

Implications of pH in Aquaponics for target plant nutrient concentrations derived from Hydroponics

A brief description of the methodology

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General

The saturation concentration of a cation in solution is determined by the least soluble salt that can be formed with the present anionic species in solution. The concentration of the salt-forming anion, on the other hand, is not reflected by its total concentration c_T that is used for the formulation of nutrient solutions such as the Hoagland solution (see Tab. 1) but determined by the pH due to speciation reactions. Thus, the true concentration of the species that is causing precipitation has to be calculated.

A **chemical species** is a *”[s]pecific form of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure.”* (IUPAC 2019). An example would be the species couple of $[\text{NH}_4^+]$ and $[\text{NH}_3]$, whose total concentration c_T is commonly termed total ammonia nitrogen (TAN). The concentration of both species at a given $\text{TAN} = c_T = 5 \text{ mmol L}^{-1}$ is a function of pH and can be calculated if the pH and the dissociation constant K of the reaction is known.

1 Calculations

1.1 Calculation of Nutrient Species Concentrations

Being directly pH-dependent, the **hydroxide** concentration can be calculated by Eq. 1.

$$[\text{OH}^-] = 10^{\text{pH}-14} \quad (1)$$

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Table 1: Total concentrations of plant nutrients in the nutrient solution after Hoagland and Arnon (Resh 2016).

Nutrient	γ [mg L ⁻¹]	c [mmol L ⁻¹]
Anions		
NH ₄ ⁺ -N	14	7.8×10^{-1}
NO ₃ ⁻ -N	196	3.16
PO ₄ ³⁻ -P	31	3.3×10^{-1}
SO ₄ ²⁻ -S	64	6.7×10^{-1}
Cations		
K ⁺	234	5.98
Ca ²⁺	160	3.99
Mg ²⁺	48	1.97
Fe ³⁺	0.6	10.7×10^{-3}
Mn ²⁺	0.5	9.1×10^{-3}
Cu ²⁺	0.02	5.5×10^{-4}
Zn ²⁺	0.05	7.6×10^{-4}
Mo ⁶⁺	0.01	1.0×10^{-4}

The concentration of **diprotic acids** [A²⁻] such as carbonic acid H₂CO₃ and sulphuric acid H₂SO₄ or **triprotic acids** [A³⁻] such as phosphoric acid H₃PO₄ can be calculated by using Eq. 2 and 3, respectively.

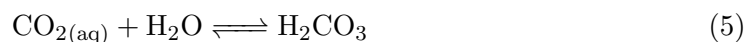
$$[A^{2-}] = c_T \cdot \frac{1}{\frac{[H^+]^2}{K_{a1}K_{a2}} + \frac{[H^+]}{K_{a2}} + 1} \quad (2)$$

$$[A^{3-}] = c_T \cdot \frac{1}{\frac{[H^+]^3}{K_{a1}K_{a2}K_{a3}} + \frac{[H^+]^2}{K_{a2}K_{a3}} + \frac{[H^+]}{K_{a3}} + 1} \quad (3)$$

Here, $K_{a,n}$ represents the acidity constants of the corresponding deprotonation levels. In the case of carbonate, it is assumed that all carbonate species in the water are originating from atmospheric CO₂ ($p = 5.4 \times 10^{-2}$ atm), neglecting the use of carbonate buffers in aquaculture. The initial **carbon dioxide concentration in water** is thus calculated by applying Henry's law.

$$[\text{CO}_2(\text{aq})] = p(\text{CO}_2(\text{g})) \cdot K_H \quad (4)$$

Eventually, the concentrations of CO₂(aq) and H₂CO₃ resulting from the reaction



are summed up as

$$[\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] = [\text{H}_2\text{CO}_3 \cdot] \quad (6)$$

as it is common practice (see e.g. Sigg and Stumm 2011). In all equations, c_T is denoting for the total molar concentration of an element and brackets are denoting for molar concentrations of the individual species. No correction for activities was done. The numeric values used for the calculations are stated in Tab. 2.

1.2 Calculation of Solubility

Salts consist of positively charged cations and negatively charged anions. The solubility of a salt is described by its solubility product constant K_{sp} as shown in Eq. 7.

$$K_{sp} = [C^{a+}]^i \cdot [A^{b-}]^j \quad (7)$$

With K_{sp} of a salt and the concentration of one of the ions in solution being known, the saturation concentration S of the other ion can be calculated. The saturation concentration is the highest possible concentration up to which no precipitation of the salt occurs.

In all equations, brackets are denoting for molar concentrations. The solubility products used for the calculation of theoretical maximum solubilities of pure salts are given in Table 3.

1.3 Constants

Table 2: Equilibrium constants of dissociation reactions.

Reaction	Abbrev.	Value	Reference
$\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_3\text{O}^+$	K_W	1.0×10^{-13}	
$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3^*$	K_H	3.4×10^{-2}	Sigg and Stumm 2011
$\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$	K_{a1}	4.46×10^{-7}	Sigg and Stumm 2011
$\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+$	K_{a2}	4.16×10^{-11}	Sigg and Stumm 2011
$\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+$	K_{a1}	7.52×10^{-3}	Küster 2011
$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$	K_{a2}	6.23×10^{-8}	Küster 2011
$\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{PO}_4^{3-} + \text{H}_3\text{O}^+$	K_{a3}	3.5×10^{-13}	Küster 2011
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_4^- + \text{H}_3\text{O}^+$	K_{a1}	1.0×10^3	Küster 2011
$\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_3\text{O}^+$	K_{a2}	1.2×10^{-2}	Küster 2011

References

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Table 3: Solubility products (K_{sp}) of some poorly soluble salts of relevant plant nutrients at 25 °C.

Compound	Solubility product	Reference
CaCO_3	3.36×10^{-9}	De Rijck and Schrevens 1998
Ca(OH)_2	5.02×10^{-6}	Lide 2007
$\text{Ca}_3(\text{PO}_4)_2$	1.00×10^{-26}	Lide 2007
$\text{Cu}_3(\text{PO}_4)_2$	1.40×10^{-37}	Lide 2007
$\text{FePO}_4 \cdot 2 \text{H}_2\text{O}$	9.91×10^{-16}	Lide 2007
MgCO_3	6.82×10^{-6}	Lide 2007
Mg(OH)_2	5.61×10^{-12}	Lide 2007
$\text{Mg}_3(\text{PO}_4)_2$	1.04×10^{-24}	Lide 2007
MnCO_3	2.24×10^{-11}	Lide 2007
$\text{Ni}_3(\text{PO}_4)_2$	4.74×10^{-32}	Lide 2007
ZnCO_3	1.46×10^{-10}	Lide 2007
Zn(OH)_2	3.00×10^{-17}	Lide 2007
$\text{Zn}_3(\text{PO}_4)_2$	9×10^{-33}	Lide 2007