Short communication

The effect of pH on phosphorus availability and speciation in an aquaponics nutrient solution

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Abstract

The interaction between the main ions in aquaponics nutrient solutions affects chemical composition and availability of nutrients, and nutrient uptake by plant roots. This study determined the effect of pH on phosphorus (P) speciation and availability in an aquaponics nutrient solution and used Visual MINTEQ to simulate P species and P activity. In both experimental and simulated results, P availability decreased with increase in pH of aquaponics nutrient solutions. According to simulations, P binds to several cations leaving less free phosphate ions available in solution. High pH values resulted in the formation of insoluble calcium phosphate species. The study also demonstrated the importance of organic matter and

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alkalinity in keeping free phosphate ions in solution at high pH ranges. It is recommended though that pH in aquaponics systems is maintained at a 5.5-7.2 range for optimal availability and uptake by plants.

Keywords: pH; phosphorus; availability; speciation; aquaponics

1. Introduction

The prospect of decreasing the availability of phosphorus ores in years to come have posed a threat to the world's agricultural systems (Cordell et al., 2011, 2009; Schröder et al., 2011). The introduction of P recycling and P use reduction can substantially improve the longevity of the natural phosphorus reserves (Koppelaar and Weikard, 2013). It is necessary to restructure agricultural practices to close the P cycle for an adequate P management in a changing world (Sharpley et al., 2015).

Closing the P loop in the agricultural sector requires a system capable of managing phosphorus with a high level of flexibility. Phosphorus has to be delivered at the right place and time, i.e., where and when plants need phosphorus the most, with no excessive environmental and economic costs (Bateman et al., 2011). Such management includes practices to recover phosphorus in usable forms from places in the food system where nutrients usually concentrate (wastewater treatment plants, livestock production facilities, compost operations, and food processing plants) and recycle it through crop production (Yorgey, 2016).

Systems that integrate agriculture with fish production are progressively becoming recognized as environment-friendly practices that combine aquatic and terrestrial crop production while promoting waste recycling (Jamu and Piedrahita, 2002). Aquaponics, an example of integrated aquaculture-agriculture, is the combination of recirculating aquaculture and soilless vegetable production in a closed-loop system. Aquaponics has received considerable attention due to system's capability to raise fish at high density, sustain adequate water quality, minimize water exchange, and produce a profitable vegetable that is responsible for the direct assimilation of dissolved fish wastes and products of microbial breakdown (Danaher et al., 2013).

An aquaponics nutrient solution is not merely a passive medium for the passage of nutrients from fish to plants. The chemical composition of aquaponics nutrient solutions is complex because of a large number of dissolved ions and organic substances resulting from the release of excretory compounds as a product of fish metabolism and feed digestion. The interaction between the main ions in solution can influence the chemical composition of aquaponics nutrient solutions. pH of the solution can also have profound effects on the uptake of nutrients by plant roots (White, 2012).

Solution pH in aquaponics systems is a compromise between microbial and plant demands. Microbial nitrification of ammonia to nitrite and nitrite to nitrate is optimized at pH 8.5, but plant nutrient uptake for many crop species is optimized near pH 6.0; thus, pH in aquaponics systems is managed near pH 7.0 (Wortman, 2015). A recent study determined that pH 6.0 was optimal for plant growth and nitrogen utilization efficiency in aquaponics at the expense of increased N_2O emission due to high denitrification (Zou et al., 2016). The forms in which phosphorus exists in solution also changes according to pH. The pKs for the dissociation of H_3PO_4 into $H_2PO_4^-$ and then into HPO_4^{2-} are 2.1 and 7.2, respectively (Schachtman et al., 1998). Therefore, in the pH range maintained in aquaponics systems, phosphorus is mostly present in the form $H_2PO_4^-$, while H_3PO_4 and HPO_4^{2-} have lower activities

Plants can only absorb P as the free orthophosphate ions $H_2PO_4^-$ and HPO_4^{2-} (Becquer et al., 2014). The rate of phosphate uptake decreases as the pH of the external solution increases, which is explained by a reduction in the concentration of $H_2PO_4^-$, which is the substrate of the proton-coupled phosphate symporter in the plasma membrane, in the pH range of 5.6 to 8.5; conversely, a decrease in pH can increase the activity of proton-coupled solute transporters and enhance anion uptake (White, 2012). Lowering the external pH from 8.0 to 4.0 increased phosphate uptake by a factor of 3 in maize roots, while the concentration of the monovalent P species (HPO_4^{2-}) was kept constant (Sentenac and Grignon, 1985).

As pH increases above 7.0 in aqueous solutions, most of the dissolved phosphorus reacts with calcium forming calcium phosphates. Gradually, reactions occur in which the dissolved free phosphate species form insoluble compounds that cause phosphate to become unavailable. In alkaline solutions, calcium is the dominant cation that reacts with phosphate (Siebielec et al., 2014). A general sequence of reactions in alkaline solutions involves the formation of dibasic calcium phosphate dihydrate, octocalcium phosphate, and hydroxyapatite. Each phosphate product formation results in the decrease of solubility and availability of phosphate (Siebielec et al., 2014).

Based on the stated above, the present study aimed to determine the effect of pH on the phosphorus speciation and availability in an aquaponics nutrient solution. Also, Visual MINTEQ, a chemical equilibrium computer model for the calculation of elements speciation and solubility of dissolved mineral phase in aqueous solution, was used to simulate the species and activity of phosphorus in an aquaponics nutrient solution as a function of pH.

2. Material and Methods

2.1. Fish culture conditions and nutrient release procedure

Tilapia juveniles were obtained from a commercial grower in Arizona (Dateland, AZ, USA). Fish were maintained in 55-L tanks in a recirculating aquaponics system under a controlled environment greenhouse at the Controlled Environment Ag Center, University of Arizona, Tucson, AZ. Fish were acclimated with a commercial fish feed (Table 1.) for a month before the trial and then fasted for 24 hours to empty all contents of their gut. 18 tilapia juveniles weighing on average 55.0 g were selected and transferred to a separate 55-L tank receiving water from the recirculating system and acclimated for another 24 hours without being fed. After the 24-hour acclimation period, fish were fed with 10 g of the same commercial feed. After one hour, fish were transferred to a 20-L tank containing 10 L of distilled water. The tank contained air stones and a 50W heater with a thermostat that maintained water temperature constant at 25ºC. Fish were kept in the tank for 24h to digest the feed ingested, and excrete all the waste resulting from digestion and metabolism.

2.2. Nutrient concentration analysis

Fish were removed from the 10-L nutrient release tank and returned to aquaponics systems. No fish died during the nutrient release procedure. The resultant nutrient solution was immediately processed. A 50-mL sample was filtered through a 0.45μm nylon syringe filter and the filtrate used for element composition analysis

The total elemental concentration in the filtered sample was determined by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) analysis. Concentrations of the anions Br^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-} were determined using ion chromatography. Ammonia (NH_3) was determined using the Hach Ammonia Low-Range Standard Method 10023 (Nitrogen-Ammonia Reagent Set, TNT, AmVer Salicilate Low Range). The alkalinity was determined using a digital titrator (Hach Model 16900). The pH was determined using a HACH Hq40d multi pH meter. Dissolved organic carbon was determined using a using a Shimadzu TOC-VCSH analyzer (Columbia, MD) with a solid state module (SSM-5000A).

2.3. Effect of pH on free orthophosphate concentration in liquid phase

50 mL aliquots of the main sample were homogeneously collected and transferred to 18 Erlenmeyer flasks. Three flasks were randomly assigned to each pH treatment [3.0, 5.5, 6.8, control (7.2), 8.5, and 10.0]. A 5.0M HCl solution was added to each Erlenmeyer flask to achieve pH values of 3.0, 5.5 and 6.8; a 5.0M NaOH solution was added to achieve pH values of 8.5 and 10.0; 7.2 was pH of the untreated solution and considered as control. pH adjustment was performed with flasks under constant agitation on a magnetic stirrer.

After the pH adjustments, a 20-mL aliquot was pipetted into separate glass vials and incubated at 25ºC in a shaking water bath for 5 hours. Vials were centrifuged for 20 minutes at 6300 RPM (5325 RCF) and the phosphate concentration in the supernatant was determined using ion-chromatography.

2.4. Visual MINTEQ simulations

In order to further investigate the experimental results obtained from the pH changes in the aquaponics nutrient solutions, the effect of pH on phosphorus availability and speciation was simulated using Visual MINTEQ 3.1.

The elemental concentrations showed in Table 1, except for phosphorus, were input in the Visual MINTEQ software and the interactions between elements were simulated at different pH values (3.0, 5.5, 6.8, 7.2, 8.5 and 10.0). The phosphate concentration used in MINTEQ was obtained from the ion chromatography analysis on the pH assay from average values obtained from the three samples at pH 3.0. The ion chromatography result for orthophosphate was preferred over the ICP-MS analysis to avoid discrepancy between simulated and observed concentrations of PO_4 in solution since the value determined by ICP-MS was slightly higher than the value determined by ion chromatography. Alkalinity was also included in the simulation, as well as dissolved organic carbon (NICA-Donnan model).

2.5. Statistical analysis

Statistical analyses were conducted using RStudio ver. 0.99.491 (RStudio Team, 2016). All the data were reported as the sample mean ± the standard deviation (S.D.). Results from the experimental assay assessing the main effects of pH on the concentration of orthophosphate in aquaponics nutrient solution were analyzed using one-way ANOVA. Differences between means were considered significant at an alpha level of 0.05 using Fisher's LSD pairwise comparisons.

3. Results and Discussion

The elemental composition of the aquaponics nutrient solution obtained with the nutrient release assay is shown in Table 1.

Table. 1 Preferred position

The pH affected the concentration of orthophosphate in the aquaponics nutrient solution (*p* = 0.001). The increase in pH lowered the overall concentration of orthophosphate, but only after pH 8.5 we detected a significant difference in PO_4 concentrations from the pH range where orthophosphate was mostly available (pH 3.0 – 5.5). However, only pH 10.0 caused a significant difference in orthophosphate concentration in comparison with the general pH maintained in aquaponics nutrient solutions (pH 6.8). Results are expressed in Fig. 1.

Fig. 1. Preferred position

The simulations in Visual MINTEQ showed a similar trend as the experimentally obtained results. Note however that model performance statistics were not calculated as there were only three data points for each pH value. In general, the modeled orthophosphate concentration in aquaponics decreased as a function of pH increase. However, the software overestimated the orthophosphate concentration at pH 6.8, 7.2 and 8.5 in comparison to experimental values (Fig 1.). Conversely, at pH 10.0, the software underestimated the concentration of free orthophosphate compared to observed values.

According to the species concentration results from Visual MINTEQ (Fig. 2), at pH 10.0 there was an increase in the formation of calcium phosphate, which represented almost 17% of all the phosphorus species in solution. Note that not all PO_4 species are described in the chart.

Fig. 2. Preferred position

Therefore, the decrease in orthophosphate predicted by the model at pH 10.0 was due to the increase in the formation of calcium phosphate. However, there was a discrepancy between predicted and simulated concentrations of orthophosphate at pH 10.0. Even though the experiment showed that at pH 10.0 the orthophosphate concentration was the lowest, it was not as low as the model predictions. By looking at the species tables provided by Visual MINTEQ, it was clear that the presence of carbonate ions and dissolved organic carbon in solution played a significant role in simulating the concentration of phosphates at high pH values. As the pH increased, it was detected that part of the calcium was bound to carbonate ions and dissolved organic carbon species. Thus, separate simulations were performed with the pH fixed at 10.0, with and without alkalinity and dissolved organic carbon being part of the model. Results are expressed in Fig. 3.

Fig. 3. Preferred position

In general, the model agreement with experimental results increased as dissolved organic carbon and alkalinity were introduced as part of the simulation. If DOC and alkalinity are not part of the simulation, Visual MINTEQ predicts a prominent decrease in the concentration of orthophosphate, mostly due to the formation of calcium phosphates (Fig. 2).

DOC and alkalinity seemed to play a major role in maintaining free orthophosphate in aquaponics nutrient solutions, possibly by protecting phosphorus from binding to free calcium ions. Alkalinity is the measurement of carbonate in aqueous solutions. The carbonate speciation is also affected by pH of aqueous solutions and has a similar behavior of the orthophosphate speciation. At high pHs, carbonate ions (CO_3^{2-}) are the dominant species in solution and react with calcium forming calcium carbonate. In aquaponics systems, alkalinity also plays an important role in the nitrification process. As ammonia is converted into nitrite and further into nitrates, H^+ ions are expelled by nitrifying bacteria and alkalinity is consumed (Timmons and Ebeling, 2007). At low alkalinities (< 100 mg L $CaCO_3$), aquaponics nutrient solutions lose buffering capacity and become susceptible to large pH fluctuations. Therefore, the present study also demonstrated that at low alkalinity concentrations, the availability of phosphorus in aquaponics nutrient solutions might also be affected. However, DOC showed a much more marked effect on the concentration of phosphorus than alkalinity. At pH 10.0, DOC species were bound to approximately 55% of the calcium in solution, which prevented Ca from binding to PO_4 ions. DOC, in the form of organic matter, has charges related to the pH-dependent characteristics of organic acid functional groups (Pierzynski et al., 2005). Under alkaline conditions, organic matter has negatively charged cation exchange sites. Therefore, ions having positive charges such as Ca^{2+} are attracted to organic matter surface by electrostatic interactions.

Conclusions

The availability of phosphorus decreased with increase in pH of aquaponics nutrient solutions. Simulations showed that phosphorus binds to several cations present in solution, leaving less free phosphate ions available for uptake by plants. High pH values influenced the formation of insoluble calcium phosphate species that precipitated from solution. The study also demonstrated the importance of organic matter and alkalinity in keeping free phosphate ions in solution at high pH ranges. It is recommended though that pH in aquaponics system is maintained at a range of 5.5-7.2 for optimal availability and uptake by plants.

Acknowledgments

Authors are indebted to the National Council for Scientific and Technological Development [CNPq, Portuguese: Conselho Nacional de Desenvolvimento Científico e Tecnológico] for the scholarship provided to BSC. Authors would also like to show their gratitude to Desert Springs for donating the fish used in this research, and Edward Hunt and Katerina Dontsova for the ion chromatography analyses.

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Figure Captions

Fig. 1. Observed and simulated concentrations of PO_4 at different pH in aquaponics solutions. Results are means ± s.d. Bars without a common letter are statistically different ($p < 0.05$).

Fig. 2. Speciation of the major forms of P in aquaponics solution as a function of pH as simulated in Visual MINTEQ for pH 10.

Fig. 3. Orthophosphate concentrations simulated by Visual MINTEQ at pH 10 with and without DOC and alkalinity.

Table 1.

Characteristics of the aquaponics nutrient solution.

Parameters	[1,2]Values
B	128.6
Na	16296.6
Mg	2162.1
Al	6.6
Si	1698.0
P	3860.0
K	12083.8
Ca	4091.4
Mn	3.4
Fe	50.1
Cu	17.1
Zn	21.5
NO_2	ND[†]
NO_3	726.3
NH_3	34000
SO_4	10703.7
Cl	17764.1
DOC[*]	21.1
Alkalinity	162
pH	7.2

[1] B, Na, Mg, Al, Si, P, K, Ca, Mn, Fe, Cu, Zn, NO_2, NO_3, NH_3, SO_4 and Cl values are expressed in µg L^{-1}

[2] DOC and alkalinity values are expressed in mg L^{-1}

[*] Dissolved Organic Carbon.

[†] Not detected.

Fig. 1.

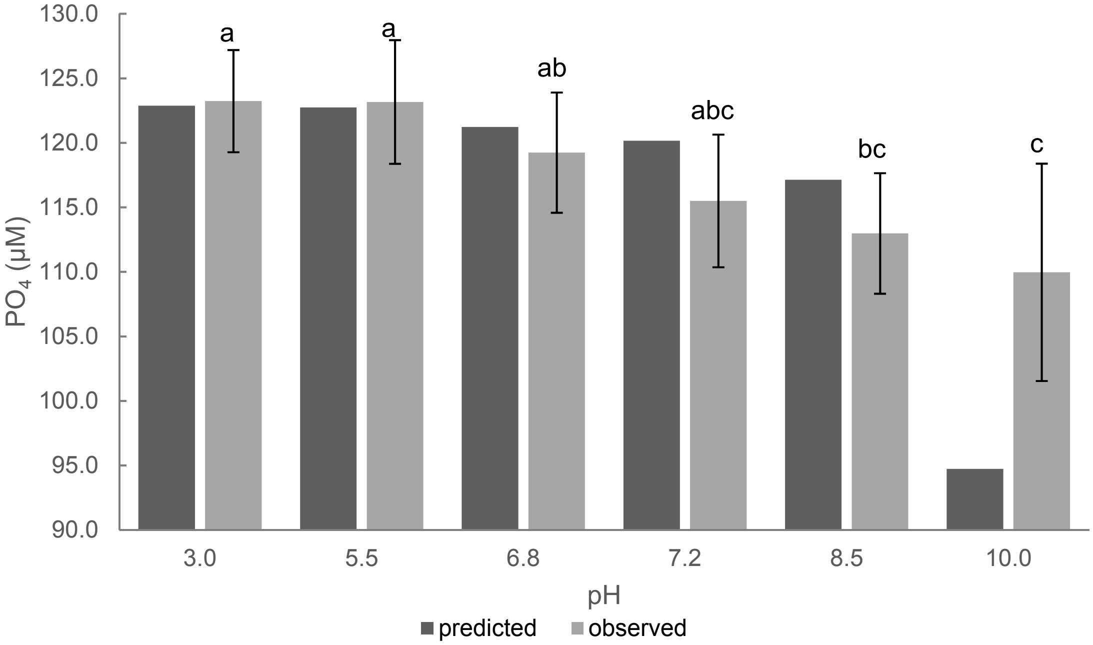

130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
PO$_4$ (μM)
a
a
ab
abc
bc
c
3.0
5.5
6.8
7.2
8.5
10.0
pH
predicted
observed

Fig. 2

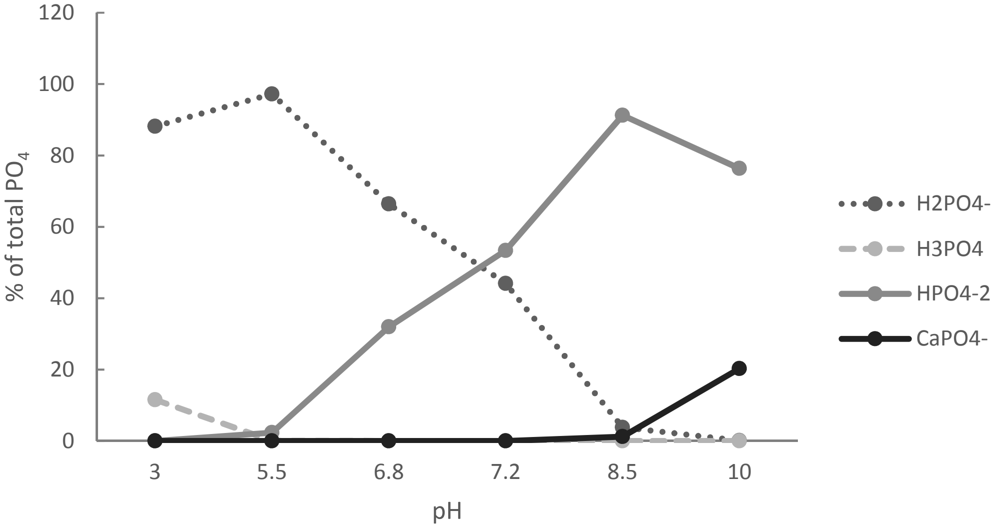
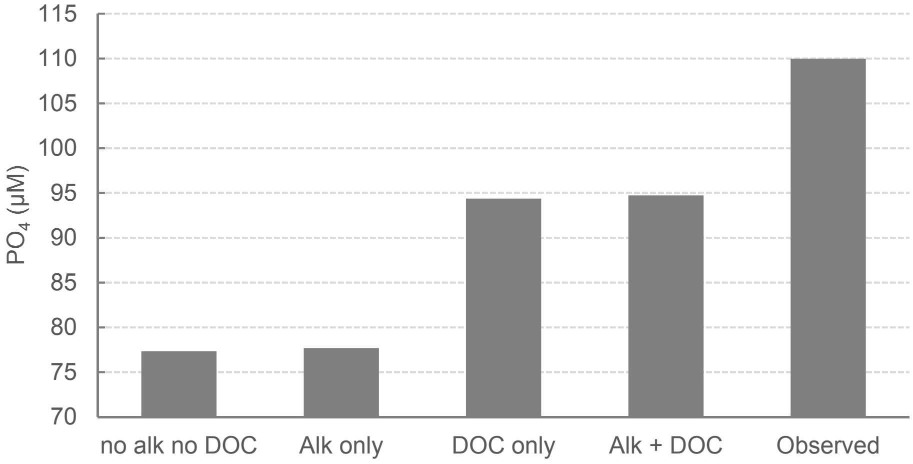

120
100
80
60
40
20
0
% of total PO_4
3
5.5
6.8
7.2
8.5
10
pH
H2PO4-
H3PO4
HPO4-2
CaPO4-

Fig. 3.



115
110
105
100
95
90
85
80
75
70
PO_4 (μM)
no alk no DOC
Alk only
DOC only
Alk + DOC
Observed