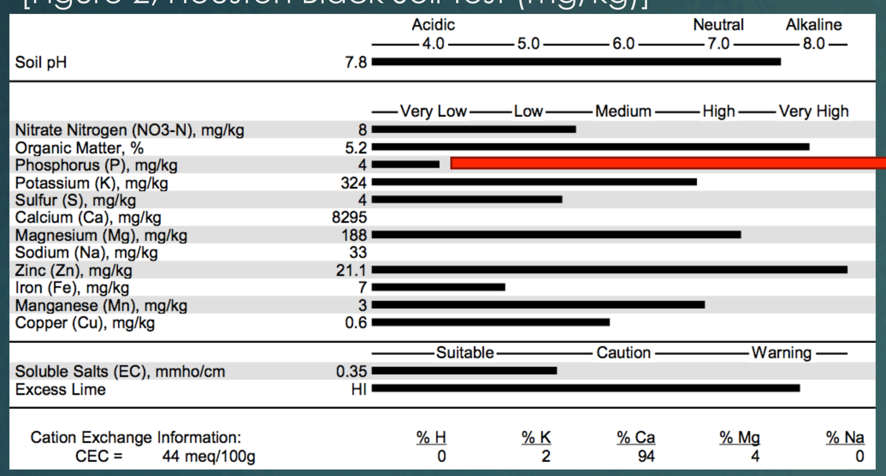
While current applications of phosphorus (P) fertilizer have played a significant role in providing sufficient harvest demands for global food production, industrial agriculture has altered the P cycle by relying on mined phosphate rock (PR) as a non-renewable fertilizer resource (Cordell & White 2011). On the other hand, most soils frequently contain enough native P for crop production (Jones et al. 2011). These soils may also contain low-molecular-weight organic acids (LMWOAs) in the rhizosphere that are used by plants and microorganisms for P-nutrient acquisition (Wang et al. 2008). Even so, high pH and high P fixation rates occur in arid soils with high concentrations of calcium carbonate ($CaCO_3$) parent material (Marschner 2002). The purpose of this study was to mimic LMWOAs commonly found in the soil rhizosphere for vegetable production. By examining their ability to solely solubilize native P from calcareous soils in semi-arid land regions LMWOAs may render a possible alternative for P fertilizer applications in future crop production systems.

[Figure 1, Tarpley Soil Test (mg/kg)]



Very low (P) availability.

[Figure 2, Houston Black Soil Test (mg/kg)]



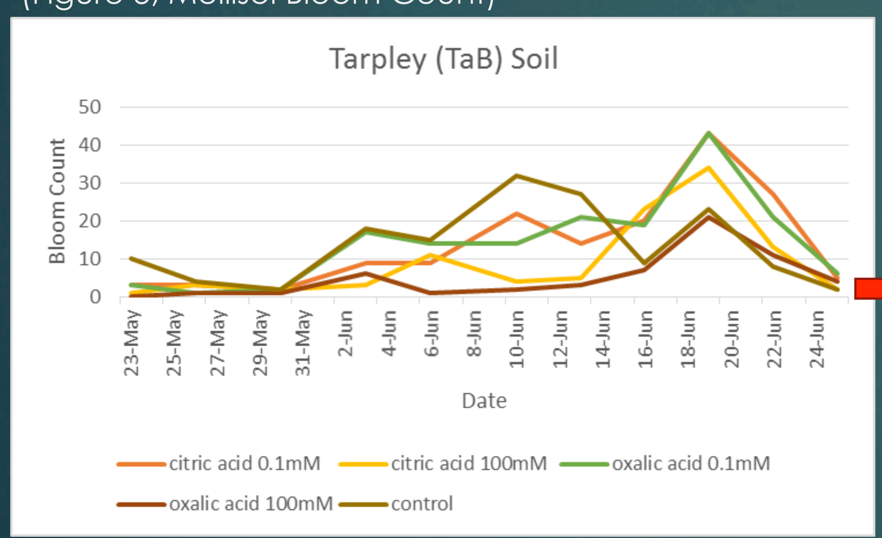
Very low (P) availability.

Objectives

Determine the effects of LMWOA applications as a substitute for conventional P fertilizer applications by:

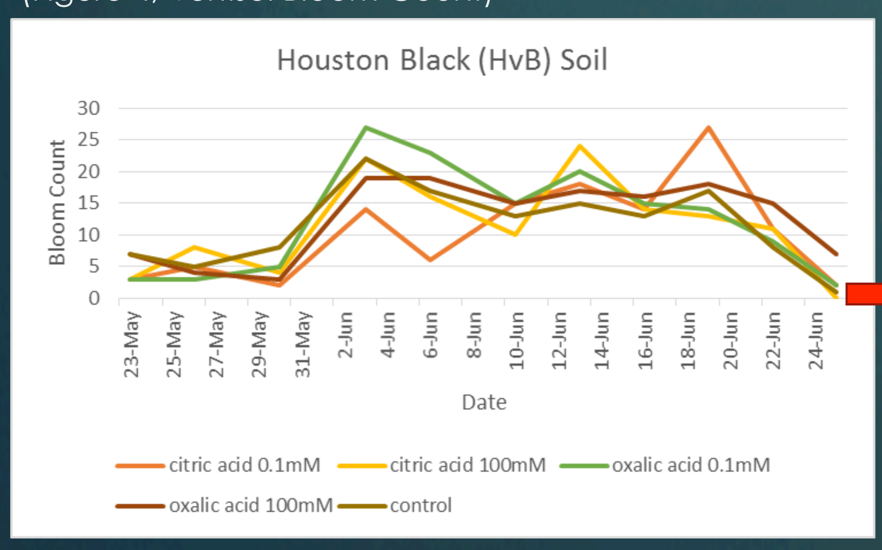
- Comparing total fruit yield (g) and bloom count of *Solanum melongena* grown solely with LMWOA treatment (mM kg) for P release versus TSP fertilizer treatment.
- Investigating significant differences in *S. melongena* production between treatments as measured by P nutrient availability (mg/kg) in each soil.

(Figure 3, Mollisol Bloom Count)



Oxalic acid 0.1mM kg treatment produced most blooms (161 total).

(Figure 4, Vertisol Bloom Count)



Oxalic acid 100 mM kg treatment produced most blooms (140 total).

Materials & Methods

As a highly dependent P nutrient crop, *S. melongena* (eggplant) was used in a pot study within a complete randomized block design using two distinct soil types native to the Central Texas region. In order to determine nutrient availability and appropriate fertilizer applications, soil samples were analyzed prior to the study (Fig. 1 & Fig. 2). Soils included a Houston Black (HvB) series Vertisol and Tarpley (TaB) series Mollisol for vegetable production. Each soil pot was treated individually with molar concentrations of oxalic or citric acid (0.1 mM kg^{-1}, 100 mM kg^{-1}). Controls received the recommended triple superphosphate (TSP) [$Ca(H_2PO_4)_2$] application from soil analysis results. Equal parts of urea (N) [$CO(NH_2)_2$] fertilizer was applied to all soil pots. During the growing period blooms were recorded for each treatment (Fig. 3 & Fig. 4). Fruit was harvested and measured to determine yield based on weight (g). P nutrient availability from soil samples of each pot was measured using a spectrophotometer (mg/kg). Two repeated-measures factorial MANOVAs further determined statistical significance between treatments in each soil for P nutrient availability and fruit production effects over time, p< 0.05.

Results

Fruit harvest totals (g) at the end of nine weeks for Houston Black soil showed citric acid 100 mM kg^{-1} as most effective for yield, while TSP treatment yielded best for Tarpley soil (Fig.5; Fig. 7; Fig. 9). MANOVA results for fruit yield (g) indicate harvest [Wilks' Λ=.323, $F(2,129)$= 135.34, p=.000], harvest*soil class [Wilks' Λ=.555, $F(2, 129)$= 51.80, p=.000], harvest*treatment [Wilks' Λ=.826, $F(8, 258)$= 3.244, p=.002], and harvest*soil class*treatment [Wilks' Λ=.800, $F(8, 258)$= 3.795, p=.000] significantly affected yield over time (Table 1). Soil test totals (mg/kg^{-1}) for treatments revealed that TSP treatment provided most P-nutrient availability for both soils (Fig. 6; Fig. 8; Fig. 10). MANOVA results indicate that soil test [Wilks' Λ=.834, $F(2,129)$= 12.838, p=.000], soil test*soil class [Wilks' Λ=.846, $F(2,129)$= 11.753, p=.000], soil test*treatment [Wilks' Λ=.735, $F(8,258)$= 5.368, p=.000] and interaction between soil test*soil class*treatment [Wilks' Λ=.626, $F(8,258)$= 8.507, p=.000] significantly affected soil test results over time (Table 2).

(Table 1. MANOVA Test, Yield)

Effect	Value	F	Hypothesis df	Error df	Sig.
Harvest	0.323	135.340	2	129	0.000
Harvest x Soil Class	0.555	51.800	2	129	0.000
Harvest x Treatment	0.826	3.244	8	258	0.002
Harvest x Soil Class x Treatment	0.800	3.795	8	258	0.000

(Table 2. MANOVA Test, Soil Test)

Effect	Value	F	Hypothesis df	Error df	Sig.
P-test	0.834	12.838	2	129	0.000
P-test x Soil Class	0.846	11.753	2	129	0.000
P-test x Treatment	0.735	5.368	8	258	0.000
P-test x Soil Class x Treatment	0.626	8.507	8	258	0.000

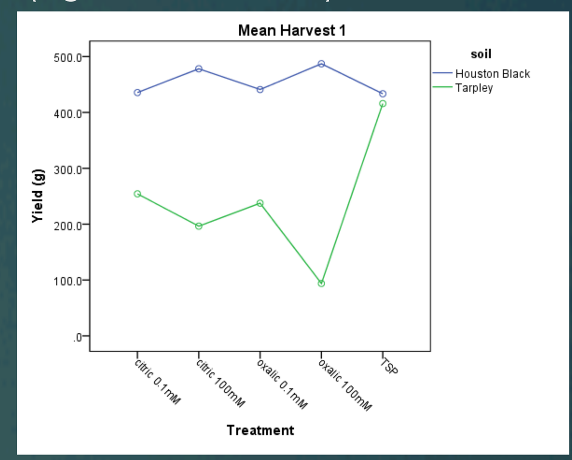
(Table 4. Post-Hoc Test, Yield)

	Measure	Mean Difference	Standard Error	Sig.	Lower Bound	Upper Bound
Houston Black						
citric 0.1 mM	citric 100 mM	-8.471	17.773	0.634	-43.633	26.690
	oxalic 0.1 mM	14.912	17.773	0.403	-20.249	50.073
	oxalic 100 mM	2.252	17.773	0.899	-32.909	37.414
	TSP	17.088	17.773	0.338	-18.073	52.249
citric 100 mM	citric 0.1 mM	8.471	17.773	0.634	-26.690	43.633
	oxalic 0.1 mM	23.383	17.773	0.191	-11.778	58.545
	oxalic 100 mM	10.724	17.773	0.547	-24.437	45.885
	TSP	25.560	17.773	0.153	-9.602	60.721
oxalic 0.1 mM	citric 0.1 mM	-14.912	17.773	0.403	-50.073	20.249
	citric 100 mM	-23.383	17.773	0.191	-58.545	11.778
	oxalic 100 mM	-12.660	17.773	0.478	-47.821	22.502
	TSP	2.176	17.773	0.903	-32.985	37.337
oxalic 100 mM	citric 0.1 mM	-2.252	17.773	0.899	-37.414	32.909
	citric 100 mM	-10.724	17.773	0.547	-45.885	24.437
	oxalic 0.1 mM	12.660	17.773	0.478	-22.502	47.821
	TSP	14.836	17.773	0.405	-20.325	49.997
TSP	citric 0.1 mM	-17.088	17.773	0.338	-52.249	18.073
	citric 100 mM	-25.560	17.773	0.153	-60.721	9.602
	oxalic 0.1 mM	-2.176	17.773	0.903	-37.337	32.985
	oxalic 100 mM	-14.836	17.773	0.405	-49.997	20.325
Tarpley						
citric 0.1 mM	citric 100 mM	36.767	17.773	0.041	1.605	71.928
	oxalic 0.1 mM	2.871	17.773	0.872	-32.290	38.033
	oxalic 100 mM	96.121	17.773	0.000	60.960	131.283
	TSP	-56.738	17.773	0.002	-91.899	-21.577
citric 100 mM	citric 0.1 mM	-36.767	17.773	0.041	-71.928	-1.605
	oxalic 0.1 mM	-33.895	17.773	0.059	-69.056	1.266
	oxalic 100 mM	59.355	17.773	0.001	24.194	94.516
	TSP	-93.505	17.773	0.000	-128.666	-58.344
oxalic 0.1 mM	citric 0.1 mM	-2.871	17.773	0.872	-38.033	32.290
	citric 100 mM	33.895	17.773	0.059	-1.266	69.056
	oxalic 100 mM	93.250	17.773	0.000	58.089	128.411
	TSP	-59.610	17.773	0.001	-94.771	-24.448
oxalic 100 mM	citric 0.1 mM	-96.121	17.773	0.000	-131.283	-60.960
	citric 100 mM	-59.355	17.773	0.001	-94.516	-24.194
	oxalic 0.1 mM	-93.250	17.773	0.000	-128.411	-58.089
	TSP	-152.860	17.773	0.000	-188.021	-117.698
TSP	citric 0.1 mM	56.738	17.773	0.002	21.577	91.899
	citric 100 mM	93.505	17.773	0.000	58.344	128.666
	oxalic 0.1 mM	59.610	17.773	0.001	24.448	94.771
	oxalic 100 mM	152.860	17.773	0.000	117.698	188.021

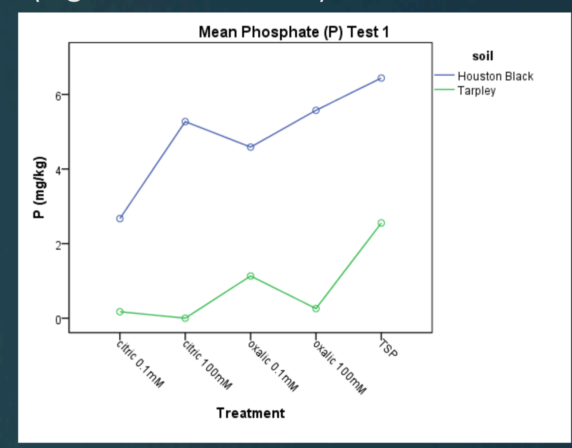
(Table 4. Post-Hoc Test, Soil Test)

	Measure	Mean Difference	Standard Error	Sig.	Lower Bound	Upper Bound
Houston Black						
citric 0.1 mM	citric 100 mM	-0.923	0.318	0.004	-1.553	-0.293
	oxalic 0.1 mM	-0.539	0.318	0.093	-1.169	0.091
	oxalic 100 mM	-1.175	0.318	0.000	-1.805	-0.545
	TSP	-1.838	0.318	0.000	-2.467	-1.208
citric 100 mM	citric 0.1 mM	0.923	0.318	0.004	0.293	1.553
	oxalic 0.1 mM	0.384	0.318	0.230	-0.246	1.014
	oxalic 100 mM	-0.252	0.318	0.431	-0.881	0.378
	TSP	-0.914	0.318	0.005	-1.544	-0.285
oxalic 0.1 mM	citric 0.1 mM	0.539	0.318	0.093	-0.091	1.169
	citric 100 mM	-0.384	0.318	0.230	-1.014	0.246
	oxalic 100 mM	-0.636	0.318	0.048	-1.266	-0.006
	TSP	-1.299	0.318	0.000	-1.928	-0.669
oxalic 100 mM	citric 0.1 mM	1.175	0.318	0.000	0.545	1.805
	citric 100 mM	0.252	0.318	0.431	-0.378	0.881
	oxalic 0.1 mM	0.636	0.318	0.048	0.006	1.266
	TSP	-0.663	0.318	0.039	-1.293	-0.033
TSP	citric 0.1 mM	1.838	0.318	0.000	1.208	2.467
	citric 100 mM	0.914	0.318	0.005	0.285	1.544
	oxalic 0.1 mM	1.299	0.318	0.000	0.669	1.928
	oxalic 100 mM	0.663	0.318	0.039	0.033	1.293
Tarpley						
citric 0.1 mM	citric 100 mM	0.140	0.318	0.661	-0.490	0.770
	oxalic 0.1 mM	-0.447	0.318	0.163	-1.076	0.183
	oxalic 100 mM	-0.127	0.318	0.691	-0.757	0.503
	TSP	-3.284	0.318	0.000	-3.914	-2.654
citric 100 mM	citric 0.1 mM	-0.140	0.318	0.661	-0.770	0.490
	oxalic 0.1 mM	-0.587	0.318	0.068	-1.216	0.043
	oxalic 100 mM	-0.267	0.318	0.404	-0.897	0.363
	TSP	-3.424	0.318	0.000	-4.054	-2.794
oxalic 0.1 mM	citric 0.1 mM	0.447	0.318	0.163	-0.183	1.076
	citric 100 mM	0.587	0.318	0.068	-0.043	1.216
	oxalic 100 mM	0.320	0.318	0.317	-0.310	0.950
	TSP	-2.838	0.318	0.000	-3.468	-2.208
oxalic 100 mM	citric 0.1 mM	0.127	0.318	0.691	-0.503	0.757
	citric 100 mM	0.267	0.318	0.404	-0.363	0.897
	oxalic 0.1 mM	-0.320	0.318	0.317	-0.950	0.310
	TSP	-3.158	0.318	0.000	-3.787	-2.528
TSP	citric 0.1 mM	3.284	0.318	0.000	2.654	3.914
	citric 100 mM	3.424	0.318	0.000	2.794	4.054
	oxalic 0.1 mM	2.838	0.318	0.000	2.208	3.468
	oxalic 100 mM	3.158	0.318	0.000	2.528	3.787

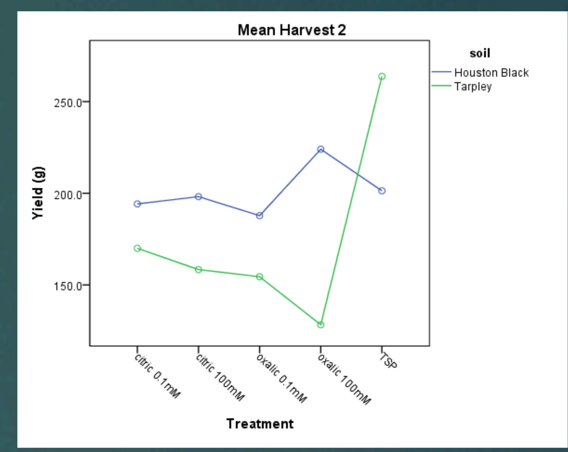
(Figure 5 , Harvest 1)



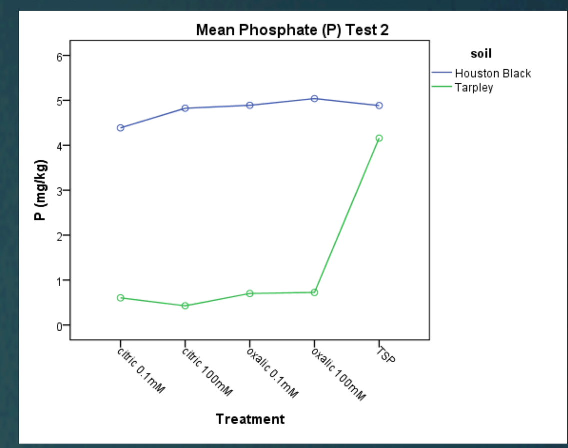
(Figure 6, Soil Test 1)



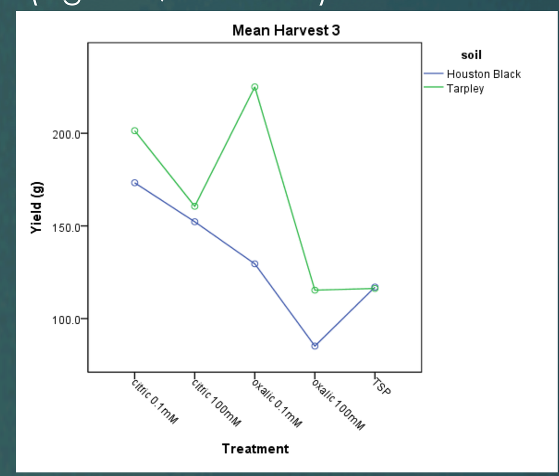
(Figure 7,Harvest 2)



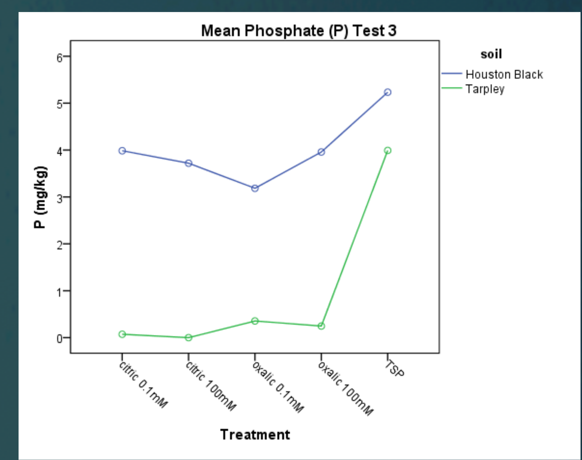
(Figure 8, Soil Test 2)



(Figure 9, Harvest 3)



(Figure 10, Soil Test 3)



Discussion

Total yield comparisons between LMWOA treatments and TSP treatment over time showed no significant differences in yield for Houston Black soils, demonstrating promising results for LMWOAs as a P fertilizer substitute in production (Table 3). This was likely due to relatively high CaCO3 and Ca^+ (8295 mg/kg^{-1}) mineral content, which easily reacted with LMWOA treatments to render soluble P nutrients through dissolution and anion exchange of existing calcium phosphate compounds as shown in a study by Jones and Darrah (1994). Similar P-test results over time showed no significant difference between treatments for Houston Black soil (Table 4), which correlate to a study by Khademi et al. (2010) in which all concentrations of citric and oxalic were effective while oxalic acid provided the most P from soil tests. As for Tarpley soil, results signify LMWOAs as a relatively weak P substitute, possibly due to buffering capacity of the soil and a negative reaction from excess iron release for oxalic 100 mM kg^{-1} treatment. According to Marschner (2002), pH of calcareous soils is dependent on the presence of $CaCO_3$ to buffer soils ranging between 7.5-8.5 pH. Nevertheless, acquiring native P from soil using LMWOAs is a method that merits further investigation as many recent studies using LMWOAs have shown to have a correlative effect on P uptake by plants (Strom et al. 2002; Allan et al. 2003; Jones et al. 2011) but research on sole LMWOA use in crop production is scarce.

References

Allan D.L., Vance C.P., Uhde-Stone C. (2003). Phosphorus Acquisition and Use: Critical Adaptions by Plants for Securing a Nonrenewable Resource. *New Phytologist*, 157, 423-447.

Cordell, D, White, S. (2011). Peak phosphorus: Clarifying the key issues of a vigorous debate about long-term phosphorus security. *Sustainability*, 3, 2027-49.

Jones, D.L., Burger E., Wenzel, W.W. (2011). Phosphorus saturation and pH differentially regulate the efficiency of organic acid anion-mediated P solubilization mechanisms in soil. *Plant Soil, 341, 363-382.*

Jones, D.L., Darrah, P.R. (1994). Role of root derived organic acids in the mobilization of nutrients from the rhizosphere. *Plant and Soil*, 166, 247-257.

Khademi, Z., Jones, D.L., Malakouti, M.J., Asadi, F. (2010). Organic acids differ in enhancing P uptake by Triticum aestivum L.—effects of rhizosphere concentration and counter ion. *Plant Soil, 334, 151-159.*

Marschner, H. (2002). Mineral nutrition of higher plants. 2nd ed. Academic Press. San Diego, California.

Strom, L., Owen, A.G., Godbold, D.L., Jones, D.L. (2002). Organic acid mediated P mobilization in the rhizosphere and uptake by maize roots. *Soil Biology & Biochemistry, 34, 703-710.*

Wang, Y., He, Y., Zhang, H., Schroder, J., Li, C., Zhou, D. (2008). Phosphate mobilization by citric, tartaric, and oxalic acids in a clay loam ultisol. *Soil Science Society American Journal, 72, 1263-1268.*