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ORIGINAL PAPER

Effect of nutrient solution pH on the quality of *Lactuca sativa* L. in a hydroponic system under struvite fertilization*

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Abstract

In this study, we proposed the application of Crystal Green as P fertilizer in lettuce cultivation in non-recirculating hydroponics in solution with a different range of pH (4.5-8.5) instead of superphosphate. The experiment was conducted at the Wroclaw University of Environmental and Life Sciences, in greenhouse conditions, in 2022. The results showed that the nutrient solution pH differences were reflected in the content of nutrients in the leaves and roots as well as the mass of lettuce plants under struvite fertilization. Macronutrients such as nitrogen, potassium, calcium, magnesium were highly available in stagnant hydroponics at pH 6.0-6.5. The phosphorus content in leaves was found to be the lowest in pH solution 7.5 and 8.5, being lower by about 34% than in control at pH 5.5. The uptake of this element was also dependent on the pH of nutrient solution. The higher pH of the solution, the lower the P uptake (42% lower at pH 7.5 and 50% at pH 8.5 compared to the control pH 5.5). A similar trend was found for K, where the higher the pH, the lower the uptake of this element (by 33% at pH 6.5, 32% at pH 7.5 and 48% at pH 8.5 compared to control). A higher amount of phosphorus was found in the root system (6459 mg kg⁻¹ dm) than in leaves (6138 mg kg⁻¹ dm). All micronutrients except boron became less available at alkaline pH. The higher the reaction of the solution, the lower the weight of lettuce leaves (8% less at pH 4.5, 11% less at pH 7.5 and 24% less at pH 8.5 compared to control), roots (30% at pH 4.5, 36% at pH 7.5 and 51% at pH 8.5 compared to the control) and the whole plants (6% in total biomass at pH 4.5, 9% at pH 7.5 and 181% at pH 8.5 compared to the control). Further study is needed to evaluate whether struvite will be suitable for the formation of nutrient solution for the next cycle of production.

Keywords: hydroponics, lettuce, struvite, pH, phosphorus, microelements

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Modern agriculture faces many challenges, including the delivery of food security, sustainable use of natural resources and farming under extreme environmental conditions (Frison et al. 2011, Singh, Singh 2019). Cultivation under controlled conditions is a key element of agriculture, especially for horticultural crops (Sardare, Adame 2013). Hydroponic systems enable soilless plant growth using a mixture of water and nutrient solution with different systems. Stagnant hydroponics has many advantages over other soilless systems, particularly in the production of leafy green vegetables (Kleiber et al. 2010). In our research, we applied stagnant hydroponics, defined as hydroponic cultivation without substrate, in which the nutrient solution supplied to the plants does not leach uncontrollably, and its level is periodically completed (Kleiber et al. 2010). Many advantages speak for this type of hydroponics: control over the nutrient composition, faster plant growth, production of high quality plants, reduction of amounts of applied pesticides (Gonnella et al. 2003, Nicola et al. 2005). Stagnant hydroponics also has a disadvantage, which is the nutrient concentration causing an increase in salt concentrations in the root zone of plants (Kleiber et al. 2010).

An important issue in hydroponic cultivation is how to control the pH of a nutrient solution, which affects the plant growth, nutrient concentration or chlorophyll content. The preferred pH in a hydroponic system is similar to pH levels in soil, but the literature reports different results/values. The most common pH for leafy greens grown hydroponically is 5.5-6.5 (Gillespie et al. 2020), while in our study it ranged from 4.5 to 8.5. Different pH can be used for specific reasons (Gillespie et al. 2020). For example, a low pH of 4 increased the nutritional and dietary value of *Taraxacum officinale* (L.) and *Reichardia picroides* (L.) in a floating hydroponic system (Alexopolous et al. 2021). Additionally, various equilibrium-based processes, such as precipitation, co-precipitation and complexation, can limit the availability of nutrients in hydroponic solutions (Sambo et al. 2019). Increased alkalinity of the nutrient solution can lead to precipitation of cations, such as copper, iron and zinc, into insoluble compounds (Lee et al. 2017). Lower pH in hydroponic nutrient solutions is generally avoided because it can lead to specific nutrient disorders and growth inhibition (Savvas, Gruda, 2018, Sambo et al. 2019). Interestingly, a number of studies suggest that hydronium and hydroxide ion toxicity occurs only at the extremes of acidity and alkalinity (Islam et al. 1980), and growth inhibition can usually be attributed to one or more pH-dependent factors, including nutrient availability, ion antagonism and precipitation of fertilizer salts (Mengel et al. 2001, Bugbee, 2004, Sambo et al. 2019).

Struvite solubility is strongly under control of pH, although the results are ambiguous, especially in hydroponic systems (Bhuiyan et al. 2007). It is worth considering experiments examining the impact of pH on the plant content of P and other elements (Penn et al. 2019). Little is known about the solubility and release of P from struvite used in hydroponics. Arcaz Pils et al. (2021), in their research, determined that 50% to 70% of struvite remains undissolved in the substrate after three lettuce cultivation cycles, thus indicating its high potential for subsequent production cycles in hydroponics. Research results pertaining to annual lettuce production with the same initial struvite indicate sustained production similar to the control. Pepper production was successful in a three-month experiment, although longer production cycles were not tested. We conducted one lettuce production cycle with different pH of the solution in order to clarify which pH would be the most beneficial for the nutrient availability in hydroponics with struvite fertilization.

We hypothesized that the use of struvite in a hydroponic system might be promising after adjusting the pH of the solution so as to increase the availability of macronutrients and micronutrients for plants. The aim of the study was to evaluate the effects of the nutrient solution pH on the macroand micro-nutrient content of lettuce (*Lactuca sativa* L.) and its mass. For this purpose, lettuce was cultivated in a stagnant hydroponic system and under a wide range of pH in the nutrient solution (from 4.5 to 8.5).

MATERIALS AND METHODS

Experiment design

The greenhouse pot experiments were conducted from September 2022 to December 2022 at the Center for Advanced Technology Psary at the Wroclaw University of Environmental and Life Sciences. The application of Crystal Green as P-fertilizer during one plant growing season was tested in two series. The one-factor experiment (each variant with pH) was conducted in six replicates. The control object were the pots with pH 5.5. The plants were grown in pots with a capacity of 7 dm³ filled with nutrient solution with different pH. Greenhouse day and night air temperatures were set at $24/16^{\circ}$ C, respectively, and humidity was 40%-50%. The experimental treatments consisted of five nutrient solutions with varied pH values, which were formulated as follows: pH 4.5 (4.5 ± 0.2), pH 5.0, pH 5.5 (5.5 ± 0.3), pH 6.5 (6.5 ± 0.2) and pH 7.5-8.5 (7.0 ± 0.1), by adding adequate amounts of HNO₃ (67% v/v) to the initial nutrient solution of pH 7.0. The solution with water was enriched with nitrogen, potassium, phosphorus and microelements. Fertilizers were dissolved in the solution before the experiment. The nutrient solution contained nutrients in following amounts (in mg dm⁻³): N-NO₃ 125, P 40, K 225, Ca 150, Mg 25, S-SO₄ 50, Fe 1, Mn 0.75, Zn 0.35, B 0.30, Cl 15, Cu 0.10, Mo 0.05. Struvite in the form of granules sold under the commercial brand Crystal Green is distributed by Ostara Nutrient Recovery Technologies Inc. Licence. White granules of struvite measured around approximately 2.4 mm in diameter (Photo 1). The chemical composi-



Photo 1. Struvite granules used in the experiment

tion of Crystal Green granules is the following: >99% struvite (NH_4MgPO_4 6H₂O) equivalent to 12% P (28% P₂O₅).

Omega F_1 variety of lettuce was selected because of its high market demand by consumers and suitability for hydroponic culture. It is an attractive, fast growing variety, which forms large, heavy and well-filled heads with very tasty light green leaves. The variety is resistant to lettuce cyst nematode BL 1-13, 17-18, 22, 24, 25. In September 2022, lettuce seeds were sown into disposable polystyrene seed trays (cell dimension $5 \times 5 \times 5$ cm) filled with peat (pH 5.5–6.5), without fertilizers, and kept in a greenhouse. At the phase of four leaves, the seedlings were transferred to a hydroponic system. The emerging seedlings were watered four times a week for three weeks.

Hydroponic components

A laboratory non-recirculating stagnate hydroponic system for lettuce was made from black plastic containers (7 dm³ volume), polystyrene plates (2.5 cm thick) and plastic cups (6.5 cm high and 5 cm wide). The black plastic containers were filled with 7.0 L of water and mineral fertilizers including struvite (Crystal Green) were added. The pH ranged from 4.5 to 8.5 and EC was 1.80-2.00 mS cm⁻¹. The pH of the nutrient solution was checked three times a week. The source of nutrients for plants were single and complex mineral fertilizers typically used in nutrient media, such as calcium nitrate, potassium sulfate, magnesium sulfate, potassium nitrate. The source of microelements was the Mikro Plus multi-component fertilizer. The source of phosphorus was struvite (Crystal Green). Calcium nitrate was used to compensate for the nitrogen. The root system of the lettuce was continuously bathed in the nutrient solution. The distance between containers and between rows was at 8 and 10 cm, respectively (Photo 2).



Photo 2. Experiment with lettuce and struvite in stagnant hydroponic system for lettuce (2023)

Biometric measurements of lettuce

At harvesting date and in each pH variant, plants from each replication were sampled. Subsequently, mass of leaves, mass of roots, mass of whole plants were assessed. The share of roots mass in the whole mass and the share of the mass of leaves in the whole mass were evaluated (Photo 3).



Photo 3. Roots system of lettuce during sampling

Leaves and roots macro-and micro-elements concentrations

Chemical analyses were performed in a laboratory at the Horticulture Department of the Wroclaw University of Environmental and Life Sciences and Institute of Agroecology and Plant Production. The nutrient content in plant material was determined after extraction with acetic acid (0.03 M). The dry matter (DM, AOAC: 934.01) in laboratory samples was determined by the gravimetric method at 105°C applied for 4 h, according to the Polish Standard. Chemical analyses were carried out according to the Official Methods of Analysis of AOAC International (AOAC): nitrogen by the Kjeldahl method, phosphorus by the vanadate-molybdate method, magnesium with titanium yellow, potassium and calcium on a flame photometer (BWB Technologies UK Ltd., Newbury, UK) using flame photometry. Mineralization of plant material was completed using sulphuric acid and perhydrol in an electric furnace at 400°C. Microelements (iron, zinc, manganese and copper) were determined by atomic absorption spectrometry AAS. To determine each of the examined microelements, the required conditions concerning wavelength, slot width, and flame height were used. The uptake of macro- and microelements was determined according to the mass of plant leaves and the content of these macronutrients.

Statistical analysis

The normality of the distribution of variables was tested using the Shapiro-Wilk normality test. All results were subjected to one-way statistical analyses, (Anova/Manova) in Statistica software (version 13.1, Statsoft, Poland) and the Tukey's test, with a significance level of a=0.05. The homogeneity of the groups was confirmed using a post-hoc test (the Tukey's test at level a=0.05). Homogeneous groups were determined from the smallest to the largest value. Correlation of traits as well as figures were prepared in Statistica software.

RESULTS AND DISCUSSION

Effect of struvite and various pH of solution on elements content in the leaves system of lettuce

Concentrations of macroelements in dry mass of lettuce grown in hydroponics varied widely among leaves and roots. The content of the macroelements analyzed in leaves of lettuce grown in hydroponics decreased in the following order: K>Ca>Mg>P>N (Table 1). Leaves of lettuce grown in high pH solutions contained less N, P, Mg than leaves of plants grown in optimum pH solutions. The content of nitrogen in the solutions with pH 4.5 and pH 8.5 is around 20% and 5% lower, respectively, than in control. The phosphorus content was significantly the lowest in the solution with pH 7.5 and 8.5, being about 34% lower compared to control. The highest concentrations of K was found in lettuce grown at pH 5.5, being 55 % higher than in the lowest pH solution and 33% higher than in the highest pH solution. In turn, the highest content of Ca was observed at pH 5.5. The content of Ca was about 59% lower at pH 4.5 and 33% lower at pH 8.5 compared to control. A different trend was observed for Mg, as the highest content of this element was found in in solution with pH 7.5 and 8.5, 26% and 24% than in control, respectively (Table 1).

Concentrations of micronutrients in lettuce leaves occurred in the following order Mn>Fe>Zn>B>Cu>Na (Table 2). As for manganese in lettuce

Table 1

pH of solution in hydroponics	N (mg kg ^{.1} dm)	P (mg kg ⁻¹ dm)	K (mg kg ^{.1} dm)	Ca (mg kg ⁻¹ dm)	Mg (mg kg ^{.1} dm)
4.5	3.46 <i>a</i>	6344b	36721a	33468a	7140a
5.5	4.34b	7346 <i>b</i>	81646c	81213d	8198 <i>a</i>
6.5	4.14 <i>ab</i>	7346b	59140b	61366c	14375c
7.5	4.26b	4807 <i>a</i>	62133b	61433c	11126b
8.5	4.12 <i>ab</i>	4848 <i>a</i>	56933b	54266b	10823b
P value	0.01**	0.001***	0.001***	0.001***	0.001***

Effect of the pH of solution on the macroelement content in lettuce leaves under struvite application

*, **, *** Analysis of variance at significance at P<0.05, P<0.01, P<0.001 respectively; Means for factors. Different letters indicate significant differences between factors (the Tukey's multiple range test).

Table 2

Effect of struvite at various pH values of the solution on the microelement and sodium content in lettuce leaves (mg $\rm kg^{1}$ dm)

pH of solution in hydro- ponics	Na (mg kg ^{.1} dm)	Fe (mg kg ^{.1} dm)	Mn (mg kg ^{.1} dm)	Cu (mg kg ^{.1} dm)	Zn (mg kg ^{.1} dm)	B (mg kg ^{.1} dm)
4.5	16.93 <i>a</i>	186.12b	966.33 <i>c</i>	56.76bc	140.86d	67.30 <i>c</i>
5.5	28.78b	283.87c	1213.33d	62.56c	149.60d	58.66a
6.5	13.66 <i>a</i>	165.87b	602.33b	88.43d	114.80 <i>c</i>	58.43a
7.5	15.69a	135.43a	450.33ab	51.17b	105.40b	63.23b
8.5	35.04c	127.40a	410.00 <i>a</i>	43.37a	74.20 <i>a</i>	66.20 bc
P value	0.001***	0.001***	0.001***	0.001***	0.001***	0.001***

*, **, *** Analysis of variance at significance at P<0.05, P<0.01, P<0.001 respectively; Means for factors. Different letters indicate significant differences between factors (the Tukey's multiple range test).

leaves, its highest content was found at pH 5.5 of solution. The higher the pH of the solution, the lower the Mn content. The lowest content, lower by around 66% than in control, was determined under alkaline reaction. Significantly higher content of sodium in the leaves was observed at pH 8.5 of the solution (about 17% higher versus the control), while the lowest was in solutions with pH of 4.5 and 6.5 (about 42% and 52% lower, respectively, compared to control object). The opposite trend was found for Fe, where the highest Fe content was determined at pH 5.5 and the lowest – in the solution with alkaline reaction (55% lower content than in control) – Table 2. In the case of Zn, its content increased in leaves as the pH of the medium decreased (at the highest pH, the Zn content was 50% lower than in the control). Higher content of boron in lettuce leaves was determined at pH 5.5 and

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 $6.5~\mathrm{pH}$ of the solution. At the highest pH, the boron content was 11% higher than in the control.

A statistically significant positive correlation was found between the following macronutrients in lettuce leaves: K and N, Ca and N, N and K, Ca and K, and K and Ca, suggesting that an increase in one element causes an increase in the other (Table 3).

Table 3

Variable	Mean	Standard deviation	Ν	Р	К	Ca	Mg
Ν	4.06	0.39	1.00	0.03	0.77*	0.78*	0.357
Р	$6\ 138.53$	1 218.26	0.03	1.00	0.26	0.29	-0.01
K	$59\ 314.87$	$15\ 005.16$	0.77*	0.26	1.00	0.98*	0.12
Ca	58 349.60	16 023.84	0.78*	0.29	0.98*	1.00	0.22
Mg	10 332.53	26 47.76	0.3	-0.01	0.12	0.22	1.00

Correlation between concentrations of macroelements in lettuce leaves

* statistically significant at α =0.05

With respect to the micronutrient content, there was both a statistically significant positive correlation (an increase in elemental content) and a negative correlation for Cu and Na, and Cu and B (Table 4).

Table 4

Variable	Average	Standard deviation	Na	Fe	Mn	Cu	Zn	В
Na	22.02	8.80	1.00	0.16	0.06	-0.56	-0.33	0.19
Fe	179.74	58.51	0.16	1.00	0.93*	0.26	0.83*	-0.49
Mn	728.47	326.73	0.06	0.93*	1.00	0.19	0.91*	-0.23
Cu	60.46	16.04	-0.56*	0.26	0.19	1.00	0.36	-0.73*
Zn	116.97	27.93	-0.33	0.83*	0.91*	0.36	1.00	-0.31
В	62.79	4.00	0.19	-0.49	-0.23	-0.73	-0.31	1.00

Correlation between concentrations of microelements and sodium in lettuce leaves

* statistically significant at α =0.05

The uptake of macroelements by lettuce leaves was significantly dependent on the pH of a solution. Overall, the lowest uptake was for nitrogen while the highest – for potassium and calcium. Significantly higher uptake of nitrogen, potassium and calcium by lettuce leaves was determined at pH 5.5 of the solution. The higher the pH, the lower the nitrogen uptake by lettuce leaves. Nitrogen uptake at the highest pH (8.5) was 30% lower and it was 10% lower at pH 7.5 and 6.5 compared to control. The use of struvite in hydroponic cultivation as phosphorus fertilizer showed the highest uptake of this element at pH 5.5-6.5. The higher the pH of the solution, the lower the P uptake (42% lower at pH 7.5 and 50% at pH 8.5 compared to the control). There was a similar trend for K, where the higher the pH, the lower the uptake of this element (by 33% at pH 6.5, 32% at pH 7.5 and 48% at pH 8.5 compared to control). A similar trend was demonstrated for calcium uptake. However, a reverse trend was observed for Mg, with its highest uptake at pH 6.5. The lower the pH, the higher the Mg uptake in lettuce leaves (Table 5).

Table 5

pH of solution in hydroponics	N uptake by lettuce (mg kg ⁻¹ dm)	P uptake by lettuce (mg kg ⁻¹ dm)	K uptake by lettuce (mg kg ⁻¹ dm)	Ca uptake by lettuce (mg kg ⁻¹ dm)	Mg uptake by lettuce (mg kg ⁻¹ dm)
4.5	0.08a	148.25b	855.73a	781.94a	166.97a
5.5	0.10b	178.58b	1983.72c	1973.10c	199.53ab
6.5	0.09ab	164.76b	1327.73b	1375.78b	321.66c
7.5	0.09ab	104.36a	1348.43b	1333.37b	241.55b
8.5	0.07a	89.67a	1054.02a	1010.17a	200.68ab
P value	0.05*	0.001***	0.001***	0.001***	0.001***

Effect of struvite at various solution pH levels on macroelement uptake by lettuce leaves

*, **, *** Analysis of variance at significance at P<0.05, P<0.01, P<0.001 respectively; Means for factors. Different letters indicate significant differences between factors (the Tukey's multiple range test).

Effect of struvite and various pH of solution on elements content in the root system of lettuce

The roots of lettuce grown in solutions with high pH contained less N and P than roots grown in solutions with optimal pH. Nitrogen and phosphorus content was significantly dependent on the pH of medium, being the highest in the medium with pH of 5.5 and 6.5 (Table 6). The nitrogen content in lettuce roots was 46% lower at pH 4.5, 49% lower at pH 7.5, and 23% lower at pH 8.5 compared to control. The phosphorus content in lettuce roots was 27% lower at pH 4.5, 21% lower at pH 7.5, and 25% lower at pH 8.5. The potassium content was the highest in the medium with pH 4.5. The potassium content was around 12% lower in the control object compared to the solution with pH 4.5. The calcium and magnesium content increased with an increasing pH of the nutrient solution (Table 6). High pH stress or nutritional deficiencies caused by high pH stress can also lead to abnormalities in the root system morphology; however, this was not detected in our study. In some cases, the concentrations of elements were statistically higher at high pH value. The magnesium content of the solution with the highest pH was 37% higher compared to the control.

The content of microelements in roots was as follows: Mn>Zn>B>Fe> >Cu>Na (Table 7), and was dependent on the pH of a solution. The highest

Table 6

pH of solution in hydroponics	N (mg kg ^{.1} dm)	P (mg kg ^{.1} dm)	K (mg kg ^{.1} dm)	Ca (mg kg ^{.1} dm)	$\begin{array}{c} Mg \\ (mg \ kg^{\cdot 1} \ dm) \end{array}$
4.5	1.92a	5620a	7443c	910 <i>1</i> a	5601a
5.5	3.57b	7763 <i>b</i>	6578ab	8863 <i>a</i>	5866a
6.5	3.13b	7101 <i>b</i>	4320 <i>a</i>	19373b	8135b
7.5	1.80a	6058a	6130 <i>b</i>	22356b	5662a
8.5	2.74ab	5753a	5983b	20490b	9406c
P value	0.01**	0.001***	0.001***	0.001***	0.001***

Effect of struvite at various pH values of the solution on the content of macroelements in the roots

*, **, *** Analysis of variance at significance at P<0.05, P<0.01, P<0.001 respectively; Means for factors. Different letters indicate significant differences between factors (the Tukey's multiple range test).

content of most microelements was found in the solutions with the lowest pH 4.5 (Na, Fe, Mn, Cu) and 5.5 (Zn). Contrary results were found for boron. The root B concentration was higher in lettuce grown in nutrient solutions with high pH than in lettuce grown in low pH solutions (Table 7). The boron content in lettuce roots was 35% higher in the control than in the variant with the highest pH 8.5.

Table 7

Effect of struvite at various pH values of the solution on microelement and sodium content in the lettuce roots (mg $kg^{_1}\,dm)$

pH of solution in hydroponics	Na (mg kg ^{.1} dm)	Fe (mg kg ^{.1} dm)	Mn (mg kg ^{.1} dm)	Cu (mg kg ^{.1} dm)	Zn (mg kg ^{.1} dm)	B (mg kg ^{.1} dm)
4.5	4.12c	51.70c	241.33c	10.98bc	72.33b	47.50b
5.5	2.01b	28.33b	227.00c	12.01c	112.27d	39.38 <i>a</i>
6.5	1.6ab	27.47b	198.67b	9.18abc	87.27c	50.73b
7.5	1.65 ab	16.37a	201.00b	8.34 <i>ab</i>	71.93b	42.83a
8.5	1.18a	29.30b	144.33a	7.87a	63.27a	60.80 <i>c</i>
P value	0.001***	0.001***	0.001***	0.001***	0.001***	0.001***

*, **, *** Analysis of variance at significance at P<0.05, P<0.01, P<0.001 respectively;

Means for factors. Different letters indicate significant differences between factors (the Tukey's multiple range test).

A significant positive correlation was found between P and N, N and P and Ca with Mg. Negative significant correlation was found between Ca and K, Mg and K, K and Ca, K and Mg (Table 8).

In the case of roots, a positive correlation was found between Fe and Na, Mn and Na, Cu and Na, Na and Fe, Na and Mn, Cu and Mn, Na and Cu, Mn

Table 8

Variable	Average	Standard deviation	Ν	Р	К	Ca	Mg
Ν	2.63	0.77	1.000	0.75*	-0.30	-0.18	0.32
Р	6459.20	893.22	0.74*	1.00	-0.33	-0.29	-0.09
K	6091.00	1115.28	-0.30	-0.33	1.00	-0.57*	-0.57*
Са	16037.00	6135.25	-0.18	-0.29	-0.57*	1.000	0.51*
Mg	6934.47	1627.25	0.32	-0.09	-0.57*	0.51*	1.00

Correlation between macroelements in the lettuce roots

* statistically significant at α =0.05

and Cu, Cu and Zn (Table 9). In turn, the statistically significant negative correlation was found between B and Mn, B and Cu, B and Zn and Mn and B, Cu and B and Zn and B (Table 9).

Table 9

Variable	Average	Standard deviation	Na	Fe	Mn	Cu	Zn	В
Na	2.13	1.08	1.00	0.84*	0.74*	0.55*	-0.03	-0.29
Fe	30.63	12.13	0.84*	1.00	0.45	0.45	-0.10	0.14
Mn	202.46	34.94	0.74*	0.45	1.00	0.74*	0.50	-0.76*
Cu	9.67	1.87	0.55*	0.45	0.74*	1.00	0.63*	-0.57*
Zn	81.41	18.04	-0.03	-0.10	0.50	0.63	1.00	-0.65*
В	48.25	7.73	-0.28	0.14	-0.77*	-0.57*	-0.65*	1.00

Correlation between microelements and sodium in the lettuce roots

* statistically significant at α =0.05

Effect of struvite and various pH of solution on the mass of lettuce and roots of lettuce

Solution pH had a significant effect on the mass of different parts of lettuce. The higher the reaction of the solution, the lower the weight of lettuce leaves (8% less at pH 4.5, 11% less at pH 7.5 and 24% less at pH 8.5 compared to control). A similar trend was found for roots. Root weight loss was found to be 30% at pH 4.5, 36% at pH 7.5 and 51% at pH 8.5 compared to the control. In turn, there was a weight loss of 6% in total biomass at pH 4.5, 9% at pH 7.5 and 181% at pH 8.5 compared to the control. Found a significant share of the root in the total weight of plants. Its largest share was at a pH of 5.5 (Table 10).

A significantly positive correlation was found between the mass of leaves and the whole plants, mass of roots and whole plants, mass of whole plants and mass of leaves, and mass of leaves and mass of roots, and mass of roots and mass of leaves and whole plants (Table 11).

pH of solution in hydroponics	Mass of leaves (g)	Mass of roots (g)	Mass of whole plant (g)	The share of roots mass in the whole mass	The share of leaves mass in the whole mass
4.5	233.76b	19.00 <i>b</i>	231.13b	8.23a	101.21
5.5	243.00b	29.60 <i>c</i>	248.27b	11.96b	97.95
6.5	224.00b	20.93b	233.37b	8.96a	96.25
7.5	217.00b	18.93b	225.58ab	8.39a	96.32
8.5	185.33a	14.44a	202.97a	7.11a	91.23
P value	0.01**	0.001***	0.05*	0.001***	ns

Effect of struvite at various pH values of solution on mass of different parts of lettuce

*, **, *** Analysis of variance at significance at *P*<0.05, *P*<0.01, *P*<0.001, respectively, ns – not significant;

Means for factors. Different letters indicate significant differences between factors (the Tukey's multiple range test).

Table 11

Variable	Average	Standard deviation	Mass of whole plants	Mass of leaves	Mass of roots
Mass of whole plants	228.26	17.51	1.00	0.81*	0.77*
Mass of leaves	220.62	22.47	0.81*	1.00	0.74*
Mass of roots	20.58	5.27	0.77*	0.74*	1.00

Correlation between mass of different part of lettuce

* statistically significant at α =0.05

Some species can grow well at pH values above the recommended range of 5.5 to 6.5, although for most vegetable species, plant growth may be limited at pH levels above 7.0 or below 5.0 (Sonneveld 2002, Sardare et al. 2013). The results of Alexopoulos et al. (2021) proved that the growth of *T. officinale* was not reduced even at the lowest pH values (pH 4.0), while another species, *R. picroides*, seemed to be more sensitive to pH changes (higher or lower than optimal). The growth of *R. picroides* was negatively affected by pH 4.0 and, to a lesser extent, by pH 7.0, despite the literature reports implicating that this species usually grows on calcareous soils (Maggini et al. 2018). In our results, the highest pH level (pH 8.5) reduced fresh weight of roots and leaves, contradictory to Alexopoulos et al. (2021), who found that the root growth was reduced by low pH levels due to the inhibition of root elongation caused by higher H+ concentrations at low pH in the nutrient solution (Rosas et al. 2007).

Stable pH of the nutrient solution is one of the key factors for obtaining predictable and accurate plant growth and mineral nutrition in hydroponics. It is often stated that the preferred pH of the medium for optimal growth is 5.5-6.5 (Gilespie et al. 2020, 2021, Alexopoulus et al. 2021). In hydroponics, a pH between 5.5 and 6.5 is optimal for plant nutrient uptake, although this value should be adjusted to genetic properties of a given plant (Resh 2008, Umamaheswari et al. 2016, Gilesspie et al. 2020). A slightly acidic pH is optimal for the nutrient uptake by plants in hydroponics and it helps to prevent the precipitation of phosphate (PO₄³), magnesium (Mg²⁺), iron (Fe²⁺), manganese (Mn²⁺), calcium (Ca²⁺) into insoluble and inaccessible salts, which can occur at water pH levels >7.0 (Resh 2004). However, low pH in the rhizosphere can induce an abiotic stress, causing directly (i.e. high H+ damage to roots) or indirectly (i.e. limited phosphorus availability) the reduced plant growth and yield (Alam et al. 1999), which is contradictory to our research results.

The pH treatments tested in the study by Alexopoulos et al. (2021) had no effect on leaf concentrations of elements in *Taraxacum officinale*, including N, Ca, Mg, Fe and B (first and second harvest of plants), P and Mn (first harvest) and Cu (second harvest). On the other hand, K (67.3 g kg⁻¹ DW in the second harvest) and Cu (5.0 g kg⁻¹ DW in first harvest) were lowest in plants grown in solution with pH 4.0. In our study, pH had a significant effect on all macroelements and microelements in lettuce leaves, but the lowest concentration of the macroelements N, K, Ca, Mg was determined in the solution with pH 4.5, and that of the microelement Na in the solutions with pH 6.5 and 7.5. The same trend was observed in the roots, i.e. the higher pH, the lower the concentration of macroelements except Ca and Mg, as well as microelements except boron. Anugoolprasert et al. (2012) found no significant effect of pH level on N concentration in *Metaxylon sagu*, while Findenegg (1987) found that pH 4.0 reduced the total N concentration in leaves of *Helianthus annuus* plants, same as in our study.

Concentrations of N, Ca, Mg and B in roots determined by Alexopoulos et al. (2021) did not depend on pH, unlike in our study. In their results, P was lowest at pH 7.0 (9.2 g kg⁻¹ DW; second harvest), K was lowest at pH 4.0 (38.5 g kg⁻¹ DW in first harvest; 33.5 g kg⁻¹ DW in second harvest), and Fe was highest at pH 4.0 (146.6 g kg¹ DW in first harvest). A decrease in the K concentration in leaves and roots caused by low pH levels (pH 4.0) was observed also in other species, such as Trifolium repens L. and Lolium perenne L. (Rosas et al. 2007), as well as in our study also at the highest pH. In our study, the lowest concentration of P was at the lowest (5620 mg kg⁻¹) and the highest (6058 and 5753 mg kg⁻¹) pH, N – at the highest pH (1.18 mg kg⁻¹), while Ca (9101 mg kg⁻¹ and 8863 mg kg⁻¹), and Mg (5601 and 5866 mg kg^{-1}) – at 4.5 and 5.5, respectively. In addition, concentrations of Mn (23.9 g kg⁻¹ DW in first harvest and 29.4 g kg⁻¹ DW in second harvest) and Cu (16.7 g kg⁻¹ DW in first harvest) were highest at pH 7.0, while in our study the Mn content was the lowest at pH 8.5 - 144.33 mg kg⁻¹ while Cu was the lowest $(7.87 \text{ mg kg}^{-1})$ in the study by Alexopoulos et al. (2021). B concentrations in leaves and roots were affected by pH values in the medium, contradictory to results reported by Alexopoulos et al. (2021).

Ca and Mg concentrations in leaves and roots in T. officinale and R. picroides were not reduced at pH 4.0, except for the Ca concentration in leaves at first harvest, which is contradictory to our results. It has been documented that higher concentrations of H+ in the nutrient solution inhibit Ca and Mg uptake by basil (Gillespie et al. 2020) and gerbera (Savvas et al. 2003), leading to instability of root cell membranes (Alam et al. 1999).

In our study, pH may have a dual effect on phosphorus availability in hydroponics and its concentration in leaves and roots. The greatest content of phosphorus available in nutrient solutions occurred at slightly acidic reaction (pH 5.5). In alkaline and strongly acidic solutions, there can be a decrease in the concentration of available ions. It has been shown in our research that there is a direct relationship between pH and the phosphorus content, with an increased phosphorus concentration at high pH (5.5-6.5 pH). Michałojć and Nurzyński (2002) and Kowalczyk and Kaniszewski (2005) found a significant decrease in phosphorus levels in the root zone at high pH values of the nutrient solution in tomato cultivation. In our study, the highest concentration of this element was found in the leaves and roots under 5.5 and 6.5 pH. In the study conducted by Komosa et al. (2004), as the pH of the nutrient solution increased, the average phosphorus content of the tomato plants decreased, same as in our research. The P concentration in leaves and roots decreased when the pH of the nutrient solution increased to 8.5, same as previously reported by Assimakopoulou et al. (2006) in spinach plants grown at high pH levels in the nutrient solution.

In a study by Dyśko et al. (2008), the marketable yield obtained with a medium at pH 5.5 was significantly higher compared to the yield obtained at pH 6.5, but was not significantly different from the yield obtained at pH 4.5, 5.0 and 6.0. Similar results were obtained by Chohura et al. (2004) investigating the effect of solution pH on tomato yield. Kowalczyk (2003), who cultivated tomato on rockwool, obtained a significantly lower commercial yield after using a medium with a high pH value (pH 6.5).

Arnon and Johnson (1942) showed that tomato, lettuce and bermudagrass can grow in nutrient solution with pH ranging from 4.0 to 8.0, although the growth rate is significantly reduced beyond the optimal pH of 5.0 to 6.0, what is in agreement with our results. Although many species may not be as tolerant of pH as low as 4.0, they can tolerate low pH when applied for short periods (Arnon, Johnson, 1942, Mengel et al. 2001, Bugbee 2004, Savvas, Gruda 2018). Accordingly, one potential management strategy may involve periodically lowering pH to 4.0 for short periods (i.e., ≈ 1 week) when disease pressure is high, such as during hot and humid conditions or after transplantation.

Several other macronutrients showed inconsistent changes in pH. In a study by Blanchar et al. (2020), nitrate assimilation into leaf tissue varied significantly with pH when measured in mid-summer 2019, showing the highest assimilation at pH 5.8 and the lowest at pH 6.5. In our study, the content of total N in the root system ranged from 1.83 (mg kg⁻¹ dm) at a pH of 7.5 to 3.57 at a pH of 5.5. In the same study by Blanchar et al. (2020), calcium uptake showed the highest levels at pH 6.5 in the late summer 2019 measurements, a 9.1% increase from 5.0 to 6.5. In our study, the greatest content of Ca was found at pH 6.5-8.5 (roots) and 6.5-7.5 (leaves) as well as a high Ca uptake (Ca – leaves at pH 5.5). According to Bugbee (2003), availability of K and P can be slightly reduced in a nutrient solution with high pH. Dyśko et al. (2008) also reported that the increase in the nutrient solution's pH led to a decrease in available P in hydroponic production of tomato (*Solanum lycopersicum* L.). Hochmuth (2001) recommended a nutrient solution's pH of 5.5-6.5 for greenhouse hydroponic production, whereas Resh (2008) recommended a little higher pH of 5.8-6.4. The effect of solution pH on nutrient availability in hydroponics depends not only on pH but also on the rate of uptake by plants via roots (Barow, Hartemik 2023).

By potentially reducing nutrient losses through a slow release of nutrients into the solution, struvite as P source can improve the plant's supply of P needs throughout the cycle (Arcas-Pilz et al. 2021). Currently, there is little information on nutrient management in hydroponics, especially when using phosphorus produced from sewage sludge. Phosphorus (P) is reported to be deficient in aquaponics due to precipitation from Ca (Bonvin et al. 2015). The mechanisms of P dissolution from struvite is not well understood. Low solubility in water may suggest that P release may be too slow for early plant growth, although Bonvin et al. (2015) found that the rate of P uptake from urine-derived synthetic struvite was fairly constant over a 30-72-day growth period.

CONCLUSIONS

Regulating the pH of the nutrient solution is an indispensable part of hydroponics while using struvite as a source of phosphorus. The greatest availability of macronutrients was stated from 5.5 to 6.5 in this study. The higher the pH of the solution, the lower the P uptake (42% lower at pH 7.5 and 50% at pH 8.5 compared to the control pH 5.5). The highest P uptake was observed at pH 5.5 (178,58 mg kg⁻¹ d.m) and the lowest – at pH 8.5 (89,67 mg kg⁻¹ d.m). Indeed, more of this element was found in the root (6459 mg kg⁻¹ d.m) than in the leaves (6138 mg kg⁻¹ dm). It is reported that an increased nutrient solution pH reduced the concentration of micronutrients. We discovered that mass of plants (leaves, the whole plant) exhibited normal growth at pH as low as 4.0. Lettuce showed adaptability in nutrient solutions with pH levels ranging from acidic to neutral (4.0, 5.5 and 8.5), although the use of pH 5.5 was more favorable while using struvite. The results of this study encourage the use of struvite in hydroponic production because of its ability to sustainably produce short-chain cycle crops in the face of phosphate depletion.

Author contributions

Conceptualization – R.R., P.C. and A.J.R., methodology – P.C, R.R., software – R.R., validation – R.R., formal analysis – A.J.R., investigation – R.R., resources – P.C., data curation – R.R., writing – original draft preparation, R.R., P.C, A.J.R, writing – review and editing – A.J.R, R.R, visualization – R.R., supervision – A. J.R., P.C., project administration – R.R. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

The authors ensure that they have neither professional nor financial connections related to the manuscript sent to the Editorial Board.

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REFERENCES

- Alam, S., Naqvi, S., Ansari, R. (1999) 'Impact of soil pH on nutrient uptake by crop plants', In Handbook of Plant and Crop Stressm Pessarakli, M., Ed.; Marcel Dekker, New York, NY, USA, pp. 51-60.
- Alexopoulos, A.A., Marandos, E., Assimakopoulou, A., Vidalis, N., Petropoulos, S.A., Karapanos, I.C. (2021) 'Effect of nutrient solution ph on the growth, yield and quality of *Taraxacum officinale* and *Reichardia picroides* in a floating hydroponic system', *Agronomy*, 11, 1118, available: https://doi.org/10.3390/agronomy11061118
- Anugoolprasert, O., Kinoshita, S., Naito, H., Shimizu, M., Ehara, H. (2012) 'Effect of low pH on the growth, physiological characteristics and nutrient absorption of sago palm in a hydroponic system', *Plant Production Science*, 15, 125-131, available: https://doi.org/10.1626/ pps.15.125
- Assimakopoulou, A. (2006) 'Effect of iron supply and nitrogen form on growth, nutritional status and ferric reducing activity of spinach in nutrient solution culture', *Scientia Horti*culturae, 110, 21-29, available: https://doi.org/10.1016/j.scienta.2006.06.010
- AOAC (2023). Official Methods of Analysis (18th ed.). Gaithersburg, USA, AOAC International (2012).
- Arcas-Pilz, V., Rufí-Salís, M., Parada, F., Petit-Boix, A., Gabarrell, X., Villalba, G. (2021) 'Recovered phosphorus for a more resilient urban agriculture: Assessment of the fertilizer potential of struvite in hydroponics', *Science of Total Environment*, 10, 799, 149424, available: https://doi.org/10.1016/j.scitotenv.2021.149424

- Arnon, D.I. and Johnson, C.M. (1942) 'Influence of hydrogen ion concentration on the growth of higher plants under controlled conditions', *Plant Physiology*, 17, 525-539.
- Bhuiyan, M.I.H., Mavinic, D.S., Beckie, R.D. (2007) 'A solubility and thermodynamic study of struvite', *Environmental Technology*, 28(9), 1015-1026, available: https://doi.org/10.1080/ 09593332808618857
- Blanchard, C., Wells, D.E., Pickens, J.M., Blersch, D.M. (2020) 'Effect of pH on cucumber growth and nutrient availability in a decoupled aquaponic system with minimal solids removal', *Horticulture*, 6(1), 10, available: https://doi.org/10.3390/horticulturae6010010
- Bugbee, B. (2004) 'Nutrient management in recirculating hydroponic culture', Acta Horticulturae, 648, 99-112, available: https://doi.org/10.17660/ActaHortic.2004.648.12
- Chochura, P., Kołota, E. (2009) 'Effect of nitrogen fertilization on the yield and quality of fieldgrown leaf lettuce for spring harvest', *Folia Horticulturae*, 71, 41-49.
- Dyśko, J., Kaniszewski, S., Kowalczyk, W. (2008) 'The effect of nutrient solution pH on phosphorus availability in soilless culture of tomato', *Journal of Elementology*, 13(2),189-198.
- Findenegg, G.R. (1987) 'A comparative study of ammonium toxicity at different constant pH of the nutrient solution', *Plant Soil*, 103, 239-243.
- Frison, E.A., Cherfas, J., Hodgkin, T. (2011) 'Agricultural biodiversity is essential for a sustainable improvement in food and nutrition security', *Sustainability*, 3, 238-253, available: https://doi.org/10.3390/su3010238
- Gillespie, D.P., Kubota, C., Miller, S.A. (2020) 'Effects of low ph of hydroponic nutrient solution on plant growth, nutrient uptake, and root rot disease incidence of basil (*Ocimum basilicum* L.)', *Hortscience*, 55(8), 1251-1258, available: https://doi.org/10.21273/HORTSCI14986-20
- Gillespie, D.P., Papio, G., Kubota, C. (2021) 'High nutrient concentrations of hydroponic solution can improve growth and nutrient uptake of spinach (*Spinacia oleracea* L.) grown in acidic nutrient solution', *HortScience*, 56, 687-694, available: https://doi.org/10.21273/ HORTSCI15777-21
- Gonnella, M., Serio., F., Conversa, G., Santamaria, P. (2003) "Yield and quality of lettuce grown in floating system using different sowing density and plant spatial arrangements', in VI International Symposium on Protected Cultivation in Mild Winter Climate, Acta Horticulturae, 614, 687- 692, available: https://10.17660/ActaHortic.2003.614.102
- Kleiber, T., Markiewicz, B. (2010) 'Tolerancja sałaty (Lactuca sativa L.) na zasolenie. Cz. I. Zróżnicowanie składu chemicznego pożywek środowiska korzeniowego', Nauka Przyroda Technologie, 4, 46.
- Komosa, A. (2002) 'Podłoża inertne postęp czy inercja?', Zeszyty Problemowe Postępów Nauk Rolniczych, Lublin, 485, 147-167.
- Kowalczyk, W., Kaniszewski S. (2005) 'The effect of pH of the nutrient on solution on phosphorus availability and nutritional status of tomato grown in rockwool', *Vegetation Crops Research Bulletin*, 63, 87-99.
- Lee, J.Y., Rahman, A., Azam, H., Kim, H.S., Kwon, M.J. (2017) 'Characterizing nutrient uptake kinetics for efficient crop production during *Solanum* lycopersicum var. cerasiforme Alef. growth in a closed indoor hydroponic system', PLoS ONE, 12, e0177041, available: https:// doi.org/10.1371/journal.pone.0177041
- Maggini, R., Benvenuti, S., Leoni, F., Pardossi, A. (2018) 'Terracrepolo (*Reichardia picroides* (L.) Roth.): Wild food or new horticultural crop?', *Scientia Horticultura*, 240, 224-231, available: https://doi.org/10.1016/j.scienta.2018.06.018
- Mengel, K., Kirkby, E.A., Kosegarten, H. and Appel, T. (2001) 'Nutrient uptake and assimilation', In K. Mengel and E.A. Kirkby (eds.), Principles of Plant Nutrition, Dordrecht, The Netherlands, Kluwer Academic, p. 111-136.
- Michalak, A. (2006) 'Phenolic compounds and their antioxidant activity in plants growing under heavy metal stress', *Polish Journal of Environmental Studies*, 15, 523-530.
- Michałojc, Z., Nurzyński, J.(2002) 'Wpływ odczynu na koncentrację składników pokarmowych

w welnie mineralnej w uprawie pomidora szklarniowego', Zeszyty Problemowe Postępów Nauk Rolniczych, 482, 385-390.

- Nicola, S., Hoeberechts, J., Fontana, E. (2005) 'Comparison between traditional and soilless culture systems to produce rocket (*Eruca sativa*) with low nitrate content', *Acta Horticultura*, 697, 549-555, available: https://doi.org/10.17660/ActaHortic.2005.697.72
- Resh, H.M. (2008) 'Hydroponic food production', 4th ed., Woodbridge Press Publishing Company, Santa Barbara, CA, USA.
- Rosas, A., Rengel, Z., Mora, M.D.L.L. (2007) 'Manganese supply and pH influence growth, carboxylate exudation and peroxidase activity of ryegrass and white clover', *Journal* of *Plant Nutrition*, 30, 253-270 available: http://dx.doi.org/10.1080/01904160601118034
- Sambo, P., Nicoletto, C., Giro, A., Pii, Y., Valentinuzzi, F., Mimmo, T., Lugli, P.,Orzes, G., Mazzetto, F., Astolfi, S., et al. (2019) 'Hydroponic solutions for soilless production systems: Issues and opportunities in a smart agriculture perspective', *Frontiers Plant Sciences*, 10, 923, available: https://doi.org/10.3389/fpls.2019.00923
- Sardare, M.D., Shraddha, V., Admane (2013) 'A review on plant without soil hydroponics', International Journal of Research in Engineering and Technology, 02,03.
- Savvas, D. & Gruda, N. (2018) 'Application of soilless culture technologies in the modern greenhouse industry – A review', *European Horticulture Science*, 83, 280-293, available: https:// doi.org/10.17660/eJHS.2018/83.5.2
- Savvas, D., Karagianni, V., Kotsiras, A., Demopoulos, V., Karkamisi, I., Pakou, P. (2003) 'Interactions between ammonium and pH of the nutrient solution supplied to gerbera (*Gerbera jamesonii*) grown in pumice', *Plant Soil*, 254, 393-402, available: https://link.springer.com/ article/10.1023/A:1025595201676
- Singh, R., Singh, G.S. (2017) 'Traditional agriculture: A climate-smart approach for sustainable food production', *Energy Ecological Environment*, 2, 296-316, available: https://link.springer.com/ article/10.1007/s40974-017-0074-7
- Sonneveld, C. (2002) 'Composition of nutrient solutions', In Hydroponic Production of Vegetables and Ornamentals, Savvas, D., Passam, H., (Eds.), Embryo Publications, Athens, Greece, pp. 179-210.
- Statistica (2014). Data Analysis Software System, Version 12, Statsoft Inc., Tulsa, OK, USA.
- Treutter, D. (2006) 'Significance of flavonoids in plant resistance: A review', *Environomental Chemistry Letter*, 4, 147-157, available: https://doi.org/10.1007/s10311-006-0068-8
- Umamaheswari, S., Preethi, A., Pravin, E., Dhanusha, R. (2016) 'Integrating scheduled hydroponic system', in Proceedings of the 2016 IEEE International Conference on Advances in Computer Applications (ICACA), Coimbatore, India, pp. 333-337.
- Voogt, W. (1995) 'Effect of the pH on rockwool grown carnation (*Dianthus caryophyllus*)', Acta Horticulture, 401, 327-336, available: https://doi.org/10.17660/ActaHortic.1995.401.39
- Zhao, J., Davis, L.C., Verpoorte, R. (2005) 'Elicitor signal transduction leading to production of plant secondary metabolites', *Biotechnology Advances*, 23, 283-333, available: https://doi. org/10.1016/j.biotechadv.2005.01.003