



Article

Struvite as a Sustainable Fertilizer in Mediterranean Soils

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Abstract: Recycled sources of phosphorus (P) and nitrogen (N), such as struvite extracted from wastewater, have the potential to substitute conventional manufactured fertilizers and mitigate environmental problems such as water eutrophication or the depletion of non-renewable resources. This study aimed to evaluate the potential of struvite as a nitrogenous and phosphate fertilizer in the Spanish Mediterranean region. Two experiments were carried out using struvite recovered from sewage sludge and different representative soils from the area. Since knowing the rates at which their nutrients are released is key for efficient use, experiment I determined the struvite N-releasing rate for 16 weeks. Experiment II studied the effect of different struvite doses (50, 100, 200 kg P₂O₅ ha⁻¹) on crop growth compared to superphosphate + ammonium nitrate. The results indicated N-releasing rates that fall in line with a slow-release fertilizer. More than 20% of applied struvite-N was unavailable for plants or in the longer term, which suggests struvite fractionation as the most efficient application method. Struvite showed similar fertilization capacity, which was even better at some points, than conventional mineral fertilization, plus adequate plant growth and good nutrient concentration at the 50 kg P₂O₅ ha⁻¹ dose. Based on this study, struvite can be considered an interesting and effective option for sustainable fertilization in the Mediterranean region.

Keywords: by-product; nutrient-releasing rate; plant growth; P and N uptake



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1. Introduction

Every year, a large amount of nitrogen (N) and phosphate fertilizers is applied to soil to increase its fertility, and excessive doses are applied to maximize crop productivity. It is estimated that ~40–70% N and ~80–90% phosphorus (P) of the total amounts applied by conventional mineral fertilizers are lost to the environment due to different soil dynamics, such as leaching or runoff [1]. Concomitant environmental problems are arising, which range from built-up soil salt to water eutrophication. Indeed, N and P contents in water bodies worldwide (rivers, lakes, seas) enhance the growth of algal blooms, which reduces light penetration and available oxygen and thus causes the death of aquatic life [2]. In addition, conventional P fertilizers are manufactured from rock phosphate, a non-renewable resource that comes mainly from a few places on Earth, namely Morocco, China, USA and South Africa and comprises 80% of the world's P. The demand for P is increasing by 1.5% each year and reserves are expected to be depleted over the next 90 years [3]. Furthermore, a new mandatory European Fertilizer Regulation, from 16 July 2022, introduces cadmium (Cd) limits in phosphate fertilizers for the first time [4]. This restricts the use of certain P fertilizers and drives some countries from the market [5]. In this context, it is crucial to optimize and reduce the use of conventional N and P mineral products, and to find new sustainable and renewable sources.

Struvite is a magnesium ammonium phosphate crystal with the chemical formula of MgNH₄PO₄·6H₂O that can be recovered from several wastewater types, including swine, dairy, landfill leachate, urine, anaerobic effluent and sewage sludge. Its theoretical fertilizer value is 12.5% P, 5.7% N and 9.9% magnesium (Mg), which varies depending on the source and recovery process [3]. Small quantities of macro- and micro-nutrients may also be

present, but heavy metal contents are lower compared to commonly available mineral fertilizers with Cd concentrations below detection limits [6,7]. It is usually free of pathogens and is non-toxic to simple invertebrate and vertebrate bioassays [3]. Struvite precipitates are usable as a magnesium ammonium phosphate fertilizer, and it also contributes to lower effluent P and N concentrations in wastewater before it is discharged to water courses. Besides being a renewable resource, struvite provides additional environmental benefits thanks to its low solubility in water. Since it is barely soluble in water within the 1–5% range, and is nearly 100% soluble in mild acids, its solubility increases in the rhizosphere when plants produce organic acids from roots [8]. Although its leaching pattern is strongly affected by soil nitrification, its placement on soil and the size of struvite particles [9], nutrients are released for longer periods compared to mineral fertilizers, which can be completely leached out in 1–3 days. A slow-release fertilizer can gradually provide N and P for crop growth by matching plants' nutrient demand during the growing season and increasing its efficiency of use [10]. Struvite can therefore be considered an interesting alternative to conventional nitrogenous and phosphate fertilizers while posing a minimal environmental impact.

Different studies have shown that struvite can be successfully used in the fertilization of different crops, such as ryegrass, ornamentals, vegetables and tree seedlings. However, most of them have focused on its interest as a P supply, and not as a N source [3,11,12]. Moreover, it is of paramount importance to evaluate its effectiveness by taking into account the local conditions where it is to be applied because results depend on the product's physical characteristics, such as the size of struvite crystals, the way that it is produced and soil characteristics.

The aim of this study was to assess the potential use of struvite as a nitrogenous and phosphate fertilizer on the east coast of Spain. Two different trials were carried out using struvite recovered from a sewage treatment plant and different representative soils in the region. The first trial was performed to determine the struvite N-releasing rate and to evaluate its availability for plants over time. The obtained results can allow decisions to be made about the most suitable times to apply struvite to meet plant requirements throughout the crop cycle. During the second trial, the effect of struvite on plant growth and nutrient status was compared to chemical fertilization by determining its optimum dose.

2. Materials and Methods

The struvite used in both trials was provided by the wastewater treatment plant E.D.A.R Cidacos (La Rioja, Spain). Struvite granules contained N (3.08%), P (7.64 %) and Mg (4.33%) (Table 1)

Table 1. Analytical characteristics of struvite used in the two experiments.

| Parameter ¹ | Value |
|------------------------------------|---------|
| Dry matter (%) | 42.9 |
| TVS (%) | 44.9 |
| pH (1:2,5) | 9.21 |
| EC (1:5, dSm ⁻¹) | 3.06 |
| N-NH ₄ ⁺ (%) | 0.00840 |
| Total N (%) | 3.08 |
| P ₂ O ₅ (%) | 17.5 |
| K ₂ O (%) | 0.130 |
| CaO (%) | 14.2 |
| MgO (%) | 7.18 |
| Na ₂ O (%) | 0.0767 |
| B (mg kg ⁻¹) | 16.9 |
| Fe (mg kg ⁻¹) | 64.9 |
| Cu (mg kg ⁻¹) | 5.30 |

Table 1. Cont.

| Parameter ¹ | Value |
|---------------------------|-------|
| Mn (mg kg ⁻¹) | 25.4 |
| Zn (mg kg ⁻¹) | 11.0 |
| Ni (mg kg ⁻¹) | 2.99 |
| Pb (mg kg ⁻¹) | 1.32 |
| Cd (mg kg ⁻¹) | 0.12 |
| Cr (mg kg ⁻¹) | 3.04 |

¹ TVS: total volatile solids; EC: electrical conductivity at 25 °C. All data, except dry matter, pH and EC, are expressed on a dry-weight basis.

2.1. N-Releasing Rate

Three soils of different textural classes were used for the experiment I: S1 (sandy soil), S2 (loamy soil) and S3 (clayey soil). They are all representative soils of the Mediterranean growing area. Soils were air-dried, ground and sieved through a 2 mm plastic mesh before analyses (Table 2). Struvite and soils were mixed carefully in replicated 125 mL plastic pots at 5.56 g kg⁻¹ soil dry matter (DM) (roughly the equivalent to an application rate of 600 kg N ha⁻¹ considering a soil bulk density of 1.8 g mL⁻¹ and a 20 cm arable layer) and incubated aerobically for 16 weeks at 25 °C, together with the controls. The water content of mixtures was adjusted weekly at 2/3 of the soil field capacity. Four samples of each soil and struvite combination were collected after 1, 2, 3, 4, 6, 8, 12 and 16 weeks. Their mineral N contents were determined following the methods by Rhine et al. [13] for N-NH₄⁺ and Sempere et al. [14] for N-NO₃. The other analytical determinations were made using the Official Methods of the Spanish Ministry of Agriculture, Food and Fisheries [15] with minor modifications. To correct the effect of native soil organic matter mineralization, mineral N was calculated at each sampling time as the difference between the values determined in the struvite-soil mixtures and that in the corresponding control (non-amended soil). By means of non-linear regressions, the mineral N data thus calculated during all eight incubation periods were adjusted to the equation described by Smith et al. [16]:

$$N_m = N_0(1 - e^{-kt})$$

where N_m is the amount of mineralized N at a specific time, N_0 is the potentially mineralizable N, k is the first-order rate constant and t is the incubation time. A first-order kinetics was considered in the same way as they are in mineralization studies of organic products, based on the assumption that struvite is a salt of low solubility and its N-releasing rate could, therefore, be like those of organic fertilizers. The Levenberg–Marquardt algorithm [17] was used for the non-linear regression analysis and to estimate kinetic parameters.

Table 2. Analytical characteristics of soils used in the experiment I (N releasing rate).

| Parameter ¹ | S1 | S2 | S3 |
|-------------------------------|--------|-------|--------|
| Texture | Sandy | Loamy | Clayey |
| Sand (%) | 92.0 | 22.0 | 9.00 |
| Silt (%) | 2.90 | 30.8 | 28.2 |
| Clay (%) | 5.10 | 47.2 | 62.8 |
| pH (1:2.5) | 8.58 | 8.33 | 8.22 |
| EC (1:5, dS m ⁻¹) | 99.7 | 161 | 182 |
| Total CaCO ₃ (%) | 31.8 | 46.6 | 21.5 |
| Organic C (%) | 0.414 | 1.04 | 0.912 |
| Organic N (%) | 0.0411 | 0.106 | 0.103 |
| C/N ratio | 10.1 | 9.82 | 8.87 |
| P (mg kg ⁻¹) | 17.4 | 40.8 | 25.9 |

¹ All data, except pH and EC, are expressed on a dry-weight basis.

2.2. Struvite Fertilizer Effect on Crop Growth

The experiment II was conducted in a greenhouse belonging to the Valencian Institute of Agricultural Research (IVIA) in Moncada (Valencia), Spain. Three soils with low Olsen P contents were used to provide a P-limiting environment and to guarantee that the P assimilated by plants came from struvite. They were all representative soils of the Mediterranean growing area but had different textural classes: S4 (sandy loam), S5 (loamy) and S6 (clay loam) (Table 3). Five P fertilizer treatments (4 replicates each) included: C (nil P fertilization, untreated control), SP (P fertilization with single superphosphate at 50 kg P₂O₅ ha⁻¹), S50 (P fertilization with struvite at an equivalent dose of 50 kg P₂O₅ ha⁻¹), S100 (P fertilization with struvite at an equivalent dose of 100 kg P₂O₅ ha⁻¹) and S200 (P fertilization with struvite at an equivalent dose of 200 kg P₂O₅ ha⁻¹). To ensure that P was the only limiting macronutrient, all the treatments received similar N and K fertilization doses. N was considered a reference for the quantity of N provided by the maximal struvite dose (200 kg P₂O₅ ha⁻¹) using NH₄NO₃ for equating N inputs. For K, K₂SO₄ was used at a dose of 45 kg K₂O ha⁻¹.

Table 3. Analytical characteristics of soils used in the experiment II (struvite fertilizer effect on crop growth).

| Parameter ¹ | S4 | S5 | S6 |
|-------------------------------|------------|--------|-----------|
| Texture | Sandy loam | Loamy | Clay loam |
| Sand (%) | 19.3 | 21.5 | 56.0 |
| Silt (%) | 18.2 | 28.7 | 37.3 |
| Clay (%) | 62.5 | 49.8 | 27.7 |
| pH (1:2, 5) | 8.69 | 8.94 | 8.75 |
| EC (1:5, dS m ⁻¹) | 175 | 140 | 152 |
| Total CaCO ₃ (%) | 40.1 | 39.2 | 27.3 |
| Organic C (%) | 1.99 | 0.980 | 1.12 |
| Organic N (%) | 0.120 | 0.0840 | 0.0920 |
| C/N ratio | 16.6 | 11.7 | 12.2 |
| P (mg kg ⁻¹) | 14.3 | 10.1 | 7.78 |

¹ All data, except pH and EC, are expressed on a dry-weight basis.

Plastic pots (5.5 L) were filled with soil-fertilizer combinations before sowing *Festuca arundinacea* at a dose of 30 g m⁻². Plants were periodically watered to maintain optimal humidity. Grass was harvested at 30, 90, 120, 150 and 180 days after sowing. Samples were dried at 65 °C, weighed and then milled before the chemical analysis. Analytical determinations were made using the Official Methods of the Spanish Ministry of Agriculture, Food and Fisheries [15] with slight modifications: N content was determined by Kjeldahl digestion [18] using a 2400 Kjeltex AutoSampler System (Foss Tecator AB, Höganäs, Sweden). The P and Mg concentrations were measured by simultaneous inductively coupled plasma atomic emission spectrometry (ICAP-AES 6000, Thermo Scientific, Cambridge, UK; [19]) after nitric-perchloric digestion [20]. The measured variables were grass DM yield, grass N concentration, grass Mg concentration and grass P concentration, which were used to calculate the P offtake in the harvested grass. Statistical analyses of the results were performed by ANOVA (F-test and LSD Multiple Range Test at $p < 0.05$). All the statistical calculations were made using the Statgraphics Plus 5.0 (Manugistics Inc., Bethesda, MD, USA) software package.

3. Results

Table 4 displays the amounts and percentage of the N released (N-NH₄⁺ + N-NO₃⁻) from struvite during the incubation period. The influence of the soil on the releasing rates was evident. In the early stages, the sandy soil clearly showed lower mineral N contents than the loamy and clayey soils, with values after 1 week of incubation of 20.4 mg kg soil⁻¹ versus 46.0 and 61.8 mg kg soil⁻¹ for loamy and clayey, respectively. However, after 4 weeks, the N amounts increased to 93.3 mg kg soil⁻¹ to equal loamy and to surpass

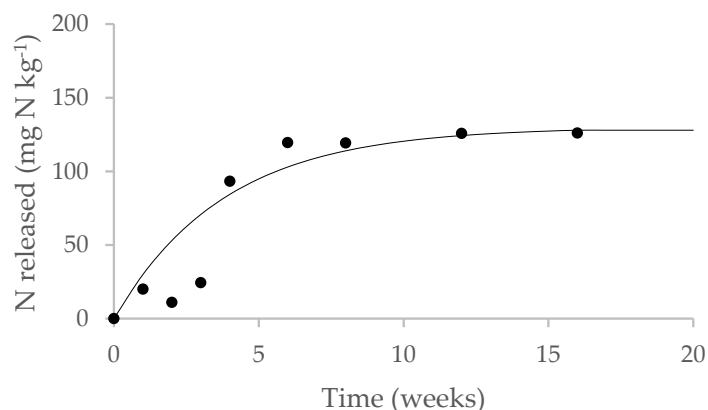
78.5 mg kg soil⁻¹ of the clayey soil, showing the highest values at 6, 8 and 12 weeks. At the end of the experiment, the soils' N contents did not statistically differ. Although the clayey soil obtained the fastest-releasing rates in the first 3 weeks with 78.4 mg kg soil⁻¹, they started to stabilize after 1 month of incubation and presented slight increments for the other measurements. During the full incubation period, the struvite N-released percentages were 55.8% in clayey and 77.0% in sandy and loamy; thus, around 25% of the fertilizer applied to the sandy and loamy soils and 44% to the clayey soil could not be used or even utilized in the long term. In the three types of soil, the release of N occurred mainly in the first month, releasing about 50% of the struvite N.

Table 4. Quantity (mg kg soil⁻¹) and percentage of the struvite N liberated.

| | Incubation Time (Weeks) | | | | | | | | | | | | | | | | | | | | | | | |
|----|-------------------------|------|---|------|------|---|------|------|---|------|------|---|------|------|----|------|------|---|------|------|---|------|------|---|
| | 1 | | 2 | | 3 | | 4 | | 6 | | 8 | | 12 | | 16 | | | | | | | | | |
| | Q | % | Q | % | Q | % | Q | % | Q | % | Q | % | Q | % | Q | % | | | | | | | | |
| S1 | 20.4 | 12.2 | a | 11.0 | 6.73 | a | 24.4 | 14.9 | a | 93.3 | 57.0 | a | 119 | 73.0 | b | 119 | 72.8 | c | 126 | 76.8 | b | 126 | 77.0 | a |
| S2 | 46.0 | 28.1 | b | 58.3 | 35.6 | b | 72.8 | 44.5 | b | 92.4 | 56.4 | a | 93.0 | 56.8 | a | 103 | 62.7 | b | 121 | 74.1 | b | 126 | 77.0 | a |
| S3 | 61.5 | 37.5 | b | 67.8 | 41.4 | b | 78.4 | 47.9 | b | 78.5 | 48.0 | a | 87.5 | 53.5 | a | 86.8 | 53.1 | a | 90.3 | 55.2 | a | 91.4 | 55.8 | a |

For each incubation time, values followed by the same letter do not differ significantly (LSD test, *p* < 0.05).

Figure 1 displays the cumulative amounts of mineral N released from struvite during incubations. Table 5 summarizes the main parameters obtained from the kinetic study of the data. In the sandy and clayey soils, the measurements taken at the beginning of the experiment considerably differed from those calculated by the first-order kinetic equation, but subsequent data were better adjusted to the mathematical approximation. The loamy soil results were the most similar ones to the model, with experimental data fitting the theoretical curve throughout the experiment. The N₀ (potentially mineralizable) values ranged from 92.6 to 130 mg kg soil⁻¹ or from 56.5 to 79.3 % of the total applied N. *k* (first-order rate constant) ranged from 0.245 to 0.323 week⁻¹. The multiplication of N₀ by its respective *k* constant (N potentially mineralizable in 1 week at an optimum soil temperature) varied from 29.9 to 34.0 mg kg soil⁻¹ week⁻¹.



(a)

Figure 1. Cont.

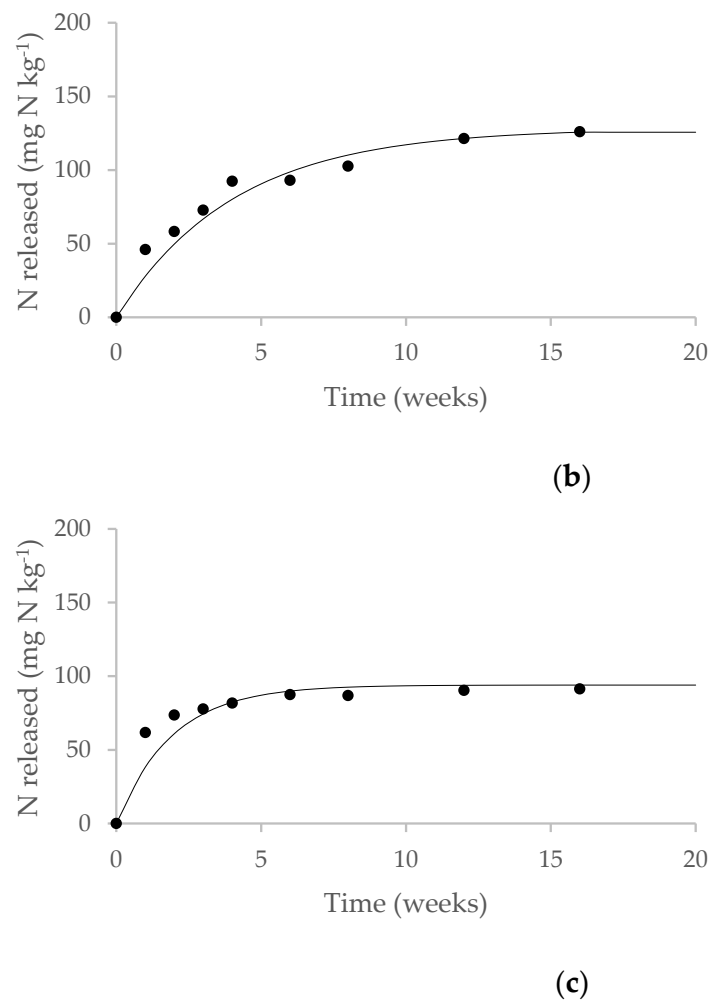


Figure 1. Amounts of N released and fitted kinetic curves for all the incubations: (a) Soil S1; (b) Soil S2; (c) Soil S3.

Table 5. Constants of the kinetic equations of N mineralization (N_0 , K) and potential index of N availability ($N_0 K$).

| Soil | N_0 ¹ (mg N kg ⁻¹ Soil) | K ¹ (Week ⁻¹) | $N_0 K$ (mg N kg ⁻¹ Soil Week ⁻¹) |
|------|--|---|---|
| S1 | 130 | 0.262 | 34.0 |
| S2 | 128 | 0.245 | 31.4 |
| S3 | 92.6 | 0.323 | 29.9 |

¹ All data are expressed on a dry-weight basis.

Struvite Fertilizer Effect on Crop Growth

Dry matter production for the grown tall fescue is shown in Tables 6–8. It is expressed as grams of biomass obtained in each cutting. Accumulated biomass was calculated by adding the five cutting values. The statistical analysis results revealed that accumulated biomass did not significantly differ among treatments in any soil. When plant growth was analyzed per cutting, significant differences ($p < 0.01$) were found in the first and second cuttings in the sandy loam soil, but only in the second cutting in the loamy and clay loam soils. In sandy loam, treatments SP, S100 and S200 showed more growth than the control in both cuttings. Struvite produced a larger plant biomass than superphosphate at the S100 dose in the first cutting, with doses S100 and S200 in the second one. In the loamy and clay loam soils, the four treatments with P-fertilization led to increased plant growth. The

struvite effect was stronger than superphosphate at three doses in loamy and at the S200 dose in clay loam.

Table 6. Dry-matter yield (g) of tall fescue in soil S4.

| Treatment | 30 Days | 90 Days | 120 Days | 150 Days | 180 Days | Accumulated |
|-----------|---------------------|--------------------|-------------------|-------------------|-------------------|-------------------|
| C | 0.152 ^a | 0.692 ^a | 1.21 ^a | 1.21 ^a | 1.30 ^a | 4.55 ^a |
| SP | 0.245 ^b | 1.17 ^b | 1.28 ^a | 1.48 ^a | 1.37 ^a | 5.54 ^a |
| S50 | 0.240 ^{ab} | 1.21 ^b | 1.01 ^a | 1.74 ^a | 1.46 ^a | 5.66 ^a |
| S100 | 0.353 ^c | 1.58 ^c | 1.10 ^a | 1.65 ^a | 1.25 ^a | 6.93 ^a |
| S200 | 0.318 ^{bc} | 1.88 ^d | 1.15 ^a | 1.43 ^a | 1.97 ^a | 6.75 ^a |

For each column, values followed by the same letter do not differ significantly (LSD test, $p < 0.05$).

Table 7. Dry-matter yield (g) of tall fescue in soil S5.

| Treatment | 30 Days | 90 Days | 120 Days | 150 Days | 180 Days | Accumulated |
|-----------|--------------------|--------------------|--------------------|-------------------|-------------------|-------------------|
| C | 0.210 ^a | 0.655 ^a | 1.04 ^a | 1.52 ^a | 1.14 ^a | 4.56 ^a |
| SP | 0.295 ^a | 0.983 ^b | 0.943 ^a | 1.35 ^a | 1.60 ^a | 5.17 ^a |
| S50 | 0.243 ^a | 1.37 ^c | 0.698 ^a | 1.23 ^a | 1.63 ^a | 5.17 ^a |
| S100 | 0.335 ^a | 1.69 ^d | 0.793 ^a | 1.01 ^a | 1.47 ^a | 5.30 ^a |
| S200 | 0.290 ^a | 1.75 ^d | 0.883 ^a | 1.12 ^a | 1.41 ^a | 5.45 ^a |

For each column, values followed by the same letter do not differ significantly (LSD test, $p < 0.05$).

Table 8. Dry-matter yield (g) of tall fescue in soil S6.

| Treatment | 30 Days | 90 Days | 120 Days | 150 Days | 180 Days | Accumulated |
|-----------|--------------------|--------------------|---------------------|-------------------|-------------------|-------------------|
| C | 0.173 ^a | 0.498 ^a | 1.29 ^a | 2.26 ^a | 1.97 ^a | 6.19 ^a |
| SP | 0.130 ^a | 1.09 ^b | 0.0480 ^a | 1.33 ^a | 1.73 ^a | 4.99 ^a |
| S50 | 0.143 ^a | 1.41 ^b | 0.638 ^a | 1.48 ^a | 2.00 ^a | 5.67 ^a |
| S100 | 0.168 ^a | 1.45 ^{bc} | 1.03 ^a | 1.76 ^a | 2.10 ^a | 6.50 ^a |
| S200 | 0.170 ^a | 1.85 ^c | 0.915 ^a | 1.39 ^a | 2.30 ^a | 6.63 ^a |

For each column, values followed by the same letter do not differ significantly (LSD test, $p < 0.05$).

As Table 9 shows, in the three soils the average grass P concentration, expressed as grams of P and as 100 g of plant biomass, significantly differed ($p < 0.01$) among treatments. The P fertilization with superphosphate did not increase the P percentages in any soil. Struvite, however, produced higher values than the untreated control at the different doses depending on soil; these values were at the rate of 50 kg P₂O₅ ha⁻¹ in sandy loam (0.278% in S50 and 0.185% in C) and in loamy (0.218% in S50 and 0.176% in C) and at the rates of 100 and 200 kg P₂O₅ ha⁻¹ in loamy (0.235% in S100, 0.237% in S200 and 0.176% in C) and clay loam (0.269% in S100, 0.327% in S200 and 0.208% in C). The fertilizer P recovery percentages ranged from 1.34% (S 50, clay loam soil) to 9.26% (S50, sandy loam soil) (Table 10). No substantial differences were found in the N biomass concentrations (Table 9), which indicates that the way N was applied (nitrate, struvite or combination of the two) did not affect plant N availability. Similarly, the Mg concentrations did not significantly differ among treatments (Table 9).

Table 9. Average nutrient concentration in tall fescue biomass (%).

| Treatment | S4 | | | S5 | | | S6 | | |
|-----------|---------------------|-------------------|--------------------|---------------------|-------------------|--------------------|---------------------|--------------------|--------------------|
| | P | N | Mg | P | N | Mg | P | N | Mg |
| C | 0.185 ^{ab} | 3.83 ^a | 0.261 ^a | 0.176 ^a | 3.59 ^a | 0.287 ^a | 0.208 ^a | 3.53 ^a | 0.406 ^a |
| SP | 0.170 ^a | 3.74 ^a | 0.239 ^a | 0.204 ^{ab} | 3.65 ^a | 0.305 ^a | 0.222 ^{ab} | 3.82 ^b | 0.331 ^a |
| S50 | 0.278 ^c | 3.83 ^a | 0.301 ^a | 0.218 ^b | 3.87 ^a | 0.310 ^a | 0.240 ^{ab} | 3.87 ^b | 0.397 ^a |
| S100 | 0.234 ^{bc} | 3.63 ^a | 0.259 ^a | 0.235 ^{bc} | 3.73 ^a | 0.292 ^a | 0.269 ^b | 3.73 ^{ab} | 0.385 ^a |
| S200 | 0.206 ^{ab} | 3.89 ^a | 0.251 ^a | 0.237 ^c | 3.62 ^a | 0.270 ^a | 0.327 ^c | 3.97 ^b | 0.355 ^a |

For each column, values followed by the same letter do not differ significantly (LSD test, $p < 0.05$).

Table 10. Percentage of fertilizer P recovery.

| Treatment | S4 | S5 | S6 |
|-----------|--------------------|-------------------|-------------------|
| SP | 1.41 ^a | 2.80 ^a | 2.83 ^a |
| S50 | 9.26 ^b | 3.88 ^a | 1.34 ^a |
| S100 | 4.49 ^{ab} | 2.61 ^a | 2.83 ^a |
| S200 | 1.76 ^a | 1.87 ^a | 2.70 ^a |

For each column, values followed by the same letter do not differ significantly (LSD test, $p < 0.05$).

4. Discussion

The struvite used herein showed lower N (3.08%), P (7.64 %) and Mg (4.33%) contents than theoretical richness, 5.7% N, 12.5% P and 9.9% [3], which indicates the presence of impurities from the recovering and crystallization process.

The study of the N-releasing rate dynamics gave values close to those reported for certain organic fertilizers. Between 91.4 and 126 mg kg soil⁻¹ of mineral N were released after 16 weeks of incubation. This coincides with a mineralization study of poultry manure, in which 99 mg kg soil⁻¹ of mineral N was obtained under similar conditions [21]. Although rates were faster than expected, around 50% struvite-N was released in the first month, with 53.5–73% released at 16 weeks. These values are comparable to those reported by Chaves et al., 2014 [22] in a mineralization study of meat and bone meals, whose values ranged between 44.6 and 63.3%. On the contrary, the results were higher than the 13% to 67% values found by Chae and Tabatabai, 1986 [23] for animal manures, and likewise higher than the 0% to 39% values reported by Serna and Pomares, 1992 [24] for sewage sludge. These differences can be explained by the fact that organic fertilizers have to be mineralized from organic to inorganic forms before being released, which is generally slower than struvite solubilization. However, if organic fertilizers have high N contents with a low C/N ratio, as in meat and bone meals, mineralization would be fast and the releasing rate would therefore be comparable to the struvite rate.

Soil texture clearly affected the N-releasing rate. The sandy soil had the lowest N contents in the first assay weeks by equaling loamy and surpassing clayey soil in the end. When struvite is applied, it partially dissolves in water in the form of N-NH⁴⁺, which is gradually nitrified by the action of soil microorganisms. Given the high correlation between soil organic matter and many biological activity indices [25–27], the sandy soil's light texture and poor content in organic matter would have brought about minor biological activity and therefore N release would be delayed. In fact, it has been stated that the rate of nutrient leaching by struvite in soil is accelerated mainly by the soil nitrification rate [9,28]. The loamy soil obtained the lowest N-released values from 1 month to the end of incubation despite its high values in the first weeks. Much of the N-NH⁴⁺ that resulted from struvite solubilization would have probably been immobilized and absorbed by the clay-humic complex to reduce the quantity of released N. Conversely to soil mineral N contents, the kinetic study of the results showed that the influence of soil texture on N₀ (potentially mineralizable N) and K (first-order rate constant) was very limited, unlike Chae and Tabatabai (1986) [23], who reported large differences depending on different soil organic waste types (sewage sludge, animal, crop waste), or Chaves et al., 2014 [22], who obtained variable K values in a meat and bone meals study according to soil. The mathematical model considered for the study proved to be adequate with some limitations. The N-releasing rate in loamy soil agrees with the model throughout the experiment; however, sandy and clayey soils show some differences in the first measurements.

Our results suggest that an important part of struvite-N (44% in the clayey soil, 23% in sandy and loamy) would not be used by plants or would be employed in the longer term. According to these release rates, applying struvite in a fractionated way would be the most suitable fertilization method for meeting crop requirements and avoiding potential N losses to the environment.

The study of struvite's capacity as a fertilizer, assessed by its effect on the growth and nutritional status of tall fescue, gave similar results, and even better ones at some

points, than conventional mineral fertilization with superphosphate and ammonium nitrate. Applied at similar doses, both struvite and mineral fertilization resulted in a higher biomass yield in the first 3 months of the study compared to the non-fertilized plants. Many authors have reported an effect of struvite with chemical fertilizers on plant growth that was comparable [7,29–31] or even superior [11]. However, other studies have obtained lower yields in struvite-treated plants [3], which suggests the need to supplement struvite with conventional mineral fertilizers to obtain adequate results. At the nutritional level, the P concentration in the plant biomass was not modified by superphosphate application, unlike struvite, which brought about significant increases at a different dose depending on soil. The N biomass concentration was independent of the N source (struvite, ammonium nitrate or a combination of both). Struvite application did not modify Mg concentrations, not even at a higher dose. The effect of struvite fertilization on nutritional plant status has been widely reported. The extensive reviews performed about this subject by Kataki et al., 2016 [11] and Naveed et al., 2018 [3] reveal quite different results ranging from no significant impact to a significant effect on P, N and Mg uptakes depending on different factors like soil, plant and climate.

Crop P recovery, calculated as the difference in P uptake from fertilized treatments and the average P uptake from control, divided by the total P struvite application, did not increase with struvite dose. Obtained values (1.34–9.26%) were in a similar range to those reported in different studies. Talboys et al., 2016 [8] found a P recovery of 11% in wheat with a struvite dose of 35 kg P ha⁻¹ after 90 days and Hertzberger et al., 2020 [32] obtained struvite P recoveries of 9.5% and 0.8% in corn and soya, respectively, after 45 days and 28.5 kg P ha⁻¹ dose. When considering both the struvite effect on plant growth and nutrient levels, the dose corresponding to 50 kg P₂O₅ ha⁻¹ produced adequate plant growth and good nutrient concentration in all three soils without having to resort to higher doses. Struvite applied in combination with ammonium nitrate, as well as struvite applied alone, gave good results. Different studies recommend applying fertilizer mixes of struvite with conventional fertilizers to provide optimal nutrient uptakes throughout the crop cycle; early in the season, nutrient demand would be provided by high-soluble fertilizers, while the late season demand would be covered by struvite nutrients [8,11]. Sometimes the limited N availability due to a low N/P ratio of struvite renders N insufficient for plant growth because the required amount of N is much bigger than the required P. If the struvite application dose increases to fulfill plant requirements, it results in a higher soil pH compared to other P fertilizers, which might affect nutrient availability and uptake. In these cases, applying struvite together with other fertilizers is recommended to obtain a balanced nutrient ratio [8]. Moreover, struvite use combined with other N sources can increase its P recovery, as in the case of struvite being applied together with ammonium, where rhizosphere acidification in response to ammonium uptake may enhance P releasing rate [33]. Either applied alone or combined, the use of struvite allows the need for conventional mineral fertilizers to be reduced, which consequently diminishes the negative environmental impact of their use. As a by-product of wastewater treatments, fertilization with struvite enables the reuse of nutrients by contributing to develop circular economy. Hence the P and N contained in different wastewaters can be regarded as resources rather than contaminants, and struvite can be ultimately considered an eco-friendly fertilizer for sustainable crop production.

5. Conclusions

Despite being an exploratory study, the obtained results indicate that struvite recovered from sewage sludge can be considered an alternative to conventional mineral N and P fertilizers in the Spanish Mediterranean region. The study of N-releasing rate dynamics gave values in accordance with a slow-release fertilizer, as well as values close to the mineralization rate reported for certain organic fertilizers such as meat and bone meals. Soil texture clearly affected N-release rates, but fractionated struvite application instead of a single application would seem to be the most suitable option in all cases. Struvite effect on

plant growth gave similar results that conventional mineral fertilizer used at the same dose. P concentration in plant biomass was increased by struvite at different doses depending on soil, in contrast to superphosphate, which did not produce any statistically significant effect. These results, together with recycling and sustainability reasons, reveal that struvite is an interesting alternative to using superphosphate as a P fertilizer. The dose corresponding to 50 kg P₂O₅ ha⁻¹ produced good plant development and an adequate plant nutrient status, without having to resort to higher doses. Regarding N availability for plants, struvite produced the same effect as ammonium nitrate independently of the applied doses. Our data support the high potential of struvite as a sustainable fertilizer in Mediterranean soils. Further field experimentation is now required to assess the effectiveness of struvite under field conditions, for a wider range of soil types and cropping systems.

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