Control of $N\text{-}NH_4^+$ and K^+ leaching in potato using a carrageenan hydrogel

Control de la lixiviación de $N\text{-}NH_4^+$ y K^+ en papa mediante un hidrogel de carragenina

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ABSTRACT

Potato cultivation requires fertilizers to sustain crop yields, but a significant percentage of added nutrients is lost by leaching. The use of coating materials for fertilizers is currently being considered to reduce these losses. The objective of this study was to determine if a carrageenin based hydrogel (CBH), used to coat fertilizer, decreases NH_4^+ and K^+ leaching from a potato crop without affecting growth, specific gravity, and tuber yield. The CBH was tested in a diploid potato crop, cultivar Criolla Colombia (*Solanum tuberosum* L., Phureja Group) using a randomized full block design including the treatments noncoated fertilizer (T1), CBH coated fertilizer (T2), and no fertilizer (T3). Mineral nutrients in soil leachates together with dry biomass, foliar area, chlorophyll, tuber specific gravity, and yield were quantified. The nutrient content in leachates from T2 were below those from T1. No significant differences between treatments were observed for growth factors, yield, and tuber specific gravity. This study confirms the controlling effect of the CBH, ensuring the retention of the nutrients added in the fertilizer and preventing them from easily leaching. Future field studies are worthwhile to establish the amount of fertilizer this coating could save.

Key words: controlled release fertilizers, soil pollution, coating, environmental protection.

RESUMEN

El cultivo de papa requiere fertilizantes para mantener su rendimiento. Sin embargo, un porcentaje significativo de los nutrientes añadidos se lixivia. Actualmente el uso de materiales de recubrimiento para los fertilizantes se está considerando para disminuir estas pérdidas. El objetivo de este estudio fue determinar si un hidrogel a base de carragenina (CBH, por sus siglas en inglés), utilizado para recubrir el fertilizante aplicado, puede disminuir la lixiviación de NH_4^+ y K^+ en un cultivo de papa, sin afectar el crecimiento, gravedad específica y el rendimiento de tubérculo. El CBH se probó en un cultivo de papa diploide, cultivar Criolla Colombia (*Solanum tuberosum* L., Grupo Phureja) utilizando un diseño de bloques completos al azar. Se evaluaron los tratamientos: fertilizante sin recubrimiento (T1), fertilizante recubierto con CBH (T2) y sin fertilizante (T3). Se cuantificaron los nutrientes minerales en los lixiviados junto con biomasa seca, área foliar, clorofila, gravedad específica del tubérculo y rendimiento. Los contenidos de nutrientes en los lixiviados de T2 fueron inferiores a los de T1, y no se observaron diferencias entre estos tratamientos para factores de crecimiento, rendimiento y gravedad específica. Los resultados evidencian que el CBH tiene potencial como material de recubrimiento para fertilizantes en papa y, se debe complementar con otros ensayos para determinar la cantidad de fertilizante que este recubrimiento podría ahorrar.

Palabras clave: fertilizante de acción controlada, polución del suelo, revestimiento, protección del medio ambiente.

Introduction

The potato has been recognized as a key product for providing food security for the growing human population, particularly in developing countries (Devaux *et al*., 2020). This food crop stands out among others because it is an accessible source of nutrients (Wijesinha-Bettoni & Mouillé, 2019) that grows in a wide range of environmental conditions (International Potato Center, 2017), and its commercial value is resilient to price volatility at the global level due to its local production and distribution (Campos & Ortiz, 2019). Therefore, potato crops are expected to strengthen a sustainable capacity to supply sufficient human nutrition. Nevertheless, there are important challenges that must be overcome to ensure environmental sustainability. One of the biggest issues in potato production is to optimize the use of fertilizers to minimize the negative impacts of current fertilization practices on the environment (Tilman, 1999). Potato is a species with high nutritional demand per kg of produced dry mass. A commercial crop of diploid

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potato extracts, in a productive cycle, 124 kg ha^{-1} of nitrogen (N), 25.4 kg ha^{-1} of phosphorus (P) and 258.2 kg ha^{-1} of potassium (K) (Suarez &Torres, 2014). The demand for nutrients implies high fertilization doses to sustain high crop yields (Rajiv & Kawar, 2016). Consequently, potatoes are one of the crops with the highest application doses using 243 kg ha^{-1} of fertilizers (FAO, 2006) for a production of 370 million t over more than 17 million ha around the world (FAOSTAT, 2019). Locally in Colombia, applications doses in commercial diploid potato are around 833.3 kg ha^{-1}, and the nutrient doses applied of added fertilizers are around to 125 kg ha^{-1} N, 54.6 kg ha^{-1} P, and 104 kg ha^{-1} K (Alvarado & Ramírez, 2018), exceeding those reported by FAO (2006).

Despite the increase in yields per unit area achieved with the application of chemical fertilizers (FAO, 1981), only 30-35% of the N, 18-20% of the P and 35-40% of K present in the chemical mixtures are actually absorbed and used by the plants in agricultural crops (Subramanian *et al*., 2015), meaning that more than half of the applied fertilizers are quickly lost into the environment through runoff, leaching, and/or volatilization (Huang *et al*., 2017). The non-absorbed N and P are the main drivers of serious environmental problems such as water pollution, eutrophication-caused reductions in biodiversity (Whitters *et al*., 2014; Diatta *et al*., 2020), global warming (Bouwnman *et al*., 2002), and reductions in the ozone layer (Molina-Herrera *et al*., 2016). Unless there is a rise in fertilizer efficiency, a significant increase in NPK fertilizer application is expected by 2050 due to the increasing demand for food (Drescher *et al*., 2011) triggering a greater negative impact on the environment.

One of the strategies for facing this issue is to optimize the use of fertilizers in potato crops by implementing controlled release fertilizers. This technology maintains constant slow rates of nutrient release into the soil allowing synchronization between the onset of nutrient uptake by the plants and availability of nutrients (Naz & Sulaiman, 2016). Meanwhile, this technology reduces leaching by rain or irrigation water, mitigating eutrophication and the release of greenhouse gases into the atmosphere (Cong *et al*., 2010). To achieve controlled release, fertilizers are encapsulated in mineral and organic polymers known as coating agents (Azeem *et al*., 2014; Ali & Danafar, 2015; Guilherme *et al*., 2015). However, the materials used in the coating agents are often non-biodegradable, costly, toxic, and inconsistent in their release patterns and rates (Azeem *et al*., 2014; Naz *et al*., 2016). Recently, a carrageenin based hydrogel (CBH) has been proposed as a new encapsulating agent for fertilizer granules. This has extra advantages: its main component is carrageenan, a sulfated polysaccharide from the wall of red algae *Hypnea musciformis* (Wulfen) J.V. Lamouroux (Rozo *et al*., 2019); the alga is abundant in the coasts and widely distributed throughout the tropics and warm temperate seas in the eastern and western Atlantic. This alga is found in Southeast Asia (Ang *et al*., 2014), the Philippines (Lastimoso & Santiañez, 2021), Asia (Titlyanova *et al*., 2016), the southern China (Phang *et al*., 2016), and the Caribbean (Camacho & Montaña-Fernández, 2012). In addition, this natural hydrogel is relatively simple in structure and chemical composition, porous, semi-permeable, easy and inexpensive to synthetize, biodegradable and non-toxic (Blakemore, 2016; Hilliou, 2021; Guo *et al*., 2022). Fertilizers coated with urea and acrylamides have existed since the 1960s. However, since 1996 alginate and chitosan biopolymers were developed with a different synthesis technology than the one used for the CBH (Fertahi *et al*., 2021). Chitosan has shown good results in corn (Kumaraswamy *et al.,* 2021). The use of kappa carrageenan as a coating material is still very new and there are still no studies evaluating this material as a coating in the field.

The CBH is a natural material that seems to have high potential as a coating to optimize fertilizers, ensuring the same yields while minimizing negative impacts in the environment; however, its efficiency at the field scale remains unexplored. Although it is known that the charges in its structure may have a natural potential to retain cations, it has not yet been explored whether, once the ions are retained, they are released from the hydrogel and absorbed by the plant. Knowledge of the integrity of the gel under the environmental conditions of the crop is absent but it is known that the encapsulating fertilizers with the CBH significantly reduced the N-NH_4^+ and K^+ in leachates from laboratory soil column experiments carried out with a soil from an Andean potato crop (Santamaría *et al*., 2019). The CBH did not have a major impact on the P leaching because in these soils this element is not leached. In general, potato crops in Colombia are in soils with high iron and aluminium content and a pH ranging between 4.5 and 6.0 (FAO, 2019), inducing the P in the fertilizer to absorb by the Fe/Al oxides (Hanyabui *et al*., 2020); therefore, P leaching is low. Furthermore, CBH encapsulation did not have a negative impact on the growth and quality of potato (*Solanum tuberosum* L., Phureja Group, cv. Criolla Colombia), since the encapsulated fertilizer was as effective as the non-encapsulated in green house experiments with plants cultivated in pots with soil (Santamaría *et al*., 2019). These results look promising; however, in order to propose the CBH as an environmentally friendly alternative to be implemented in potato crops, an evaluation of its efficacy in field experiments is necessary. The objective of this study was to test whether the CBH coating around granulated fertilizer could reduce NH_4^+ and K^+ leaching without impacting plant growth, specific gravity, and yield of a commercial potato crop.

Materials and methods

Study area

This study was conducted in a *Solanum tuberosu*m L. crop at the San Isidro farm in the municipality of Sibaté (4°25'42"N; 74°17'58.4"W), located at 2720 m a.s.l. (Cundinamarca, Colombia) that supplies local markets of the Cundinamarca region. The production cycle took place between August and December of 2018, a period with an average temperature of 12.7ºC and a maximum/minimum of 15.3/7.1ºC. Collected soil samples were analyzed at the CIAT analytical laboratory for the physicochemical properties of the top (0 to 15 cm) soil layer (Tab. 1). Based on the levels of nutrient availability, the soil had a deficit in the amount of assimilable nitrogen (16.8 kg ha^{-1}), since 1 ha of the cv. Criolla Colombia potato extracts on average 124 kg of nitrogen (Suarez &Torres, 2014). Both phosphorus and potassium are present in optimal concentrations with respect to the concentration requirements of the crop (Suarez & Torres, 2014).

TABLE 1. Main soil properties at the San Isidro farm.

Property	Method	Value
pH	1:1 Soil water	4.92
Organic carbon	Walkley-Black	25.40%
Total N	Acid digestates-(sulfuric-salicylic)	5094 mg kg^{-1}
$N-NH_4^+$	1 M KCl-extraction	9.7 mg kg^{-1}
Extractable P	Bray II	31.6 mg kg^{-1}
Extractable K	Bray II	0.252 cmol kg^{-1}
Ca	1 M KCl-extraction	5.16 cmol kg^{-1}
Mg	1 M KCl-extraction	0.44 cmol kg^{-1}
Al	1 M KCl-extraction	1.245 cmol kg^{-1}
Fe	Dilute double acid extraction: 1 M HCl and 5 M H_2SO_4	6,62 cmol kg^{-1}
CECe	Sum of interchangeable bases plus Al	7.10 cmol kg^{-1}

Data source: soil samples collected at the study site and analyzed at CIAT analytical laboratory.

Field experiment

Experimental design

Three treatments were compared in a randomized block design with three replicates for a total of nine experimental plots of 15 m^2 each. Each plot was planted with two rows spaced 1 m apart and 25 plants per row with 0.3 m between plants in a row for a population of 33,333 plants ha^{-1}. The treatment of the plot T1 was fertilized with the nonencapsulated fertilizer and the treatment plots T2 were fertilized with the CBH hydrogel encapsulated fertilizer. A control treatment T3 was established with no fertilizer added to the plots. We used cv. Criolla Colombia (*S. tuberosum* L., Phureja Group), because this is the most cultivated diploid variety in Cundinamarca, with 120 d of cultivation cycle at 2600 m a.s.l (Ñústez & Rodríguez, 2020) and because of its excellent nutritional attributes (Thomas *et al*., 2021) and high required fertilizer applications (Alvarado & Ramírez, 2018), demand the design of innovative management strategies to reduce environmental impact. Also, the Phureja group is diploid and displays superior performance of agronomic traits, unlike *Solanum tuberosum* L. that is autotetraploid (Tai & Xiong, 2003) and has restrictions in the advancement of genetic improvement (Camadro & Mendiburu, 1988).

Fertilization treatments

Field preparation and management practices followed those used at the San Isidro farm. The land was dredge plowed and the furrows were constructed using a manual hoe. Fertilizer treatments with and without coating, consisted of 25 g of a granulated fertilizer (Vecol 15-15-15-11 with N 15%, P_20_5 15%, K_2O 15%, S 11% (Phosagro, Rusia) that contains only ammoniacal N) applied once per plant at the time of sowing. This amount corresponded to 833.3 kg ha^{-1}. In T2, the 25 g of fertilizer were distributed in 11 capsules of the CBH hydrogel. The capsules had a cylindrical shape of 15.4 cm^3 and contained 2.27 g of fertilizer (14% w/v). The encapsulated fertilizer was prepared as described in Santamaría *et al.* (2019). For both treatments, the 25 g of fertilizer were placed at 10 cm around the seed (Fig. 1). Finally, fertilizer and seed were covered with a layer of about 5 cm of soil. Selected seed tubers, about 5 cm in diameter, of the cv. Criolla Colombia were obtained from farmers of the region.

Rainfall was recorded daily using a conventional rain gauge. Precipitation registered a total of 481 mm during the production cycle. This precipitation corresponded to the second rainy peak at this locality. Supplemental irrigation was not performed.

Collected samples

Soil leachates

To collect leachates containing the nutrients not absorbed by the roots, three suction lysimeters were installed (SSAT

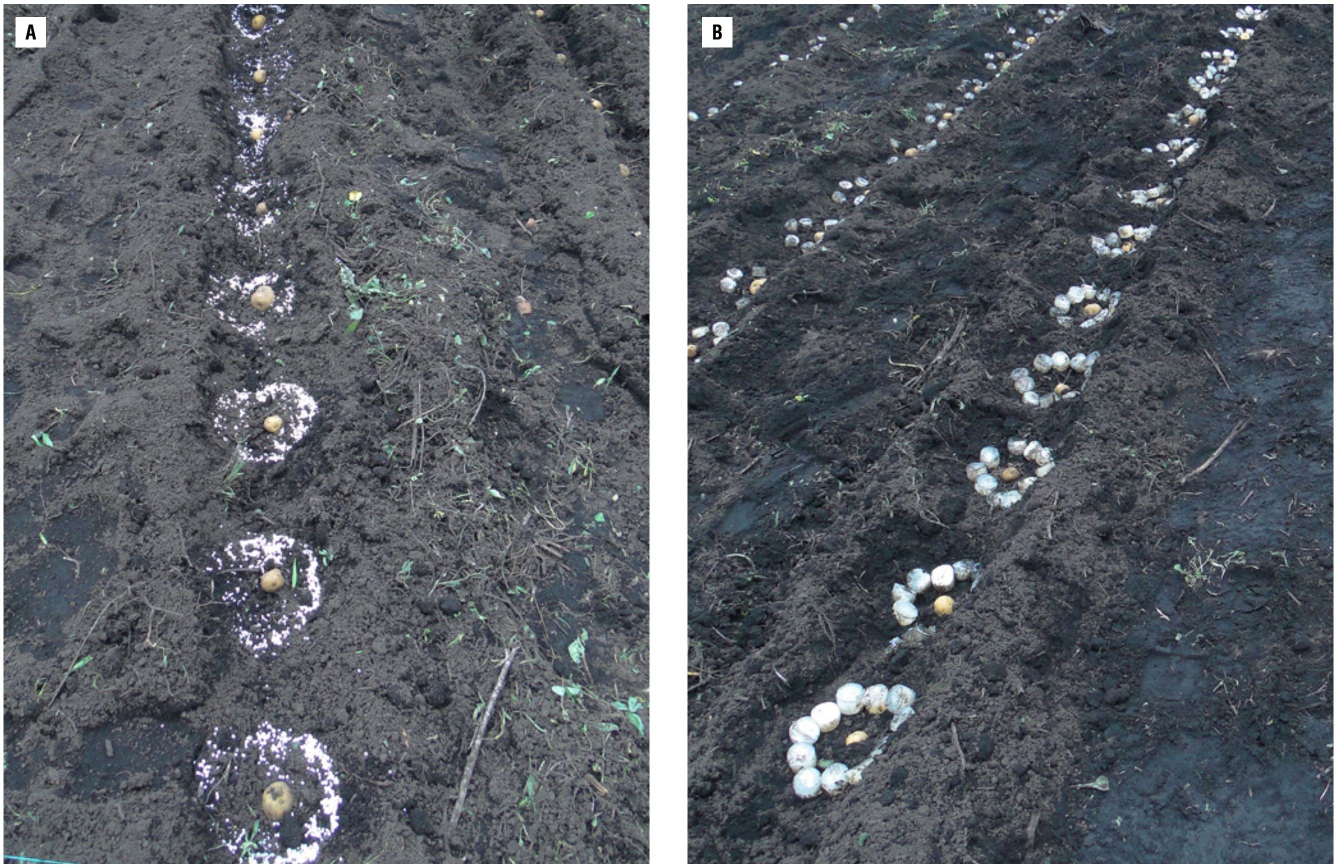

FIGURE 1. Fertilizer distribution around the potato seed. A) Treatment 1=noncoated fertilizer and B) treatment 2=CBH coated fertilizer.

Model, Irrometer Company, Inc., USA) the planting day in each experimental plot. Lysimeters were installed at 40 cm depth to ensure that the sampling of soil draining water not absorbed by the plants. At this depth, the leachates have moved beyond the reach of the roots that are typically 30 cm long in the cv. Criolla Colombia (C. Ñústez, personal communication, February 15, 2019). Lysimeters were placed next to the plants. Leachate volumes were sampled weekly up until 50 d after sowing (das). This time interval included the phenological growth stages of germination (BBCH 0), leaf development (1), formation of lateral shoots (2), longitudinal growth (BBCH 3), development of harvestable vegetative parts (BBCH 4), and appearance of floral organs (BBCH 5) based on the BBCH scale of phenological growth stages (Hack *et al*., 1993). Their content of NH_4^+ and K^+ was quantified in the Analytical Services Laboratory of the International Center for Tropical Agriculture (CIAT). The NH_4^+ was analyzed by the automated spectrophotometry method using a Skalar Sanplus Analyzer SA 3000/5000 Mode 5000-01 (Skalar Analytical B.V, Netherlands) and atomic absorption spectrophotometry (Unicam Solar 969 spectrophotometer, Unicam company, England) was used to quantify K^+.

Plant material samples and measured growth variables

To compare plant growth among the treatments, destructive samplings were conducted on three plants from each experimental plot fortnightly from 14 d after emergence (dae), until 8 d before harvest, which took place 126 d after planting. We quantified the total plant dry mass (PDM) (g), tuber dry mass (TDM) (g), foliar area (FA) (cm^2), and chlorophyll content (SPAD units). In all cases, the result was expressed as the average of the nine sampled plants.

The PDM was the sum of the dry weight of leaves, stems, flowers, and tubers on each plant. Dry weight of plant organs was determined after dehydration of the fresh samples in an oven at 70°C until they reached constant weight. Tuber dry mass content was determined by chopping all the tubers from the same plant and drying this material in an oven at 70°C until a constant weight was reached. Leaf area was quantified using a digital camera (Canon EOS-Rebel T3) and following the methodology of Campillo *et al.* (2008). The relative content of chlorophyll was measured with a portable chlorophyll meter (SPAD-502 plus, Konica Minolta, Inc., Japan) on the third or fourth fully expanding leaf of the upper third in three plants per experimental plot. Three measurements per leaf were averaged.

At the time of harvest, we conducted destructive sampling to quantify tuber weight and size. Tubers from 30 different plants from each plot were classified according to the local commercial category bases on tuber diameters: > 4 cm, between 2 and 4 cm and < 2 cm. The tuber yield per plot was expressed in t ha^{-1}. The specific gravity, a commercial quality indicator, was determined for 10 tubers (> 4 cm diameter) randomly taken from each treatment after harvest, using both the weight in water and weight in air method (Bonierbale *et al.*, 2010).

Data analysis

The assumptions of normality were verified by the Shapiro-Wilk and Kolmogorov-Smirnov tests. The homogeneity of variance was verified by the Levene test. If any variable did not meet the assumptions, a Box-Cox transformation was performed, and an analysis of variance was performed again.

Concentrations of $N\text{-}NH_4^+$ and K^+ in leachates did not meet the assumptions after transformation. Therefore, we tested if the treatment and the das explained the concentrations of $N\text{-}NH_4^+$ and K^+ in the leachates using generalized linear models (GLM, R core packages Stats version 3.6.2) followed by model selection. We conducted two independent models, one for each nutrient. The response variable was the concentration (mg L^{-1}), while the treatment and das were the fixed effects. We used a GLM from a Gaussian family, since a preliminary analysis, (Supplementary material 1 [S1]) showed our data deviated from the linear regression assumptions only slightly. To increase the robustness of our analysis, we used the corrected Akaike's information criterion (AICC) and dredge automated model selection tool (dredge, R package MuMIn; Bartón, 2020), instead of minimum squares to determine the significance of each predictor. We report the model averaged coefficients and 95% confidence intervals (considered significant if they did not overlap with 0) of the resulting models. Models with ΔAICC < 2 were not considered different, so the simpler model was preferred for that case. All statistical analyses were performed in R 3.6.3 (R Core Team, 2018).

Regarding plant growth and yield evaluation, a main effects analysis of variance (ANOVA) was applied to determine differences among treatments. The data from each sampling date were analyzed separately to determine the treatment effect on a phenological crop stage. Average values were compared by the Tukey's HSD post hoc analysis. These statistical analyzes were conducted with the software STATISTICA (version 7: StatSoft Inc., Tulsa, USA), with a significance level of α=0.05.

Results and discussion

Nutrient leaching

Overall, the greatest effect of the CBH on nutrient leaching occurred from the second week after sowing (Fig. 2 A, B). The highest leachate concentrations of $N\text{-}NH_4^+$ occurred in T1 (1.05±0.51 mg L^{-1}, mean ±standard deviation [SD]) at 15 das (Fig. 2A), a time at which the plants had not yet developed a root system to take the nutrients supplied through the fertilizer. The $N\text{-}NH_4^+$ in the leachates collected in T2 at 15 das (0.16±0.03 mg L^{-1}), was lower than in T1 and showed similar $N\text{-}NH_4^+$ values to those in leachates from the control treatment T3 (0.12±0.005 mg L^{-1}). Likewise, at 22 das the $N\text{-}NH_4^+$ in the leachates from T2 (0.12±0.01 mg L^{-1}) was lower than in T1 (0.423±0.145 mg L^{-1}), although the difference between T1 and T2 decreased. At 29 das, an important reduction in the $N\text{-}NH_4^+$ concentration was observed in leachates from T1 (0.28±0.13 mg L^{-1}) with closer but still higher values to those observed in T2 (0.13±0.01 mg L^{-1}) and T3 (0.10±0.002 mg L^{-1}). After 36 d, high N values were observed in the leachates from T1, but leachates from T2 and the control remained as in the previous sampling dates. Regarding the K^+ ion (Fig. 2B), its concentration in the leachates from T2 (4.18±0.75 mg L^{-1}) was lower than in T1 (6.39±1.09 mg L^{-1}) from 15 d.

In previous studies, the mathematical models that follow the ions leaving the gel as a function of time describe a gradual release (Rozo *et al.*, 2019). Results for AIC model selection criteria (S2) showed that only the variable treatment had an effect on the concentration of $N\text{-}NH_4^+$ and K^+ in the soil. Results of the linear models are shown in Table 2. The estimate for T1 was different from the control, indicating that the application of uncoated fertilizer increased the ammonia and potassium ions in leachates. Conversely, T2 was no different from the control for any of the two nutrients, indicating that the coating reduced nutrient leaching to the same level as the control, reducing the environmental risk of using fertilizers.

It is important to highlight the large variation for $N\text{-}NH_4^+$ concentration in the leachates from plots under T1 (Fig. 2A). This may be the result of non-homogeneous fertilizer distribution in the crop soil plus the lateral flow of the water produced by the soil heterogeneity and the land slope that together may change the expected downward vertical transport of the infiltration water towards horizontal

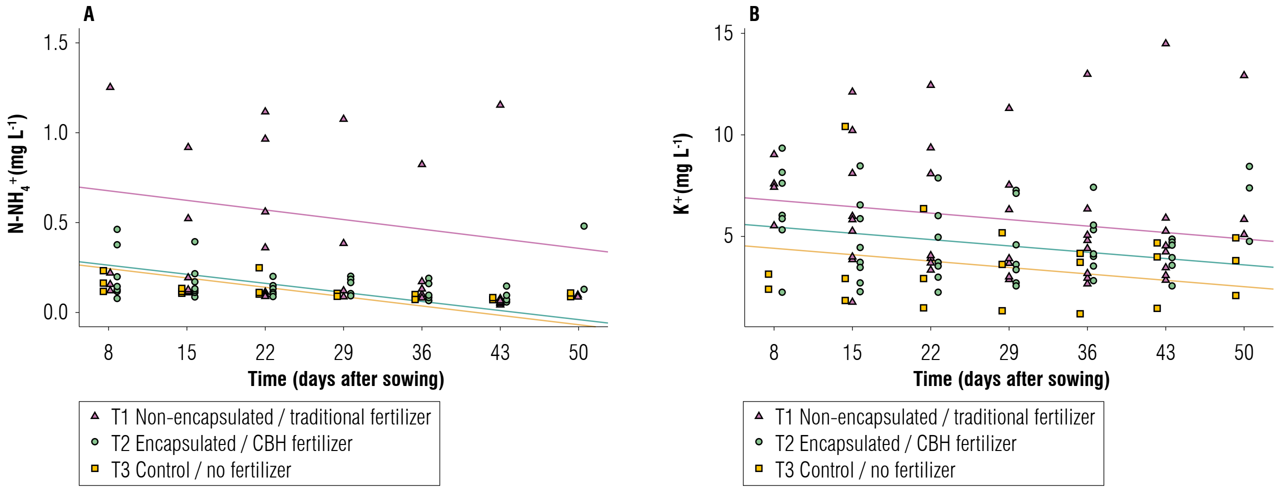

FIGURE 2. Nutrient concentration in soil leachates over time. The first seven weeks of the crop cycle in the San Isidro Farm are shown. A) Generalized linear models-GLM for $N\text{-}NH_4^+$ and B). generalized linear models-GLM for K^+. Number of analyzed leachate samples per treatment 1 and 2 in each sampling date=9.

TABLE 2. Results of the generalized linear models for the concentrations of the $N\text{-}NH_4^+$ and K^+.

	R^2 (%)	Parameter	Estimate	95% C.I.
		Intercept	0.305	
$N\text{-}NH_4^+$ (mg L^{-1})	10.15	Time	-0.007	-0.0148; 0.0017
		T1 (Uncoated fertilizer)	0.384	**0.0758; 0.6992**
		T2 (Coated fertilizer)	0.015	-0.2874; 0.3179
		Intercept	4.169	
K^+ (mg L^{-1})	12.38	Time	-0.019	-0.0556; 0.0172
		T1 (Uncoated fertilizer)	2.469	**1.1169; 3.8220**
		T2 (Coated fertilizer)	1.151	-0.1946; 2.4971

The estimates for each parameter are shown. The intercept corresponds to ion concentration in the control (no fertilizer) at the beginning of the experiment (d=0). The parameter "Time" indicates the change in concentration according to the d, which is constant for all treatments (no interactions). The percentage of variance explained is shown as the R^2 in %. The effect of each treatment (coated or uncoated) was determined as the difference between their intercept and the control given by a 95% confidence interval (C.I.) around the estimate. The intervals that indicate a significant difference from the control (those that do not overlap with 0) are highlighted in bold.

transport of the water (Hardie *et al.*, 2012; Kim & Mohanty, 2016). Ideally, diffused nutrients from the fertilizer placed around the tuber seed would be expected to be mobilized primarily vertically into deeper layers of the soil profile by water infiltration. As a result, the fraction of the volume of the water infiltration sucked by the lysimeters placed in T1 plots would be expected to contain a high concentration of nutrients in all leachate samples. Nevertheless, the redistribution of the infiltration that resulted from the preferential water flow could avoid the infiltration water to move vertically into deeper layers of the soil profile towards the lysimeter (Bundt *et al.,* 2001; Starr & Timlin, 2001; Zhang *et al*., 2018). Therefore, some lysimeters in the T1 plots probably collected infiltrated water coming from soil areas not directly influenced by the fertilizer, yielding lower contents of $N\text{-}NH_4^+$ for some of the leachate samples. On the other hand, the variation in nutrient content of leachates collected from T2 was small and similar to that of the control, indicating that plots under T2 had a homogeneous low $N\text{-}NH_4^+$ concentration across the soil surface as a result of the control that CBH exerts on the exit rate of $N\text{-}NH_4^+$ from the fertilizer.

The CBH is more efficient regulating the $N\text{-}NH_4^+$ than the K^+ leaching. When the mean ion concentration in T2 is subtracted from T1, the difference is higher for K^+ than for $N\text{-}NH_4^+$, suggesting a greater effect of the CBH on K retention. However, there was a wider range of K^+ concentration values in leachates sampled in T2 (from 22 d until the last sampling date) than the one registered for $N\text{-}NH_4^+$ in T2 (Fig. 2B), pointing out that the CBH exerts less control over the diffusion of this ion from the fertilizer granule and reiterating previous laboratory results. This occurs because the presence in the hydrogel network of carboxyl and sulfate negative charges had a greater influence on the retention of the ammonium ion as a result of a greater hydration radius in NH_4^+ than in K^+ (Guilherme *et al.,* 2015; Xu, 2019). Anyway, less variation was observed for K^+ in T2 than in T1 due to the presence of the CBH. Greater retention of potassium in the CBH could be achieved by using carrageenan with a higher content of sulfates.

Subsequent field trials with an experimental design including a greater number of replicates and plots are necessary. This is essential to measure the amount of fertilizer that can be saved using the CBH encapsulated fertilizer.

Crop growth and yield

From the beginning of tuberization detected at 42 d after emerging (dae), the PDM, FA, and TDM tended to have lower values in the plots treated with the CBH encapsulated fertilizer, but no significant differences were found among T1 and T2 for most sampling dates (Fig. 3).

No significant differences were observed among treatments for chlorophyll content (Fig. 3D) and specific gravity that showed an average value of 1.081 (±0.003) for T1, 1.078 (±0.010 SD) for T2 and 1.106 (±0.025) for T3 (Fig. 4A). Potatoes in T2 had lower mean yields than T1 in all categories of tuber diameter, although there were no significant differences between treatments (Fig. 4B). The lowest yields were recorded in T3.

The lower PDM and TDM trend in plants under T2 warns of the possibility that the current CBH formulation might decrease the crop yield below that achieved by using the non-CBH encapsulated fertilizer. The CBH could be retaining nutrients around the fertilizer, harming the development of the leaf area, and diminishing the interception of photosynthetically active radiation, hence affecting the total biomass production (Allen & Scott, 1980; Santos Castellanos *et al*., 2010; Gómez *et al*., 2017). Nonetheless, more field trials are needed to confirm a negative effect of the

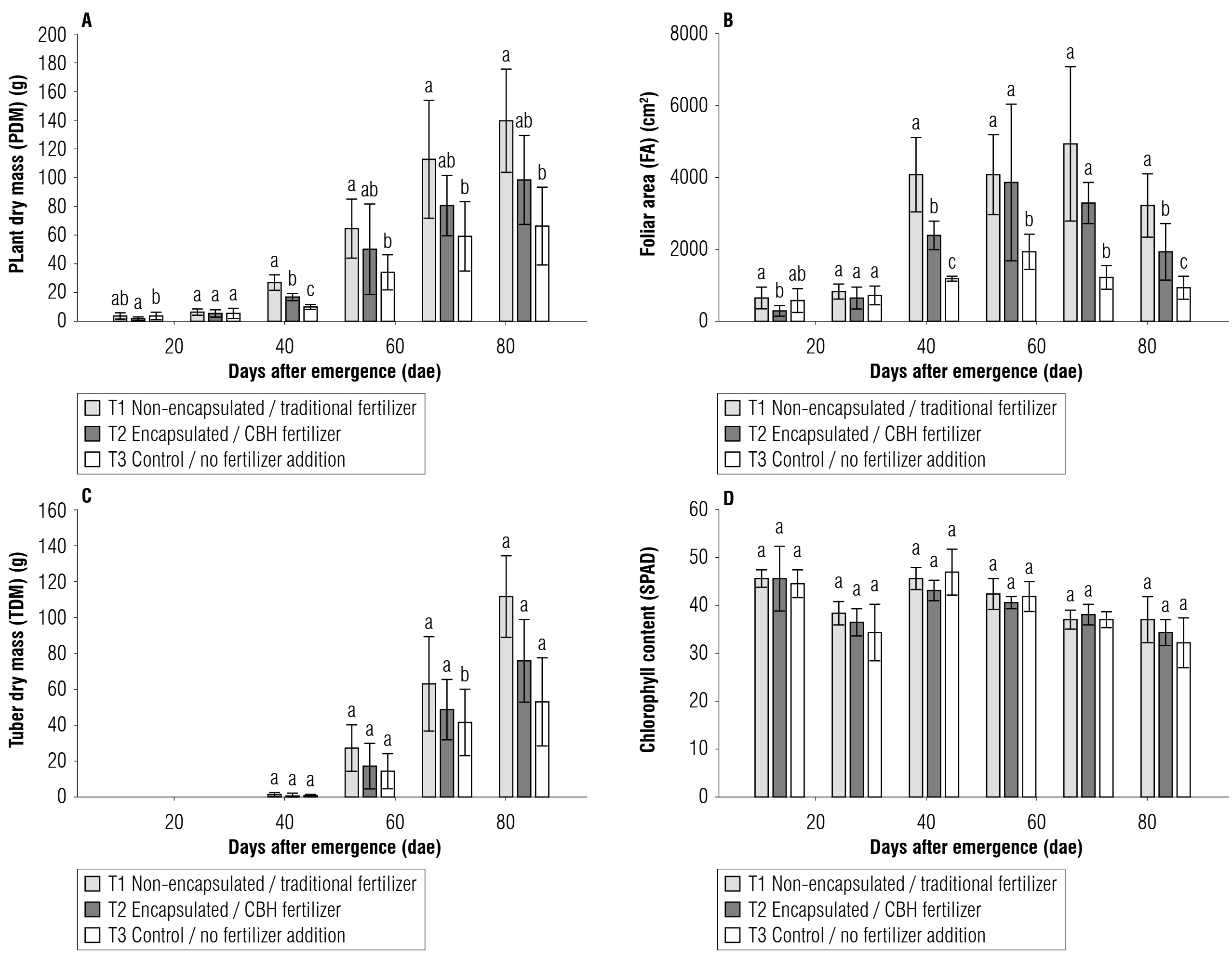

FIGURE 3. Plant dry mass A), foliar area B), tuber dry mass C) and chlorophyll content D) (mean ± standard deviation [SD]); n=9. Different letters above the bars indicate differences between treatments at P<0.05 (Tukey HSD P-values). Bars=SD.

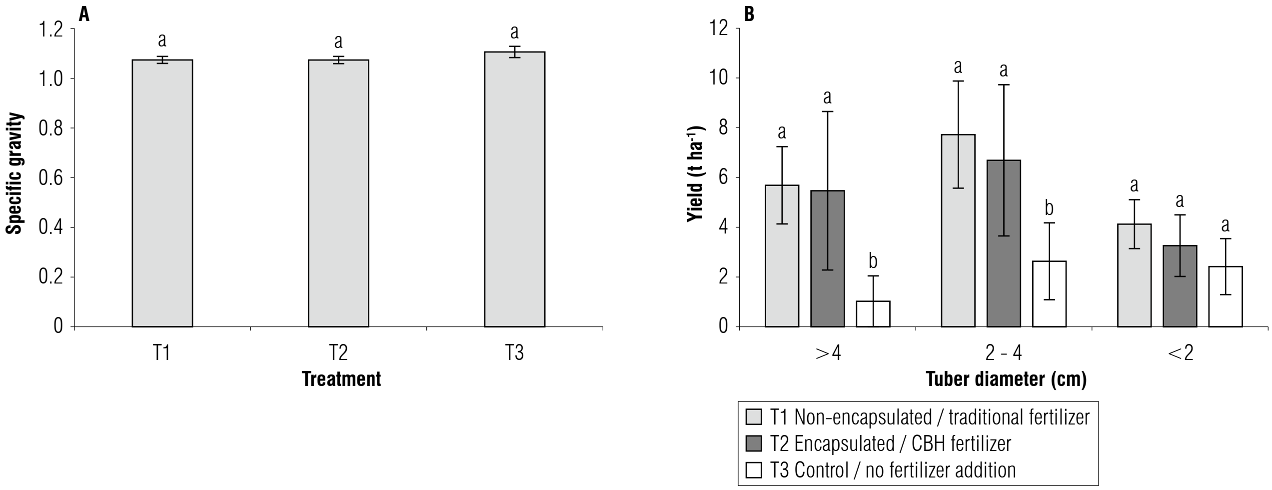

FIGURE 4. Specific gravity A) and yield B) (mean ± standard deviation [SD]); n per treatment for the yield data=3 blocks (30 plants per block) and n for the specific gravity=10 plants per treatment. The same letters above the bars indicate no differences between treatments (Tukey HSD, P>0.05). Bars=SD.

CBH on biomass production. Despite this trend towards a lower FA and PDM in T2, the chlorophyll content and the specific gravity were not affected. The chlorophyll ranged between 34.47 and 46.9 SPAD units between the 14 and 84 dae, coinciding with values previously reported by Ariza *et al.* (2020) for the cv. Criolla Colombia (42 SPAD at 70 das) under optimal irrigation and fertilization conditions. Therefore, in this study, normal chlorophyll levels were maintained with all treatments so nitrogen may not be a limiting factor in any of the treatments for chlorophyll synthesis. The specific gravity, an important quality indicator for the industrial processing of potato and directly correlated with the dry matter and starch content (Lulai & Orr, 1979), showed values (T1=1.081±0.003 and T2=1.078 ± 0.01) recommended for most processed products (Kirkman, 2007) like those reported for the cv. Criolla Colombia in previous studies (Rozo & Ñústez, 2011). The total tuber yield reported for cv. Criolla Colombia ranged between 11.15 and 20.48 t ha^{-1} in six localities in Antioquia department (Rodriguez *et al.*, 2009). The tuber yield result in this experiment is within this reported range, except for T3, a result that was expected due to lack of fertilizer.

Even so, contrary to the expected, a slight trend towards a lower yield was observed when CBH is used. This is not desirable because this would translate into a lower profit at the time of harvest. It is necessary to verify whether this effect is a consequence of the CBH nutrient retention that would make it necessary to modify the hydrogel formula to ensure the right flow of nutrients at the beginning of tuber development. It might also be an effect of the field trial size and the number of samples collected for yield estimation. Therefore, new trials should include larger crops and larger samplings.

Conclusions

This study confirmed the controlling effect of the CBH on the exit of nutrients from the soil solution at the field scale and during a rainy season, ensuring the retention of the nutrients added in the fertilizer on the soil surface and preventing them from easily leaching, especially at the beginning of the productive cycle when the seed potato tubers have not emerged and do not have roots to absorb the nutrients. At the same time, it was confirmed that the CBH is less efficient controlling the exit of K^+. The encapsulated CBH fertilizer allowed the same yield for crops at a field scale as the traditional fertilizers, with the additional advantage of reducing the negative environmental impact of leachates.

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Conflict of interest statement

The author´s declare that there is no conflict of interest regarding the publication of this article.

Author's contributions

JSV and GRT formulated the overarching research goals and aims, JSV and GRT obtained the financial support for the project leading to this publication. JSV and CEÑL developed or designed the methodology. NPM and JSV conducted the research. JSV, NPM, GRT and CEÑL contributed to the data analysis. JSV, NPM and GRT wrote the article. All authors reviewed the manuscript.

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S.1. Linear models

The effect of our predictors over the concentration of ammonia N-NH_4^+ (mg L^{-1}) and potassium K^+ (mg L^{-1}) was tested.

The model was set as: Concentration ~ Treatment + Days. The interaction between treatment and d was not considered, since there was not a powerful reason to believe that the effect of the treatments on the leachates would vary over time. This is because this is the first study of the performance of our carragean-based gels as coating for fertilizers at a field scale. In addition, it was done to prevent overfitting in our model.

The equation of the model was $Y = \beta 0 + \beta 1\ T1 + \beta 2\ T2 + \beta 3\ T3 + \alpha\ Days$, where Y represents the concentration, $\beta 0$ is the overall intercept, the value when all predictors are 0 (no biological meaning). $\beta 1$, $\beta 2$, $\beta 3$ are the values of the effect of each of the three treatments, uncoated fertilizer, coated and control, respectively. Finally, α represents the slope, *i. e.*, the effect of time over the concentration in the leachates.

The distribution of the residuals of the model was analyzed in order to determine if the suppositions of a linear regression are met. We evaluated if residuals ~ N (0, θ). Results are shown in Figure S1 for ammonium and S2 for potassium. In both cases, the general pattern seems to be the same: the residuals are distributed regardless of the treatments and

TABLE S1. Results for the linear models. The units of the Estimate and standard error are mg L^{-1} . The percentage of variance explained is shown as the R^2 in %, and the *P*-values indicating significant effects are highlighted in bold.

	R^2 (%)	Parameter	Estimate	Std error	*P*-value
N-NH_4^+ (mg L^{-1})	10.15	Intercept	0.305	0.1774	0.088
		Time	-0.007	0.0041	0.116
		T1*	0.384	0.1556	**0.015**
		T2**	0.015	0.1529	0.921
K^+ (mg L^{-1})	12.38	Intercept	4.169	0.7954	<0.001
		Time	-0.119	0.0183	0.298
		T1*	2.469	0.6827	**0.0004**
		T2**	1.151	0.6793	0-092

*T1 = Uncoated fertilizer, **T2 = Coated fertilizer.

time (Figs. S1A and S2A). Residuals are distributed with means approximately 0. Slight deviations from homoscedasticity and normality are observed, but mostly driven by the outliers. Overall, the analysis of residuals suggests the assumptions for linear regressions are met with only subtle deviations.

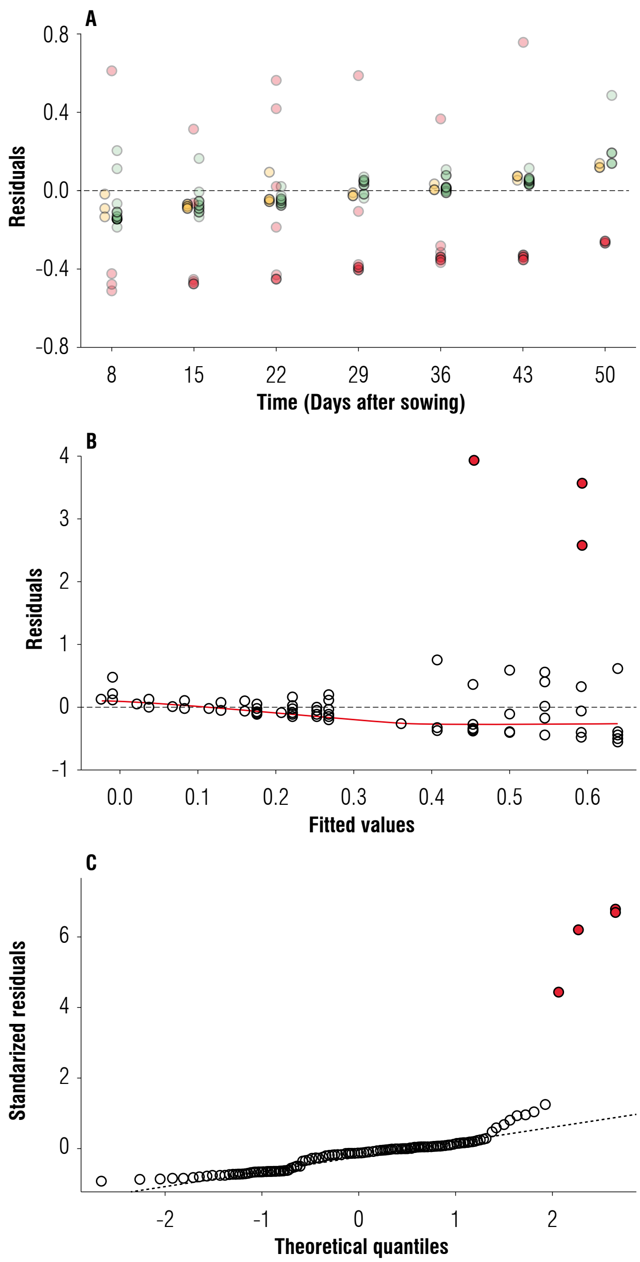

FIGURE S1. Analysis of residuals from the linear model of Ammonium concentration ~ Treatment + Days. A) Residuals vs. Predictor plot. Residuals show a similar distribution without any distinguishable pattern regardless of the treatment (yellow=T3/control, red=T1/Uncoated, green=T2/Coated). Outliers (n=3) omitted to facilitate visualization of differences in the y axis. B) Residual vs. Fitted values plot. Mean is approximately 0. Interestingly, the variance is relatively homogeneous only with slight alterations at higher values of concentration. Outliers shown in red. C) Normality Q-Q plot. Overall, the standardized residuals correspond to the expected quantile without red. Subtle deviations are shown in the tails. Larger deviations in the outliers shown in red.

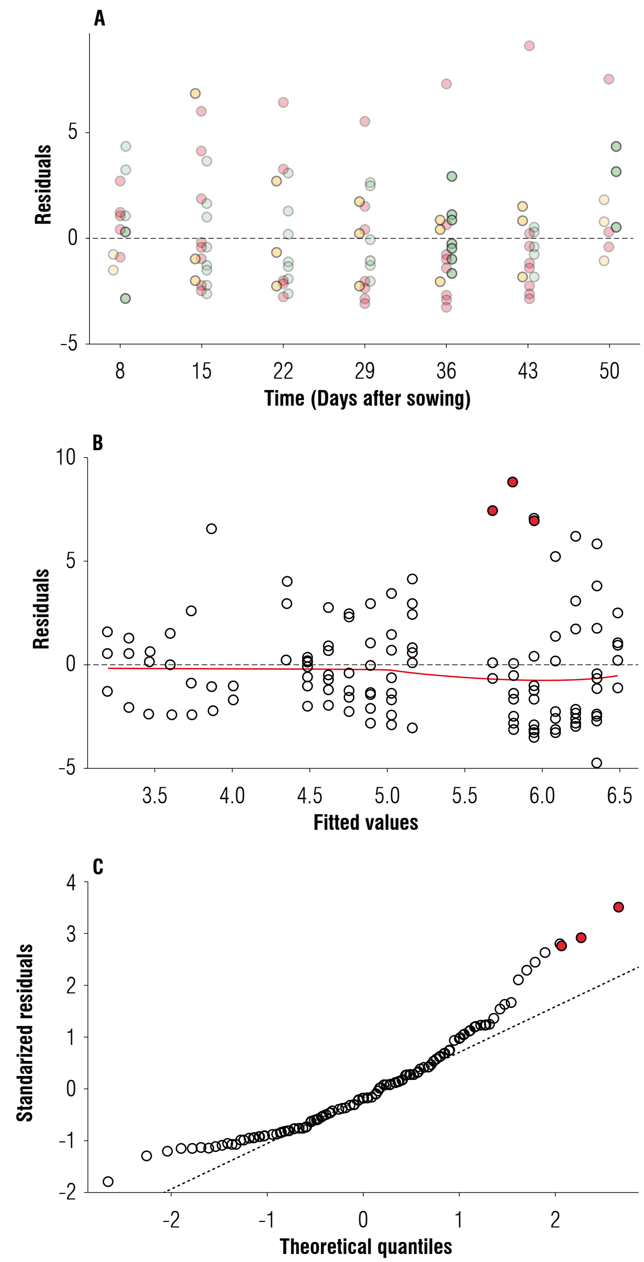

FIGURE S2. Analysis of residuals from the linear model of Potassium concentration ~ Treatment + Days. A) Residuals vs. Predictor plot. Residuals show a similar distribution without a distinguishable pattern regardless of the treatment (yellow=T3/control, red=T1/Uncoated, green=T2/Coated). B) Residual vs. Fitted values plot. Mean is approximately 0. Outliers shown in red. C) Normality Q-Q plot. Overall, the standardized residuals correspond to the expected quantile without red. Subtle deviations are shown in the tails. Outliers shown in red.

S2. Model selection tables

Each table shows the summary of likelihood and AIC criteria for each possible model that can be constructed with the combination of variables in this experiment. Each row represents one model and the columns represent the following: intercept (Intrc), the estimates for the two variables Days and Treatment (Trtmn), the degrees of freedom (df), log likelihood (LogLik), AIC value, ΔAICC (Difference in AIC with the model of minimum AIC) and the standardized weight of the model.

TABLE S2.1. Model selection table with the concentration of ammonia as a response variable. Model 3 was preferred over model 4 since the ΔAICC < 2. This means that the variable 'Days' does not help to explain the variability in the response variable. The only variable with a considerable effect was Treatment.

Model	(Intrc)	Time	Trtmn	df	logLik	AIC	ΔAICc	weight
4	0.3053	-0.00657	+	5	-111.698	233.4	0	0.554
3	0.1148		+	4	-112.975	234	0.56	0.42
1	0.2771			2	-118.442	240.9	7.49	0.013
2	0.4456	-0.00601		3	-117.46	240.9	7.52	0.013

TABLE S2.2. Model selection table with the concentration of potassium as a response variable. Model 3 was preferred since it has the best AIC (minimum). The only variable with a considerable effect was Treatment.

Model	(Intrc)	Time	Trtmn	df	logLik	AIC	ΔAICc	weight
3	3.593		+	4	-276.909	561.8	0	0.605
4	4.169.	-0.1918	+	5	-276.348	562.7	0.88	0.39
1	5.125			2	-284.143	572.3	10.47	0.003
2	5.744	-0.02212		3	-283.479	573	11.14	0.002