

# 1 General

The nutrients relevant for plant growth are the following:

## Macronutrients

- N
- P
- K
- Ca
- Mg
- S

## Micronutrients

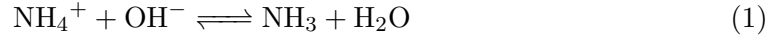
- Fe
- Cu
- Zn
- B
- Mn
- Mo
- Ni

The solubility of a salt is generally determined by

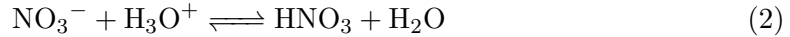
- its solubility product ( $K_{S0}$ ),
- the temperature (T),
- the pH, affecting speciation,
- the pE, affecting speciation,
- the partial pressure of  $\text{CO}_2(\text{g})$  ( $p_{\text{CO}_2}$ ),
- the presence of common ions,
- the ionic strength of the solution,
- and the presence of chelating agents.

The solids with the lowest solubility are assumed to control the total solubility of the contained compounds in aquatic systems.

The **pH** of an aquaculture system would typically range between 6.5 to 8.0. A higher pH would lead to an equilibrium shift of the chemical equilibrium between  $\text{NH}_4^+$  and  $\text{NH}_3$



, with  $\text{NH}_3$  being a toxic species for fish. It is thus not desirable to raise the pH above a value of 8. On the other hand, a low pH leads to the shift of the equilibrium between  $\text{NO}_3^-$  and  $\text{HNO}_3$



, with the latter being a toxic component. Furthermore, the decreased pH hampers the transport of  $\text{CO}_2$  into the adjacent water and thus poses direct physiological implications for the fish. A third downside of a low pH is the decrease of nitrification efficiency due to suboptimum conditions for nitrifying bacteria.

The average **temperature** depends on the fish species reared, while the temperature range is determined by whether the system is cooled or heated using technical equipment or exposed to natural fluctuations. In most aquaponic systems, the species of choice are either African catfish (*Clarias gariepinus*) or Nile tilapia (*Oreochromis niloticus*) with an average temperature preference of 25 °C. The fish production system in aquaponics would usually be a recirculation aquaculture system (RAS) with temperature control. Fluctuations are thus expected to be within a range of 1 °C.

## 1.1 Hydroxides

The formation of hydroxides is determined by the pH. With increasing pH, the concentration of  $\text{OH}^-$  ions increases as well.

## 1.2 Carbonates

Aquaculture systems can be considered open systems where the partial pressure of  $\text{CO}_2(\text{g})$  is constant. The total concentration of  $[\text{CO}_2(\text{aq})]$  and consequently  $[\text{H}_2\text{CO}_3^*]$  is thus depending on the pH and  $T$  of the system. Under the conditions in an aquaponic system, and considering  $pK_{a2} = 10.4$  of the carbonate system, the availability of free  $[\text{CO}_3^{2-}(\text{aq})]$  is limited. However, carbonate speciation is pH dependent, as visible in Figure 1. If  $[\text{H}_2\text{CO}_3^*]$  is removed due to an increasing pH and shift of the equilibrium towards a higher proportion of  $[\text{HCO}_3^-]$  and eventually  $[\text{CO}_3^{2-}]$ , further gaseous  $\text{CO}_2$  can be dissolved in water and is thus raising the total concentration of these carbonaceous compounds in the water.

## 1.3 Phosphates

Phosphorus is entering an aquaculture system via the feed. While the average digestibility of phosphorus is ranging between 50 % to 90 %, the excreted form of phosphorus

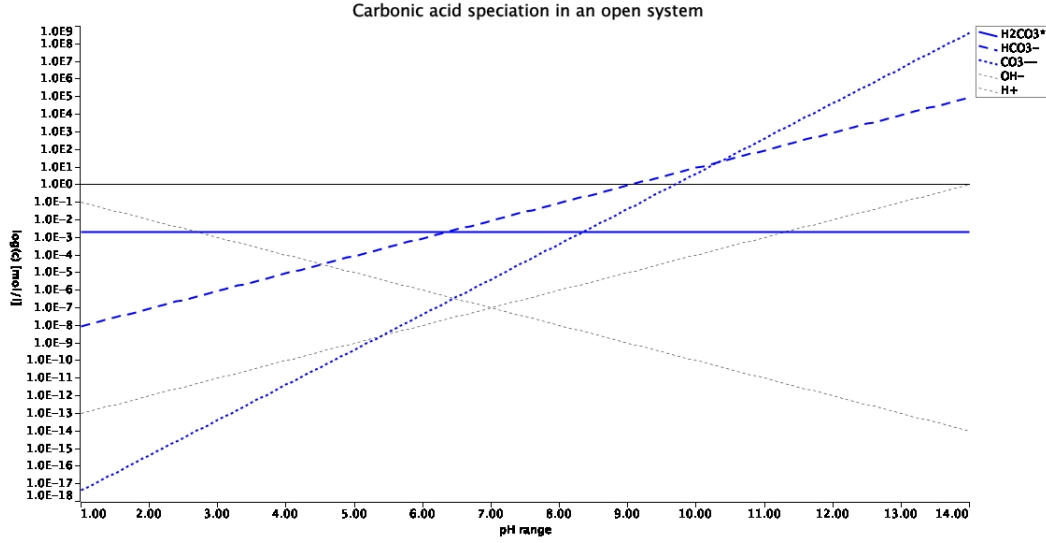


Figure 1: Carbonate speciation in an open system

depends on the form in which it is present in the feed. Phosphorus can be added to the feed in form of phosphate salts, for instance Mono-calcium phosphate, or bound as phytic acid, which is present in plant ingredients and considered as anti-nutritional factor due to its indigestibility. Phosphates are prone to be excreted via the urinary system in form of free ions. Indigestible compounds, on the other hand, are excreted as part of the faeces and are thus considered solids and bound to organic carbon. Phosphate speciation is ph-dependent as can be seen in Figure 2.

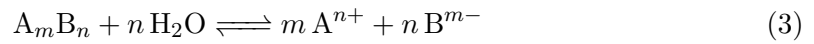
## 1.4 Nitrates

## 1.5 Sulphates

As described for phosphates, the speciation of sulphates is heavily depending on the pH of the solution.

# 2 Equations and data used

The dissolution of a salt in  $H_2O$  can be described as



. Considering the concentration of  $H_2O$  being constant ( $[H_2O] = 1$ ), the solubility product  $K_{S0}$ , which is equal to the ion product of a saturated solution of the salt, can be written as

$$K_{S0} = [A^{n+}]^m \cdot [B^{m-}]^n \quad (4)$$

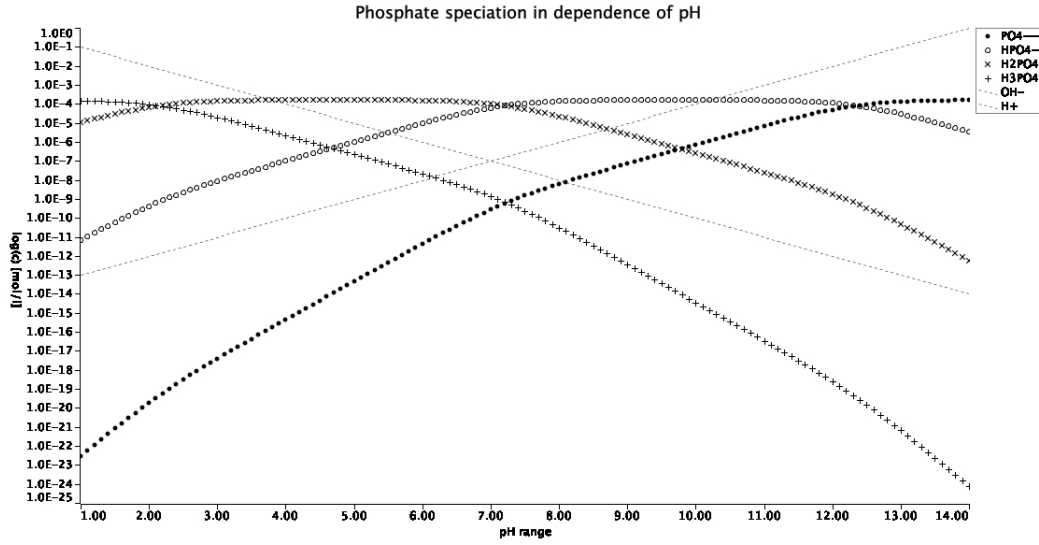


Figure 2: Phosphate speciation

in a generalised way. To calculate the maximum solubility  $S$  of a salt in  $H_2O$  based on  $K_{S0}$ , the proportions in which the cation and anion are present in the salt have to be considered as shown in equation 3. Substitution of the concentration of one ion by the concentration of the other leads to the generalised formula

$$S = \sqrt[m+n]{\frac{K_{S0}}{n^n \cdot m^m}} \quad (5)$$

. The result has then to be multiplied by the corresponding stoichiometric factor resulting from the mass balance of the compounds of the salt.

The solubility products used for the calculation of theoretical maximum solubilities of pure salts are given in Table 1. As result of the stoichiometry of the salts

### 3 Results of calculations

Initially, the solubilities of the main plant nutrients were calculated using reported mass percentages of a number of their salts at saturation concentration. In case of slightly soluble salts, the saturation concentration was calculated using the solubility product  $K_{S0}$ .

Table 2: Calculated solubilities in  $\text{mol L}^{-1}$  for a number of salts.

Formula	Salt	Cation	Anion
$NH_4H_2PO_4$	3.5	3.5	3.5

NH <sub>4</sub> NO <sub>3</sub>	$2.6 \times 10^1$	$2.6 \times 10^1$	$2.6 \times 10^1$
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	5.8	$1.2 \times 10^1$	5.8
B(OH) <sub>3</sub>	$9.3 \times 10^{-1}$	$9.3 \times 10^{-1}$	2.8
CaCO <sub>3</sub>	$5.8 \times 10^{-5}$	$5.8 \times 10^{-5}$	$5.8 \times 10^{-5}$
CaCl <sub>2</sub>	7.4	7.4	$1.5 \times 10^1$
Ca(OH) <sub>2</sub>	$1.1 \times 10^{-2}$	$1.1 \times 10^{-2}$	$2.2 \times 10^{-2}$
Ca(NO <sub>3</sub> ) <sub>2</sub>	8.7	8.7	$1.7 \times 10^1$
KH <sub>2</sub> PO <sub>4</sub>	1.8	1.8	1.8
CaSO <sub>4</sub>	$7.0 \times 10^{-3}$	$7.0 \times 10^{-3}$	$7.0 \times 10^{-3}$
CaSO <sub>4</sub> · 2 H <sub>2</sub> O	$5.6 \times 10^{-3}$	$5.6 \times 10^{-3}$	$5.6 \times 10^{-3}$
CuCl <sub>2</sub>	5.6	5.6	$1.1 \times 10^1$
Cu(NO <sub>3</sub> ) <sub>2</sub>	7.7	7.7	$1.5 \times 10^1$
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	5.2	$1.0 \times 10^1$	5.2
CuSO <sub>4</sub>	1.4	1.4	1.4
CuS	$2.4 \times 10^{-8}$	$2.4 \times 10^{-8}$	$2.4 \times 10^{-8}$
FeCO <sub>3</sub>	$5.6 \times 10^{-6}$	$5.6 \times 10^{-6}$	$5.6 \times 10^{-6}$
Fe(OH) <sub>2</sub>	$2.3 \times 10^{-6}$	$2.3 \times 10^{-6}$	$4.6 \times 10^{-6}$
FeSO <sub>4</sub>	1.9	1.9	1.9
FeS	$2.4 \times 10^1$	$2.4 \times 10^1$	$2.4 \times 10^1$
FeCl <sub>3</sub>	5.5	5.5	$1.7 \times 10^1$
Fe(OH) <sub>3</sub>	$1.0 \times 10^{-10}$	$1.0 \times 10^{-10}$	$3.0 \times 10^{-10}$
Fe(NO <sub>3</sub> ) <sub>3</sub>	3.6	3.6	$1.1 \times 10^1$
MgCO <sub>3</sub>	$2.6 \times 10^{-3}$	$2.6 \times 10^{-3}$	$2.6 \times 10^{-3}$
MgCl <sub>2</sub>	5.9	5.9	$1.2 \times 10^1$
Mg(OH) <sub>2</sub>	$1.1 \times 10^{-4}$	$1.1 \times 10^{-4}$	$2.2 \times 10^{-4}$
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$1.1 \times 10^{-7}$	$3.4 \times 10^{-7}$	$2.3 \times 10^{-7}$
Mg(NO <sub>3</sub> ) <sub>2</sub>	4.8	4.8	9.6
Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$1.7 \times 10^{-8}$	$5.0 \times 10^{-8}$	$3.3 \times 10^{-8}$
MgSO <sub>4</sub>	3.0	3.0	3.0
MnCO <sub>3</sub>	$4.7 \times 10^{-6}$	$4.7 \times 10^{-6}$	$4.7 \times 10^{-6}$
MnCl <sub>2</sub>	6.2	6.2	$1.2 \times 10^1$
MnS	$5.5 \times 10^3$	$5.5 \times 10^3$	$5.5 \times 10^3$
FePO <sub>4</sub> · 2 H <sub>2</sub> O	$3.1 \times 10^{-8}$	$3.1 \times 10^{-8}$	$3.1 \times 10^{-8}$
Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$6.3 \times 10^{-6}$	$1.9 \times 10^{-5}$	$1.3 \times 10^{-5}$
MnSO <sub>4</sub>	4.2	4.2	4.2
NiCO <sub>3</sub>	$3.8 \times 10^{-4}$	$3.8 \times 10^{-4}$	$3.8 \times 10^{-4}$
NiCl <sub>2</sub>	5.2	5.2	$1.0 \times 10^1$
Ni(OH) <sub>2</sub>	$5.2 \times 10^{-6}$	$5.2 \times 10^{-6}$	$1.0 \times 10^{-5}$
Ni(NO <sub>3</sub> ) <sub>2</sub>	5.4	5.4	$1.1 \times 10^1$
NiSO <sub>4</sub>	2.6	2.6	2.6
K <sub>2</sub> CO <sub>3</sub>	8.0	$1.6 \times 10^1$	8.0
KCl	4.8	4.8	4.8
KHCO <sub>3</sub>	3.6	3.6	3.6
KOH	$2.1 \times 10^1$	$2.1 \times 10^1$	$2.1 \times 10^1$

Ni <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$2.1 \times 10^{-7}$	$6.4 \times 10^{-7}$	$4.3 \times 10^{-7}$
KNO <sub>3</sub>	3.8	3.8	3.8
K <sub>3</sub> PO <sub>4</sub>	5.4	$1.6 \times 10^1$	5.4
K <sub>2</sub> SO <sub>4</sub>	$6.9 \times 10^{-1}$	1.4	$6.9 \times 10^{-1}$
ZnCO <sub>3</sub>	$1.2 \times 10^{-5}$	$1.2 \times 10^{-5}$	$1.2 \times 10^{-5}$
ZnCl <sub>2</sub>	$3.0 \times 10^1$	$3.0 \times 10^1$	$6.0 \times 10^1$
Zn(OH) <sub>2</sub>	$2.0 \times 10^{-6}$	$2.0 \times 10^{-6}$	$3.9 \times 10^{-6}$
Zn(NO <sub>3</sub> ) <sub>2</sub>	6.3	6.3	$1.3 \times 10^1$
ZnSO <sub>3</sub>	$1.2 \times 10^{-2}$	$1.2 \times 10^{-2}$	$1.2 \times 10^{-2}$
ZnSO <sub>4</sub>	3.6	3.6	3.6
ZnS	$1.7 \times 10^{-1}$	$1.7 \times 10^{-1}$	$1.7 \times 10^{-1}$

The obtained molar concentrations were then converted into mass concentrations.

Table 4: Calculated solubilities in mg L<sup>-1</sup> for a number of salts.

Compound	Formula	Salt	Cation
Ammonium dihydrogen phosphate	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	$4.0 \times 10^5$	$6.3 \times 10^4$
Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	$2.1 \times 10^6$	$4.8 \times 10^5$
Ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	$7.6 \times 10^5$	$2.1 \times 10^5$
Boric acid	B(OH) <sub>3</sub>	$5.8 \times 10^4$	$1.0 \times 10^4$
Calcium carbonate	CaCO <sub>3</sub>	5.8	2.3
Calcium chloride	CaCl <sub>2</sub>	$8.1 \times 10^5$	$2.9 \times 10^5$
Calcium hydroxide	Ca(OH) <sub>2</sub>	$8.0 \times 10^2$	$4.3 \times 10^2$
Calcium nitrate	Ca(NO <sub>3</sub> ) <sub>2</sub>	$1.4 \times 10^6$	$3.5 \times 10^5$
Potassium dihydrogen phosphate	KH <sub>2</sub> PO <sub>4</sub>	$2.5 \times 10^5$	$7.1 \times 10^4$
Calcium sulfate	CaSO <sub>4</sub>	$9.5 \times 10^2$	$2.8 \times 10^2$
Calcium sulfate dihydrate	CaSO <sub>4</sub> · 2 H <sub>2</sub> O	$9.6 \times 10^2$	$2.2 \times 10^2$
Copper chloride	CuCl <sub>2</sub>	$7.6 \times 10^5$	$3.6 \times 10^5$
Copper nitrate	Cu(NO <sub>3</sub> ) <sub>2</sub>	$1.4 \times 10^6$	$4.9 \times 10^5$
Ammonium monohydrogen phosphate	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	$6.9 \times 10^5$	$1.9 \times 10^5$
Copper sulfate	CuSO <sub>4</sub>	$2.2 \times 10^5$	$8.7 \times 10^4$
Copper sulfid	CuS	$2.4 \times 10^{-3}$	$1.6 \times 10^{-3}$
Iron(II) carbonate	FeCO <sub>3</sub>	$6.5 \times 10^{-1}$	$3.1 \times 10^{-1}$
Iron(II) hydroxide	Fe(OH) <sub>2</sub>	$2.1 \times 10^{-1}$	$1.3 \times 10^{-1}$
Iron(II) sulfate	FeSO <sub>4</sub>	$2.9 \times 10^5$	$1.1 \times 10^5$
Iron(II) sulfid	FeS	$2.2 \times 10^6$	$1.4 \times 10^6$
Iron(III) chloride	FeCl <sub>3</sub>	$9.1 \times 10^5$	$3.1 \times 10^5$
Iron(III) hydroxide	Fe(OH) <sub>3</sub>	$1.1 \times 10^{-5}$	$5.6 \times 10^{-6}$
Iron(III) nitrate	Fe(NO <sub>3</sub> ) <sub>3</sub>	$8.7 \times 10^5$	$2.0 \times 10^5$

Magnesium carbonate	MgCO <sub>3</sub>	$2.2 \times 10^2$	$6.3 \times 10^1$
Magnesium chloride	MgCl <sub>2</sub>	$5.6 \times 10^5$	$1.4 \times 10^5$
Magnesium hydroxide	Mg(OH) <sub>2</sub>	6.5	2.7
Calcium phosphate	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$3.5 \times 10^{-2}$	$1.4 \times 10^{-2}$
Magnesium nitrate	Mg(NO <sub>3</sub> ) <sub>2</sub>	$7.1 \times 10^5$	$1.2 \times 10^5$
Copper phosphate	Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$6.4 \times 10^{-3}$	$3.2 \times 10^{-3}$
Magnesium sulfate	MgSO <sub>4</sub>	$3.6 \times 10^5$	$7.2 \times 10^4$
Manganese carbonate	MnCO <sub>3</sub>	$5.4 \times 10^{-1}$	$2.6 \times 10^{-1}$
Manganese dichloride	MnCl <sub>2</sub>	$7.7 \times 10^5$	$3.4 \times 10^5$
Manganese sulfid	MnS	$4.8 \times 10^8$	$3.0 \times 10^8$
Iron(III) phosphate dihydrate	FePO <sub>4</sub> · 2 H <sub>2</sub> O	$5.9 \times 10^{-3}$	$1.8 \times 10^{-3}$
Magnesium orthophosphate	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1.6	$4.6 \times 10^{-1}$
Manganous sulfate	MnSO <sub>4</sub>	$6.3 \times 10^5$	$2.3 \times 10^5$
Nickel carbonate	NiCO <sub>3</sub>	$4.5 \times 10^1$	$2.2 \times 10^1$
Nickel chloride	NiCl <sub>2</sub>	$6.7 \times 10^5$	$3.1 \times 10^5$
Nickel hydroxide	Ni(OH) <sub>2</sub>	$4.8 \times 10^{-1}$	$3.0 \times 10^{-1}$
Nickel nitrate	Ni(NO <sub>3</sub> ) <sub>2</sub>	$9.9 \times 10^5$	$3.2 \times 10^5$
Nickel sulphate	NiSO <sub>4</sub>	$4.0 \times 10^5$	$1.5 \times 10^5$
Potassium carbonate	K <sub>2</sub> CO <sub>3</sub>	$1.1 \times 10^6$	$6.3 \times 10^5$
Potassium chloride	KCl	$3.5 \times 10^5$	$1.9 \times 10^5$
Potassium hydrogencarbonate	KHCO <sub>3</sub>	$3.6 \times 10^5$	$1.4 \times 10^5$
Potassium hydroxide	KOH	$1.2 \times 10^6$	$8.4 \times 10^5$
Nickel phosphate	Ni <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	$7.8 \times 10^{-2}$	$3.8 \times 10^{-2}$
Potassium nitrate	KNO <sub>3</sub>	$3.8 \times 10^5$	$1.5 \times 10^5$
Potassium orthophosphate	K <sub>3</sub> PO <sub>4</sub>	$1.1 \times 10^6$	$6.3 \times 10^5$
Potassium sulfate	K <sub>2</sub> SO <sub>4</sub>	$1.2 \times 10^5$	$5.4 \times 10^4$
Zinc carbonate	ZnCO <sub>3</sub>	1.5	$7.9 \times 10^{-1}$
Zinc chloride	ZnCl <sub>2</sub>	$4.1 \times 10^6$	$2.0 \times 10^6$
Zinc hydroxide	Zn(OH) <sub>2</sub>	$1.9 \times 10^{-1}$	$1.3 \times 10^{-1}$
Zinc nitrate	Zn(NO <sub>3</sub> ) <sub>2</sub>	$1.2 \times 10^6$	$4.1 \times 10^5$
Zinc sulfite	ZnSO <sub>3</sub>	$1.8 \times 10^3$	$8.1 \times 10^2$
Zinc sulfate	ZnSO <sub>4</sub>	$5.8 \times 10^5$	$2.3 \times 10^5$
Zinc sulfid	ZnS	$1.7 \times 10^4$	$1.1 \times 10^4$

For the following calculations, it is assumed that pH = 7.5, T = 25 °C,  $K_{H,CO_2} = 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ , and  $p_{CO_2} = 5.4 \times 10^{-2} \text{ atm}$ .

### 3.1 Hydroxides

In an aquaculture system with an assumed average pH = 7.5, the hydroxide concentration would be

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-(14-\text{pH})} = 10^{-(14-7.5)} = 3.2 \times 10^{-7} \quad (6)$$

Table 1: Solubility products ( $K_{S0}$ ) of poorly soluble salts of relevant plant nutrients at 25 °C.

Compound	Solubility product
$\text{Ca}_3(\text{PO}_4)_2$	$2.07 \times 10^{-33}$
$\text{Cu}_3(\text{PO}_4)_2$	$1.40 \times 10^{-37}$
$\text{Fe}(\text{OH})_3$	$2.79 \times 10^{-39}$
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	$9.91 \times 10^{-16}$
$\text{Mg}_3(\text{PO}_4)_2$	$1.04 \times 10^{-24}$
$\text{MnCO}_3$	$2.24 \times 10^{-11}$
$\text{Ni}_3(\text{PO}_4)_2$	$4.74 \times 10^{-32}$
$\text{Zn}(\text{OH})_2$	$3.00 \times 10^{-17}$

### 3.2 Carbonates

Assuming that  $K_{H,\text{CO}_2} = 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ , and  $p_{\text{CO}_2} = 5.4 \times 10^{-2} \text{ atm}$ , the resulting  $[\text{H}_2\text{CO}_3^*]$  would equal to  $\approx 2 \times 10^{-3} \text{ mol L}^{-1}$ . Within a pH-range from 7 to 8.5, the predominant species would be  $\text{HCO}_3^-$ , while the concentration of  $\text{CO}_3^{2-}$  would range between  $4.2 \times 10^{-6} \text{ mol L}^{-1}$  and  $4.2 \times 10^{-3} \text{ mol L}^{-1}$ .

### 3.3 Phosphates

The initial mass fraction of all phosphates present in the system was assumed to be  $5 \text{ mg L}^{-1}$ , resulting in a  $c_T$  of  $1.6 \times 10^{-4} \text{ mol L}^{-1}$ . This data is taken from [?].

At a pH = 7, the predominant phosphate species are  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ . Given  $c_T$ , this would result in  $[\text{H}_2\text{PO}_4^-] \approx 6 \times 10^{-2} \text{ mol L}^{-1}$  and  $[\text{HPO}_4^{2-}] \approx 4 \times 10^{-2} \text{ mol L}^{-1}$ .

## 4 Comparison with empirical results

In the following, theoretical concentrations of compounds relevant for plant nutrition and concentrations found empirically are compared in Table 6. The theoretical concentrations are referring to the maximum concentration possible, considering only solubility product constants and neglecting complexing agents such as humic substances present in the water.

Table 6: Table



## 5 Discussion