An Empirical Model to Estimate Nutrients Concentration in Controlled Release Fertilizers Aqueous Solutions

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Abstract. Controlled release fertilizers (CRFs) insure controlled release of nutrients due to their coating. The aim of this study was to investigate the effect of nutrient solution parameters as well as time on the evolution of NO_3, NH_4, PO_4 and K concentrations. For this reason, 0.5 g of Multicote fertilizers 14-14-14 and 15-7-15 dissolved in 100 mL and 300 mL of deionized water respectively. The solutions remained at 24°C and their pH was adjusted once during their preparation at 5.5, 6.0 and 6.5 or adjusted every three days for a 24 days period. A linear empirical mathematical model was developed for the prediction of the above mentioned nutrients concentrations (C_X) in relation to the remaining (Vs) and the removed (dVs) volume of the nutrient solution, its pH and time (t) from its preparation. The model output compares favorably with data for the prediction of the concentration of these nutrients.

Keywords: soilless culture, hydroponics, multicote, fertigation, CRF

1 Introduction

Controlled release fertilizers (CRF) were introduced in the global market in recent years, in an attempt on behalf of the fertilizer industries to find ways to cover different needs either of crops, or of the producers themselves (Shaviv & Mikkelsen, 1993). The CRFs, according to their specifications, promise controlled release of nutrients, well synchronized in time with the needs of the crops (Trenkel, 2010). The time for the gradual release of nutrients from these fertilizers may range from 20 days to 18 months (Shoji & Gandeza, 1992). For this reason the use of CRFs in many crops like maize, wheat, rice etc. reduced significantly the production cost and the environment pollution. Recently the use of CRFs to high value crops (in particular ornamental, vegetables and orchards) led to the conduction of experiments in order to determine the release rate of nutrients in soil and aqueous solutions (Kinoshita, 2012).

In experiments concerning the use of CRFs in free water solutions and water saturated substrates, it is referred that the type of medium affect the nutrients release rate (Du et al, 2006). Besides that, the release of each nutrient element depends on

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several parameters such as fertilizers polymer coating, diffusivity, the concentrations of nutrient elements and the water content of the medium as well as its temperature (Du et al, 2004). Based on the above parameters, mathematical models have already been developed to describe the nutrient release rate of CRFs in soil. In addition, some research works revealed that the type of the fertilizers coating membrane play a key role for nitrate release in aqueous solutions, followed by other parameters like temperature (Du et al, 2008).

This paper examined the effect of some major characteristics of the solution such as pH, volume and temperature, the type of CRFs and the time from solution preparation on the alterations of nutrients concentrations. The results were used to develop an empirical mathematical model for the prediction of the evaluation of NO_3, NH_4, PO_4 and K concentration in aqueous solutions.

2 Materials & Methods

2.1 Treatments

For the purposes of the experiment, two types of Multicote fertilizers 14-14-14 and 15-7-15 (100% coated) were used for the preparation of two groups of aqueous solutions (six solutions in each group). Each solution in the first group had 100 ml volume and was prepared with the use of 0.5g of 14-14-14 fertilizer, while in the second group each solution had 300 ml volume and was prepared with the use of the same weight of 15-7-15 fertilizer. In two of the solutions from each group, the pH was initially (t_0) adjusted to 5.5, 6.0 and 6.5. In half of the above mentioned solutions the pH was adjusted once during their preparation (no buffered solutions), while in the other half solutions the pH was adjusted every three days (buffered solutions), in the initial value (namely 5.5, 6.0 and 6.5), with the addition of NaOH or HCl. During the experiment period the solutions were kept at a fixed temperature (24°C). The concentrations of NO_3, NH_4, PO_4 and K, the volume of the solutions remained after sampling and the pH were measured every three days for a 24 days period. The above measurements performed using LAMOTTE Smart 2 colorimeter, volumetric cylinder and HI991300 Portable pH/EC/TDS meter.

2.2 Statistical Analysis

Data were statistically analyzed by analysis of variance (ANOVA) using Statgraphics Centurion XVI. Duncan's multiple range test was used at a significance level of 0.05.

3 Results and Discussion

3.1 Evolution of pH in buffered and no buffered solutions

The pH evolution in no buffered solutions, where the pH was adjusted once at t_0 at 5.5, 6.0 and 6.5, is shown in Figure 1. However in these solutions the initial pH value and the type of CRF used for the preparation of the solution seems to affect significantly the evolution of pH during the experiment period.

In the above mentioned solutions with 300 ml volume prepared with the use of 15-7-15 fertilizer, pH varied slightly from the initial pH. As shown in Figure 1, when pH was initially adjusted to 5.5 or 6.0 it stabilized after fifteen days from the solution preparation close to 5.7, while in solution where the pH was adjusted initially to 6.5, it remained almost stable to the initial pH. In contrast, the pH in solutions with 100 ml volume prepared with the use of 14-14-14 fertilizer, increased significantly during a period of three days after its preparation. After this period the pH in all solutions stabilized at a value which was also relative to the initial pH of solutions. In solutions where pH was initially adjusted to 5.5 it stabilized at 6.0, while in solution where the pH was adjusted initially to 6.0 or 6.5 it stabilized at 6.5. The highest pH stability over most of the experiment period of solutions prepared with the use of 15-7-15 fertilizer compared to those prepared with the use of 14-14-14 fertilizer, may be due both to the type of the fertilizer and the volume of the solution.

In consequence pH adjustment was more efficient in solutions with volume 300 ml prepared with the use of 15-7-15 fertilizers than in those with volume 100 ml prepared with the use of 14-14-14 fertilizers, when it was attempted every three days, as presented in Table 1.

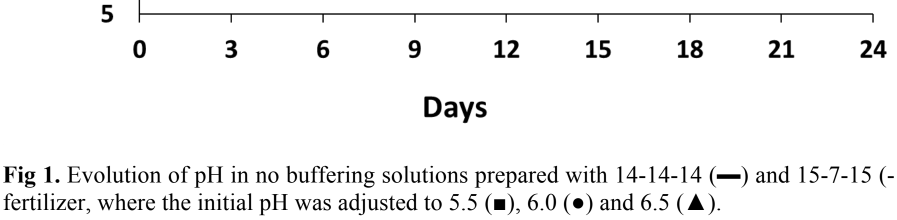

Fig 1. Evolution of pH in no buffering solutions prepared with 14-14-14 (▬) and 15-7-15 (- -) fertilizer, where the initial pH was adjusted to 5.5 (■), 6.0 (●) and 6.5 (▲).

Table 1. Average value of pH during the experiment period in buffered solutions prepared with the use of 14-14-14 and 15-7-15 fertilizer where the pH was adjusted every three days at the values 5.5, 6.0 and 6.5.

Fertilize Type	Volume of the Solution (ml)	Target pH 5.5	6.0	6.5
14-14-14	100	5.9±0.31	6.4±0.32	6.7±0.23
15-7-15	300	5.53±0.08	5.92±0.12	6.49±0.18

In specific, both pH stability and the efficient pH adjustment observed in solutions prepared with the use of 15-7-15 is due probably to the lower content in P_2O_5 this type of fertilizer has, compared to 14-14-14 fertilizer. It is a notable property of phosphate fertilizers to develop an alkaline pH in aqueous solutions when they are in presence. In addition the ability to predict the pH evolution of aqueous solution prepared with the use of CRFs, is of particular importance when it concerns nutrient solutions for soilless cultures.

3.2 Evolution of nutrient elements concentration in buffered solutions

The results of the measurements concerning the alteration of NO_3, NH_4, PO_4 and K concentration in solutions where the pH was adjusted every three days to the initial value, reviled a similar evolution of the concentration of these elements, regardless to the type of CRF used for solutions preparation. However, the concentrations that reached each one of the nutrients were significantly affected by the pH of the solution and probably by their volume (Figure 2). As seen in the above mentioned figure, both concentrations of NO_3 and K increased significantly during a period of nine days from t_0 where 14-14-14 fertilizer was used for nutrient solution preparation (Figure 2 A_1 and B_1) and three days from t_0 where 15-7-15 fertilizer was used for the same purpose (Figure 2 A_2 and B_2). The concentration of the above mentioned nutrients decreased during the next six days and it reached the minimum value twelve to fifteen days from t_0, where 14-14-14 fertilizer was used for nutrient solution preparation (Figure 2 A_1 and B_1), and six to nine days after t_0, where 15-7-15 fertilizer was used for the same purpose (Figure 2 A_2 and B_2). A similar alteration pattern was observed for both nutrient elements during the next period until the end of the experiment.

The concentration of NH_4 in solutions prepared with different CRF type, altered following almost the same pattern (Figure 2 C_1 and C_2). The pH and probably the volume of the solution seems that also in this case affected the rate and the concentration increment as well as the higher concentration level that NH_4 reached in these solutions.

However similar higher concentration levels of NO_3, NH_4 and K were observed in the solutions prepared with the different CRFs, probably because of their similar composition concerning N and K. The decrease of NO_3, NH_4 and K concentration shown in Figure 2 may be attributed to the KNO_3 and NH_4NO_3 complexes, formatted in the solution, when the concentration of NO_3, NH_4 and K was increased. In that solutions precipitations were visible.

In contrast PO_4 concentration was continuously increased after solutions preparation except from the solution with volume 100ml prepared with the use 14-14-14 having pH 5.5 where a decrease of PO_4 was observed fifteen days after t_0 (Figure 2 D_1 and D_2). This may be occurred to KH_2PO_4 and $NH_4H_2PO_4$ complexes formed in the solution due to the high concentration of K and NH_4. In that solutions precipitations were visible. In addition the above complexes formation may be favored because of the higher content in PO_4 that 14-14-14 fertilizer has.

According to the above, since pH affect significantly the release, and therefore the concentration of nutrients in the solutions, may become an alternative to the temperature in order to control efficiently the nutrients elements concentration in nutrient solutions used in soilless culture.

3.3 Model development

The above mentioned results reveal that the pH, the volume of the solution, the time from their preparation and the type of the CRF fertilizer play a significant role on the evolution of NO_3, NH_4, PO_4 and K concentration. Specifically the pH of the aqueous solution and undoubtedly their volume seems to affect both the nutrients release rate and the level of their concentration, regardless to CRF type used for their preparation. The time is another parameter that also undoubtedly affect the release rate of the nutrients since in CRFs fertilizers coating membrane plays exactly this role, to control the nutrients release in a course of time (Wang et al., 2011).

Taking into account all the above mentioned parameters, an empirical mathematical equation to estimate the NO_3, NH_4, PO_4 and K concentration in aqueous solutions prepared with 14-14-14 and 15-7-15 CRF fertilizers was developed. The form of the equation if the following:

$$C_X = a + b * Vs + c * dVs + d * pH + e * t \qquad \textbf{(1)}$$

Where: C_X = the concentration of NO_3, NH_4, PO_4, K at time t
Vs = the sum of the volume removed by sampling
dVs = the volume of the solution removed in each sampling
pH = the pH at time t
t = the time (in days) from the preparation of the solution

To calibrate the model described with equation (1), measurements performed in 100 and 300ml solutions prepared with the use of 14-14-14 and 15-7-15 CRF, were used. Statgraphics Centurion XVI software was used in order to estimate the a, b, c, d and e parameters used in equation (1) and presented in Table 2 and 3.

Figure 3 shows the 1:1 linear correlation between measured and estimated from the equation (1) values of the concentration of NO_3, NH_4, PO_4 and K in aqueous solutions prepared with the use of 14-14-14 and 15-7-15 CRF. The correlation of the following values is linear, since the equation describing the relation between the measured and calculated values has the form of y = a * x + b, in which a and b do not differ statistically from the values 1 and 0 respectively (Gauch et al, 2003).

4 Conclusions

In this work similarities concerning the evolution of NO_3, NH_4, PO_4 and K concentration were reviled among aqueous solutions with different volumes, which were prepared by using CRFs with different composition. In all these solutions parameters such as pH, the volume of the solution, the type of CRF fertilizer used for their preparation, as well as the time from their preparation affected significantly the rate of nutrients release and the evolution of nutrients concentration.

Based on the above mentioned parameters an empirical mathematical model was developed and calibrated in order to predict the concentration of NO_3, NH_4, PO_4 and K in aqueous solutions prepared with the use of CRFs. The model output compares favorably with data for the prediction of the concentration of these nutrients.

Although most of the researchers refer that temperature is the most important factor that influence the diffusion and therefore CRFs nutrients release, the above measurements revealed that pH might affect significantly the release, precipitation and the final concentration of nutrients in aqueous solutions.

However additional research is necessary to identify other parameters that may affect the release of nutrients from the CRFs in aqueous solutions. This information could be used to improve the mathematical model efficiency. With the perspective of using CRFs to prepare nutrient solutions, the above mentioned model can be used to determine the optimal solution management.

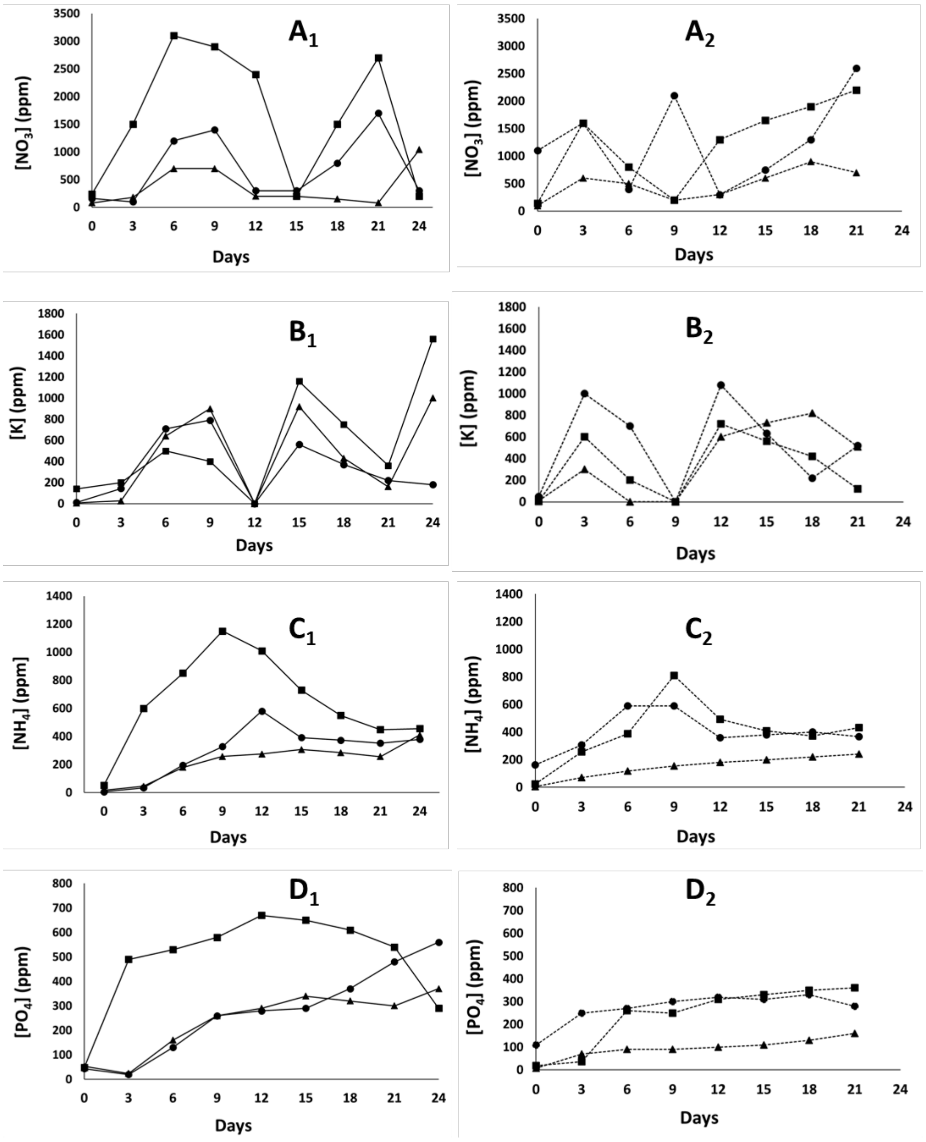

Fig 2. Alteration of NO_3, NH_4, PO_4 and K concentration, in solutions prepared with the use of 14-14-14 (▬) and 15-7-15 (- -) fertilizer, where the pH was adjusted in the initial value 5.5 (■), 6.0 (●) and 6.5 (▲).

Table 2. The values of a, b, c, d and e parameters used in equation (1) for the estimation of NO3, NH4, PO4 and K, when 14-14-14 fertilizer was used for the preparation of the solution.

Nutrients Concentration	**Parameters**					
C_X	**a**	**b**	**c**	**d**	**e**	R^2
C_{NH4}	-3852,33	15016,7	-1071,11	-405,556	-473,889	0,78
C_{PO4}	-1301,58	3016,67	- 945,278	61,1111	-77,2222	0,99
C_{NO3}	-6347,5	63500	-3191,67	-3333,33	-2233,33	0,99
C_K	25692,5	-40300	-525	-1000	1260	0,91

Table 3. The values of a, b, c, d and e parameters used in equation (1) for the estimation of NO3, NH4, PO4 and K, when 15-7-15 fertilizer was used for the preparation of the solution.

Nutrients Concentration	**Parameters**					
C_X	**a**	**b**	**c**	**d**	**e**	R^2
C_{NH4}	15863,4	3307,4	-1800,14	-2997,53	-106,619	0,86
C_{PO4}	-1553,17	-170,333	-573,763	350,805	13,5193	0,99
C_{NO3}	-49865	-8680,61	1338,12	9695,82	349,24	0,95
C_K	-32142,2	1629,09	1654,68	5543,73	13,8593	0,82

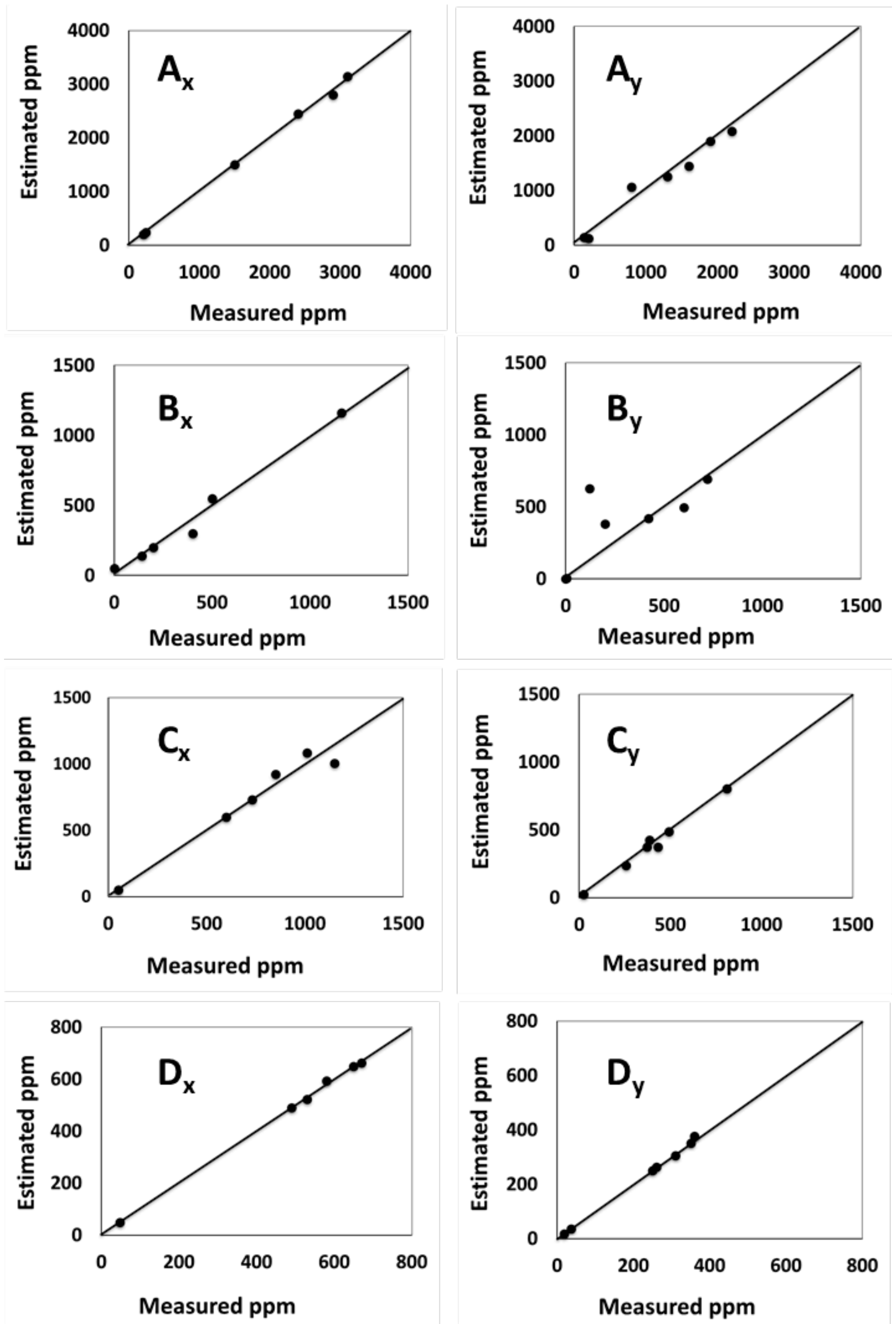

Fig. 3. The 1:1 linear correlation between measured and estimated from the equation (1) values, of the concentration of NO_3 (**A**), K (**B**), NH_4 (**C**) and PO_4 (**D**) in aqueous solutions prepared with the use of 14-14-14 (**x**) and 15-7-15 (**y**) CRFs.

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