ELEMENTAL BIOAVAILABILITY IN NUTRIENT SOLUTIONS IN RELATION TO PRECIPITATION REACTIONS

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ABSTRACT

In hydroponic plant nutritional research, nutrient solutions can be considered as aqueous solutions of inorganic ions. In this aqueous solution the ions are submitted to the laws of aquatic inorganic chemistry. This means that the ions are involved in the dynamic equilibria between complexation, dissociation and precipitation reactions. These chemical reactions seriously impact elemental speciation and bioavailability. As a result, plant roots experience a different nutritional composition.

Ions withdrawn from the nutrient solution due to precipitation reactions, change the nutritional composition and are not available for uptake by plant roots. Like complexes, precipitates can buffer a nutrient solution, exchanging nutrients as these decrease by plant uptake.

This research looks into the precipitation reactions that occur in hydroponic nutrient solutions. In the concentration range of nutrient solutions no precipitates are formed involving potassium, nitrate, ammonium or sulphate, while Ca^{2+} and Mg^{2+} form mainly at a higher pH precipitates with HPO_4^{2-} . Preparing nutrient solutions with tap-water, CaCO_3 is likely to precipitate.

A good knowledge of the chemical reactions occurring in nutrient solutions is the first prerequisite in hydroponic plant nutritional research.

INTRODUCTION

The laws of aquatic inorganic chemistry distribute the ions in nutrient solutions among their various chemical and physical forms like: free ions, soluble complexes, chelates, ionpairs, solid and gaseous phases and different oxidation states, called “elemental speciation”. Each of these chemical and physical forms possesses a different reactivity, mobility and different physicochemical properties, changing bioavailability.

The inorganic ions present in nutrient solutions can form precipitates. Precipitated elements are not available for uptake by plants. In this way, precipitation reactions like dissociation and complexation reactions change the mineral composition of nutrient solutions (De Rijck *et al.*, 1997a, 1997b).

The precipitation reactions involving the six essential macronutrients (K^+ , Ca^{2+} , Mg^{2+} , NO_3^- , $H_2PO_4^-$ and SO_4^{2-}) are elaborated. Since hydroponic nutrient solutions sometimes contain ammonium and bicarbonate in a millimolar range, also the precipitation reactions involving these two ions are considered.

MATERIAL AND METHODS

Calculations

The calculations are carried out with the conditional equilibrium constants of the computer speciation program Geochem PC version 2.0 (Parker *et al.*, 1995), adjusted at an ionic strength of 30 mmol/l, the concentration range of nutrient solutions. This means that the calculations are correct if beside the considered chemical entity other ions are present, inert for the considered chemical reactions, at a concentration so that the total ionic strength equals 30 mmol/l.

The effect of temperature, atmospheric pressure and atmospheric composition is not taken into account. All the calculations are made for closed systems (no CO_2 exchange with the atmosphere) at a temperature of 25 °C, an atmospheric pressure of 0.1 Mpa and a total ionic strength of 30 mmol/l.

Precipitation reactions

In a precipitation reaction certain cations combine with certain anions to form an insoluble solid called a precipitate (Skoog *et al.*, 1976):

with: l : valence of the anion

m : valence of the cation

The solubility product constant “ K_{sp} ” is a measure for the equilibrium between a precipitate and its ions in a saturated solution (Cotton *et al.*, 1980):

$$K_{sp} = [M^{m+}]^k [L^{-}]^n \quad (2)$$

Considering equation (1), it is clear that for each mole of M_kL_n that dissolves k moles of M^{m+} and n moles of L^{-} appear in the solution. If S is the molar solubility of M_kL_n , then a saturated solution of M_kL_n contains $k S$ mol/l M^{m+} and $n S$ mol/l L^{-} . The molar solubility (S) of M_kL_n is calculated as follows:

$$K_{sp} = [M^{m+}]^k [L^{-}]^n = (k S)^k (n S)^n \quad (3)$$

The molar solubility (S) can be expressed with the following equation:

$$S = (n+k) \sqrt[n+k]{\frac{K_{sp}}{k^k n^n}} \quad (4)$$

Precipitation reactions are influenced by phenomenons like pH, common ion effect (precipitation effect), salt effect (activity effect) and ion pair formation (complexation). A precipitate is pH dependent if its cation or anion takes part in an acid - base equilibrium.

The common ion effect is also called the ”primary salt effect”. If a certain concentration of XL is added to a saturated M_lL_m solution, a certain amount of M_lL_m will precipitate, resulting in a lower $M^{m+}_{(aq)}$, and a higher $L^{-}_{(aq)}$ concentration.

The presence of other ions also impacts solubility. This effect is opposite to the common ion effect and was called the “secondary salt effect”. If other ions are dissolved, the total ionic concentration of the solution increases and interionic attractions become important. Activities become smaller than the stoichiometric or measured concentrations. Higher concentrations of the ions are necessary before

equilibrium is established (Petrucci *et al.*, '93). This means that the solubility increases in solutions of higher concentrations.

Ion pair formation or complexation increases the solubility. In a saturated solution of M_1L_m there exist combinations of one $M^{m+}_{(aq)}$ ion and one $L^{l-}_{(aq)}$ ion present in solution as the ion pair $ML^{m-l}_{(aq)}$. The amount of ions taking part in the formation of ion pairs reduces the concentration of the dissociated ions. Higher amounts of the solute must be dissolved to maintain the required ion concentration to satisfy the solubility product constant.

For slightly soluble salts ($CaSO_4 \cdot 2H_2O$, $CaHPO_4$, ...) the solubility product constants are used in a correct way. If moderately or highly soluble salts ($MgNO_3$, KNO_3 , ...) are used, the K_{sp} value must be based on ion activities rather than on concentrations.

In an aqueous solution of the six essential macronutrients K^+ , Ca^{2+} , Mg^{2+} , NO_3^- , $H_2PO_4^-$ and SO_4^{2-} the following precipitation reactions have to be taken into account:

Tetracalciumhydrogentriphosphate, tricalciumdiphosphate and trimagnesiumbiphosphate are very insoluble precipitates. At the pH range of nutrient solutions almost no PO_4^{3-} is present. Should this case arise considerable amounts of the respective cations and anions would precipitate.

In nutrient solutions containing ammonia and inorganic carbonate also the following precipitation reactions have to be considered:

Using tap-water, magnesium and calcium ions may precipitate, changing the mineral composition of the nutrient solution. Potassium and ammonium ions are not involved in precipitation reaction.

RESULTS AND DISCUSSION

Ca₃(PO₄)₂ and Mg₃(PO₄)₂

Figure 1 represents the solubility of Ca₃(PO₄)₂ and Mg₃(PO₄)₂ as a function of the PO₄³⁻ concentration and the concentration of the respective cation. For each PO₄³⁻ concentration the maximum allowed Ca²⁺ or Mg²⁺ concentration can be calculated. Both Ca₃(PO₄)₂ and Mg₃(PO₄)₂ are very insoluble. Only very small concentrations of both cation and anion are present in a saturated solution. For a total phosphate concentration of 2.25 mmol/l there is only 3 · 10⁻¹² mmol/l of PO₄³⁻ present at pH 5. Due to this low PO₄³⁻ concentration in a general hydroponic nutrient solution, no Ca₃(PO₄)₂ nor Mg₃(PO₄)₂ precipitates.

CaHPO₄ and MgHPO₄

Hydrogenphosphate forms precipitates with both calcium and magnesium. In a nutrient solution with a total phosphate concentration of 2.25 mmol/l, there is 0.026 mmol/l HPO₄²⁻ present at pH 5. At this HPO₄²⁻ concentration and taking only the respective precipitation reactions into account, the maximum allowed calcium and magnesium concentrations is 39 and 197 mmol/l respectively (Figure 2). So, at this pH nor CaHPO₄ nor MgHPO₄ precipitates in the concentration range of nutrient solutions. However, as the pH of the nutrient solution increases, CaHPO₄ and MgHPO₄ may precipitate.

CaSO₄ and Ca(OH)₂

Considering only precipitation reactions, no CaSO₄ precipitates at the concentration range of calcium and sulphate in nutrient solutions (Figure 3).

Due to the high solubility product constant ($K_{sp} = 10^{-5.16}$) no Ca(OH)₂ precipitates in the pH range of nutrient solutions (Figure 4). At a Ca²⁺ concentration of 2.25 mmol/l, 55 mmol/l OH⁻ or a pH of 12.7 is necessary to precipitate Ca(OH)₂.

Ca₄H(PO₄)₃

The solubility of octo-calcium phosphate is pH dependent (Figure 5). Increasing pH, increases the solubility of Ca₄H(PO₄)₃. Due to the low PO₄³⁻ concentration in nutrient solutions no Ca₄H(PO₄)₃ precipitates.

MgSO₄ and Mg(OH)₂

At the Mg²⁺ and the SO₄²⁻ concentrations present in nutrient solutions no MgSO₄ precipitates (Figure 6). For a Mg²⁺ concentration of 1.5 mmol/l, a SO₄²⁻ concentration of 15.6 mol/l is necessary before MgSO₄ precipitates.

In a general hydroponic nutrient solution no Mg(OH)₂ precipitates (Figure 7). At a Mg²⁺ concentration of 1.5 mmol/l, an OH⁻ concentration of at least 3 mmol/l or a pH of 11.5 is necessary before Mg(OH)₂ precipitates.

CaCO₃ and MgCO₃

At a Ca²⁺ concentration of 5 mmol/l, CaCO₃ precipitates if the CO₃²⁻ concentration is 3 μmol/l or higher (Figure 8). In tap-water with a total inorganic carbonate concentration of 5 mmol/l and a pH of 7, CO₃²⁻ is present at a concentration of 2 μmol/l. To prevent precipitation in preparing a nutrient solution using tap-water, the pH is to be lowered first. Reducing the pH also reduces the CO₃²⁻ concentration.

Since the solubility product constant of MgCO₃ ($K_{sp} = 10^{-6.93}$) is about 10 times higher than that of CaCO₃ ($K_{sp} = 10^{-7.83}$) no MgCO₃ precipitates in nutrient solutions (Figure 9).

The solubility of Mg₅(OH)₂(CO₃)₄ strongly decreases as pH increases (Figure 10). In nutrient solutions no Mg₅(OH)₂(CO₃)₄ precipitates.

CONCLUSIONS

In nutrient solutions no precipitates are formed involving potassium, nitrate, ammonium or sulphate.

At a higher pH, Ca²⁺ and Mg²⁺ may form precipitates with HPO₄²⁻. In the pH range of nutrient solutions H₂PO₄⁻ is the dissociation form that is mainly present. In the concentration range of nutrient solutions no precipitates are formed with the different dissociation forms of phosphates. However, if the pH and/or the concentration range of nutrient solutions increases these precipitates can not be prevented.

If tap-water is used to prepare nutrient solutions CaCO₃ precipitates. This can be prevented by lowering the pH of tap-water before adding the nutrients. Reducing the pH also reduces the amount of CO₃²⁻ present.

Although in general no precipitates are formed at the concentration range of standard nutrient solutions, this may well be the case in the concentrated stock solutions or in the fertigated substrates. For tomato cropping on rockwool, nutrient solutions with an electric conductivity (EC) of 4 mS/cm or more are used. This increases the chance on the formation of precipitates. Furthermore, due to salt accumulation the nutrient solution in the substrates may easily reach an EC of 10 mS/cm.

Precipitation reactions are not only harmful because of the fact that elements are withdrawn from the nutrient solution and the mineral composition changes. The formation of precipitates on valves and trickle irrigation systems results in blockages. These blockages result in a heterogeneous production, diminishing the quality of the produce.

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FIGURE 6: Precipitation of MgSO_4
(I = 30 mmol/l)