

## Article

# Evaluation of the Use of a Material with Struvite from a Wastewater Treatment Plant as N Fertilizer in Acid and Basic Agricultural Soils

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**Abstract:** Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) has been widely studied as an emerging recycled phosphorous fertilizer despite its low solubility. However, there are few studies on the use of this mineral as an N fertilizer. This article evaluates the use of two powder struvite-containing materials from wastewater treatment as an N fertilizer in agricultural soils. A 9-week soil incubation experiment was conducted to compare the effectiveness of this mineral as an N fertilizer in two soils with different pH values (8.2 and 6.7), using two different doses and a control soil. The use of these materials has a positive effect on soil fertility, especially in acidic soils where struvite seems to be more soluble. Thus, struvite can be a potential N fertilizer for agricultural soils and can promote circular economy opportunities for the wastewater industry, especially in acid soils (concentrations of mineral N between 453–339 mg/kg were obtained in the mixtures with acid soil, and values between 408–212 mg/kg in the mixtures with the basic soil after 6 weeks of soil incubation). However, associated with this process, an increase in soil salt content was observed (EC values reaching 3.9 dS/cm in mixtures with the acid soil and 2.8 dS/cm in the mixtures with the basic soil after nine weeks of soil incubation). Therefore, this parameter should be controlled in the case of continuous applications of the amendments, especially in conditions of poor drainage and/or non-percolating water regime, since it can be a limiting factor in crop development. These processes should be studied in detail in the future considering that the N soil cycle has a significant impact on soil chemistry and fertility and on the soil microbiological community.

**Keywords:** struvite; agricultural soil; N fertilizer; wastewater treatment; soil acidification; soil carbonates



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## 1. Introduction

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) is a P mineral generated from wastewater treatment plants (WWTP) by precipitation [1], which can decrease the operational and maintenance cost of WWTP, promoting the optimization of operational and environmental performance [2]. Struvite precipitation can act as a fast, efficient, and environmentally friendly pre-treatment step to remove P and reduce N from wastewater, and it can simultaneously be sold as fertilizer, reducing resource depletion by replacing fossil-fuel-based P [2]. Its precipitation as stable orthorhombic crystals can be used to sustain the nutrient loop in agriculture because it can be used as a slow-release fertilizer in crop production equal to the traditional chemical fertilizers [3]. Consequently, the recovery of P and N from the precipitation of struvite in WWTPs could promote circular economy opportunities for the wastewater industry.

The high demand for phosphorous as a crop nutrient and the finite resources of P in the world [1] have led to the search for new materials that can be used as P fertilizers.

The global demand for P fertilizers is estimated to be 47.0 million tons of  $P_2O_5$  due to intensive agriculture's heavy reliance on the input of fertilizers to sustain food production [4,5]. Since about 90% of commercially available P is sourced from phosphate rock, a non-renewable and geographically restricted resource with no meaningful reserves in the European Union [6], the European Union has recognized P as a critical resource [7]. In this sense, P recovery through struvite precipitation from wastewater has received much attention.

There are numerous articles about the effectiveness of struvite as a P fertilizer [1,7–20] because struvite has a theoretical P content close to that of phosphate rock (12.6%) [6]. These studies have demonstrated that struvite has improved the growth and development of different crops such as corn, wheat, barley, oats, etc., and some vegetables, such as cabbage, tomato, lettuce, spinach, etc. [3], especially in acid soils [6]. Another example is the article by [15], where the use of struvite in greenhouse experiments led to biomass yields and phosphorous uptakes comparable to or higher than those induced by a commercial mineral fertilizer. Contrary to these results, Ackerman et al. [8] reported that the biomass yield per unit of P uptake was smaller with struvite due to the lower solubility of the mineral in alkaline soils. Thus, the pH of the soil seems to be an important factor. Another factor to consider is the temperature, as the solubility of struvite is influenced by temperature, reaching its maximum at 35 °C [21]. Consequently, its application may not be suitable in some areas where those temperatures are not reached. Finally, the mineral form is also crucial since dissolution and hence plant availability of P is slower for granular compared to ground struvite [22]. Therefore, the fertilizer's effect in different soils and forms should be considered in future investigations [20].

On the other hand, despite the fact that the mineral also contains  $NH_4^+$  (6.5%), the behavior of this mineral as an N fertilizer has not been completely studied and is merely reported [5,23], mainly because of its low N/ $P_2O_5$  ratio [23]. According to the conclusions of Arcas-Pilz et al. [7], future research should focus on the role of  $NH_4^+$  supplied by struvite on plant development. Therefore, the use of struvite as a potential fertilizer still presents a challenge because the N dynamics after its application in soils remain unknown.

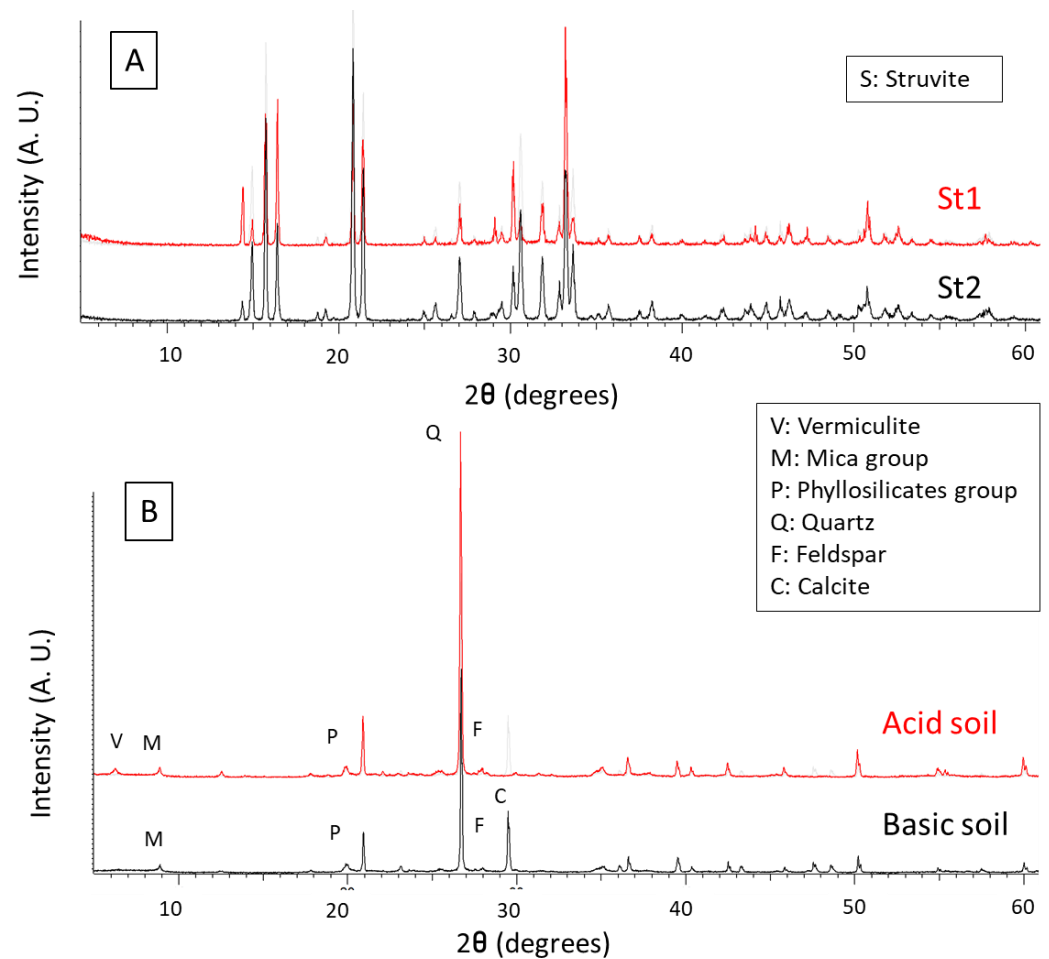
Nitrogen is generally considered the main factor limiting plant growth [5], so an increase in fertilizer nutrient input has been shown to contribute significantly to the improvement of crop yields around the world [24,25]. For this reason, N fertilizers have been widely used globally, and their use is expected to increase in the coming decades [26]. According to the FAO, the total fertilizer nutrient demand was 185,063 million tons in 2016, and this demand was forecasted to grow to reach 200,919 million tons in 2022 [27], leading to the search for new sources of N fertilizers. On the other hand, rational use of N fertilizers is necessary, since long-term N fertilization can deeply affect the physiochemical and biological soil properties associated with pH buffering capacity. Furthermore, N fertilization could induce the dissolution of carbonates in soils [28]. In addition, the incomplete capture and poor conversion of N fertilizer could also cause water pollution and global warming through emissions of nitrous oxide [29]. Therefore, it is crucial to evaluate the effectiveness of new fertilizers in the future, not only considering the productivity of the crops but also studying their effect on soil properties and the environment.

In this framework, the objective of this work is to evaluate the use of materials containing struvite from WWTPs as N fertilizers in soils with different pH values, under controlled laboratory conditions. It is crucial to understand the N dynamics after its application in order to define the overall fertilizer efficiency in soils with different pH values, taking into account that the continued use of nitrogenous fertilizers can cause problems in agricultural soils, such as acidification. This is particularly important because, in contrast to commonly used soluble fertilizers, the persistence of undissolved struvite at the end of the growing season can influence the evaluation of soil nutrient availability for the next cropping season [1].

## 2. Materials and Methods

### 2.1. Materials

Two materials obtained from two WWTPs from a stream of high concentrations of salts were used in the laboratory experiments: St1, which came from an uncontrolled precipitate in a stream with activated sludge treatment, and St2, which came from a pilot plant with a trickling filter of a stream with high carbonate concentration. Both materials contained struvite in their mineral composition (Figure 1A). Both materials were homogenized and ground to less than 2 mm using a mechanical mill.



**Figure 1.** X-Ray diffraction patterns of the materials from the WWTPs (A) and the studied soils (B).

The characterization of the samples was achieved according to standard methods [30] and by X-Ray diffraction (XRD) in a Bruker D8 advance Eco X-Ray diffractometer fitted with a Cu anode. The operating conditions were 40 mA, 45 kV, divergence slit of  $0.5^\circ$ , and 0.5 mm reception slits. The samples were scanned with a step size of  $0.0167^\circ$  ( $2\theta$ ) and 150 ms per step. The characterization of samples was carried out using the random power method operating from  $5^\circ$  to  $80^\circ$  ( $2\theta$ ) [31]. Table 1 and Figure 1 show the characterization of the samples containing struvite.

**Table 1.** Chemical characterization of the materials from the WWTPs.

Sample	pH	EC (dS/m)	N (%)	P ( $P_2O_5$ , %)	C (%)
St1	8.02	0.72	5.20	28.3	0.25
St2	8.46	1.09	4.15	15	0.20

Two soils of real agricultural plots of long duration (>10 years) were selected for this study. Both soil samples were collected with a shovel at the depth of the tilled layer (0–30 cm) and these samples were subsequently air-dried, homogenized, and sieved to 2mm. The first studied soil (S1) corresponds to a basic pH soil with a high content of carbonates (21.6%) from the practice agricultural field of the Higher Technical School of Agricultural Engineering and Biosciences (ETSIAB) in the Public University of Navarre (Pamplona, Spain). It is a representative soil of the non-irrigated cereal area of the Pamplona basin. The second studied soil (S2) corresponds to soil with acid pH values from an experimental agricultural plot managed by the regional public extension service (INTIA), in the north of Navarre (Spain), near Mount Remendia. In this case, the soil corresponds to the grassland area of the north-central zone of Navarre.

The soils used in the incubation experiments were characterized in terms of soil texture, pH, electrical conductivity (EC), total organic carbon, total N, P (Olsen), and cation exchange capacity (CEC) according to the official soil properties determinations [30]. In addition, the carbonate content of the soil samples was analyzed by a modified Bernard's calcimeter after quantifying the CO<sub>2</sub> produced after treating a soil sample ground to a powdery consistency with HCl 6M [32] and their mineralogical composition was determined using XRD. Table 2 and Figure 1B, show the characterization of the agricultural soils. The mineralogical composition of both soils is similar: mica minerals (vermiculite was detected in the acid soil), phyllosilicates, quartz, and a small amount of feldspar. In the basic soil, calcite is also present (Figure 1B).

**Table 2.** Physicochemical characterization of the soil samples.

Sample	pH	EC (dS/m)	N (%)	P Olsen (mg/kg)	C (%)	CEC (cmol+/kg)
S1	8.21	0.21	0.26	87.7	5.2	24.4
S2	6.74	0.06	0.16	77.5	1.7	12.1
Sample	Sand (%)	Silt (%)	Clay (%)	Texture	CaCO <sub>3</sub> (%)	Field Capacity (g/g)
S1	31	40	29	Clay Loam	21.6	0.32
S2	32	52	16	Silt Loam	0	0.34

## 2.2. Laboratory Soil Incubations

Laboratory incubation of soils under controlled temperature and soil moisture conditions was used in the evaluation of materials with struvite from the WWTPs as N fertilizer. Two soil incubation experiments (one soil incubation for each studied material) of 9 weeks duration were conducted. They evaluated the effectiveness as an N fertilizer of two powder materials (<2 mm) from the WWTPs (St1 and St2) in two types of soils (S1 (basic soil) and S2 (acid soil)), using two different N doses (d1 and d2).

The doses correspond to half of the dose of N recommended for the fertilization of a corn crop (d1) and the dose of N fertilization for this crop (d2) according to Urbano Terrón [33]. Specifically, 50 g of soil (S1 or S2) was mixed with 1 g (d1) or 2 g (d2) of the material with struvite (St1 or St2). These calculations were made taking into account the N content of the soils and of the samples with struvite. The mixtures (soil + struvite) were made at the beginning of the laboratory experiment. As a control of the experiment, the two soils were tested under the same conditions without adding the struvite samples (Figure 2A).



**Figure 2.** Laboratory soil incubations. (A): scheme of the laboratory soil incubation. (B): picture of the plots in the laboratory soil incubations.

According to the literature, the ideal temperature and moisture conditions for the development of microorganisms in this type of experiment are 25 °C and soil moisture between 60 to 100% of the field capacity of the samples (0.32 g/g and 0.34 g/g in the mixtures with S1 and S2, respectively) [18,34–37]. All the samples were maintained at these conditions during the 9 weeks of the experiment using a laboratory incubator (SANYO cooled incubator MIR 254) at 25 °C.

To maintain the correct moisture conditions of the samples (between 60 to 100% of the field capacity of the samples), the moisture control was checked twice a week. The irrigation of the samples was carried out by capillarity action. The samples were in 150 mL pots with four small holes, and these pots were placed on a plate where they were watered twice per week to maintain hydration between 60 and 100% of the field capacity. Therefore, the irrigation water could rise by capillarity action (Figure 2B).

A complete control of the samples was performed every three weeks, and characterization of the samples was carried out at the beginning of the trial and at 3, 6, and 9 weeks. All samples were analyzed in triplicate (Figure 2) in order to present the data as mean values with standard errors. Therefore, a total of 72 samples were prepared for each soil incubation (Figure 2A).

The following samples were analyzed (Figure 2A):

- S1: basic soil control samples; 50 g of S1 soil.
- S2: acid soil control samples; 50 g of S2 soil.
- S1 + St<sub>1</sub>\_d1: a mixture of the basic soil (50 g of S1) and the uncontrolled material with struvite with half the N recommended for the fertilization of corn (1 g of St<sub>1</sub>).
- S1 + St<sub>1</sub>\_d2: a mixture of the basic soil (50 g of S1) and the uncontrolled material with struvite with the N recommended for the fertilization of corn (2 g of St<sub>1</sub>).
- S2 + St<sub>1</sub>\_d1: a mixture of the acid soil (50 g of S2) and the uncontrolled material with struvite with half the N recommended for the fertilization of corn (1 g of St<sub>1</sub>).
- S2 + St<sub>1</sub>\_d2: a mixture of the basic soil (50 g of S2) and the uncontrolled material with struvite with the N recommended for the fertilization of corn (2 g of St<sub>1</sub>).
- S1 + St<sub>2</sub>\_d1: a mixture of the basic soil (50 g of S1) and the controlled material with struvite with half the N recommended for the fertilization of corn (1 g of St<sub>2</sub>).

- S1 + St2\_d2: a mixture of the basic soil (50 g of S1) and the controlled material with struvite with the N recommended for the fertilization of corn (2 g of St2).
- S2 + St2\_d1: a mixture of the acid soil (50 g of S2) and the controlled material with struvite with half the N recommended for the fertilization of corn (1 g of St2).
- S2 + St2\_d2: a mixture of the basic soil (50 g of S2) and the controlled material with struvite with the N recommended for the fertilization of corn (2 g of St2).

### 2.3. Analysis of the Samples

The characterization of the samples was carried out at the beginning of the trial and at 3, 6, and 9 weeks. The mixtures and the control soil samples were characterized in terms of pH, EC, and mineral N ( $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations) according to the official soil properties determinations [30]. This characterization made it possible to study the evolution of the pH, EC, and  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations in soil laboratory incubations. In addition, the carbonate content of the basic soil (S1) and their mixtures with St1 and St2 at different doses after 9 weeks of the experiment were analyzed by the protocol of [32] in a modified Bernard's calcimeter. A statistical *t*-test analysis was used to compare the results of the samples at the beginning and after 9 weeks of incubation, using SPSS 17.0. Significant differences were based on a probability level of  $p < 0.05$ . The data obtained from the incubation experiments are presented as  $\pm$ standard deviation of the mean values obtained from the analyses of three replicates (Figure 2A).

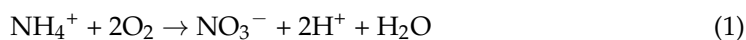
## 3. Results and Discussion

### 3.1. pH and Electrical Conductivity Values

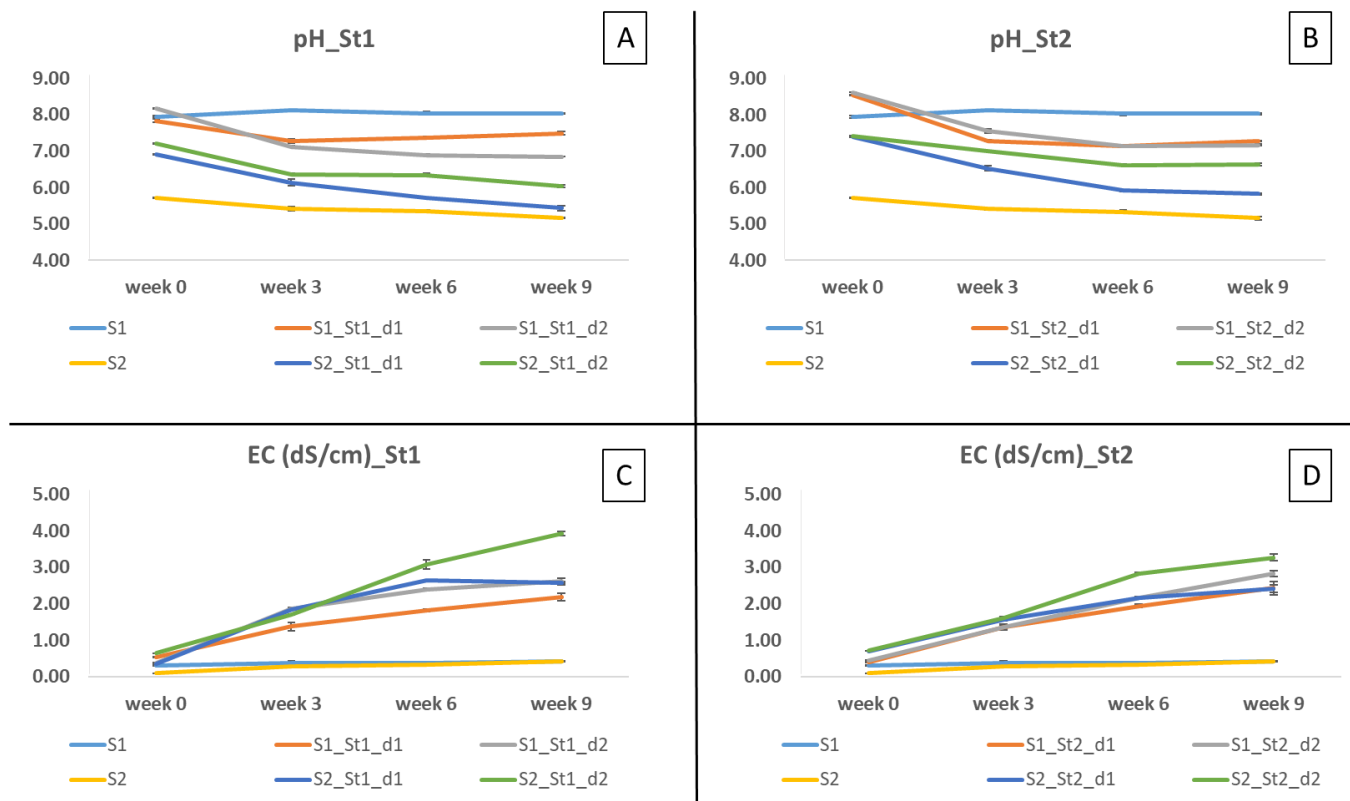
Figure 3A,B show the evolution of the pH in the two experiments. Amendment additions significantly affected the pH of the mixtures in both trials; the pH value of soils increased at the beginning of the test, especially in the acid soil. Statistically significant differences were observed when comparing the pH value of the control soil with the pH value of the soils at the end of the trials. In the acid soil (S2), the two materials from the WWTPs (St1 and St2) could be used as liming agents because the pH of the acid soil had increased, reaching pH values from 6.7 to 7–7.5 in the first week of the laboratory experiment (Figure 3A,B). This increase was slightly greater in the case of the mixtures with St2 than in the mixtures with St1, possibly due to the fact that St2 has an initial pH value somewhat higher than that of St1 (Table 1). According to these findings, these materials from the WWTPs could be an effective soil amendment for remedying soil acidity, and thus increasing productivity and soil fertility. The incorporation of liming materials can neutralize the protons released, hence reducing soil acidity and its adverse impacts on soil environment, food security, and human health [38]. On the contrary, in the basic soil (S1), an increase in the pH values at the beginning of the laboratory experiment was observed only in the mixtures with St2. These samples presented an increase in pH values from 8 to 8.5, but this increase was not seen in the mixtures with St1 (Figure 3A,B). These results are in agreement with previous studies [3,39]; their conclusion was that, generally, acid soils are found to be more suitable for struvite application because they improve its solubility and therefore increase the fertilizer's efficiency. This same conclusion was reached by Ackerman et al. [8], who reported a lower solubility of the mineral in alkaline soils. Therefore, the soil pH values seem to be a crucial factor in the evaluation of these materials with struvite as a fertilizer.

From week 3 onward, soil acidification was observed in all the mixture samples studied (Figure 3A,B). Soil acidification in agricultural lands principally results from the increased release of protons ( $\text{H}^+$ ) from the transformation reactions of C-, N-, and S-containing compounds [38]. In this case, the soil acidification after 3 weeks of the experiment is related to the soil N cycle. The major process leading to acidification during this cycle

is nitrification, since nitrification of 1 mol of ammonium to nitrate releases 2 mol of H<sup>+</sup> ions [40], according to Equation (1):



Thus, nitrification explains why there was a decrease in pH values in all the mixtures but not in the control soil samples (Figure 3A,B).



**Figure 3.** Results of pH and electrical conductivity (dS/cm). (A): pH results in the laboratory experiments with St1. (B): pH results of the laboratory experiment with St2. (C): EC results in the experiment with St1. (D): EC results in the experiment with St2. Bars indicate the standard deviations of the means of three replicates of each sample.

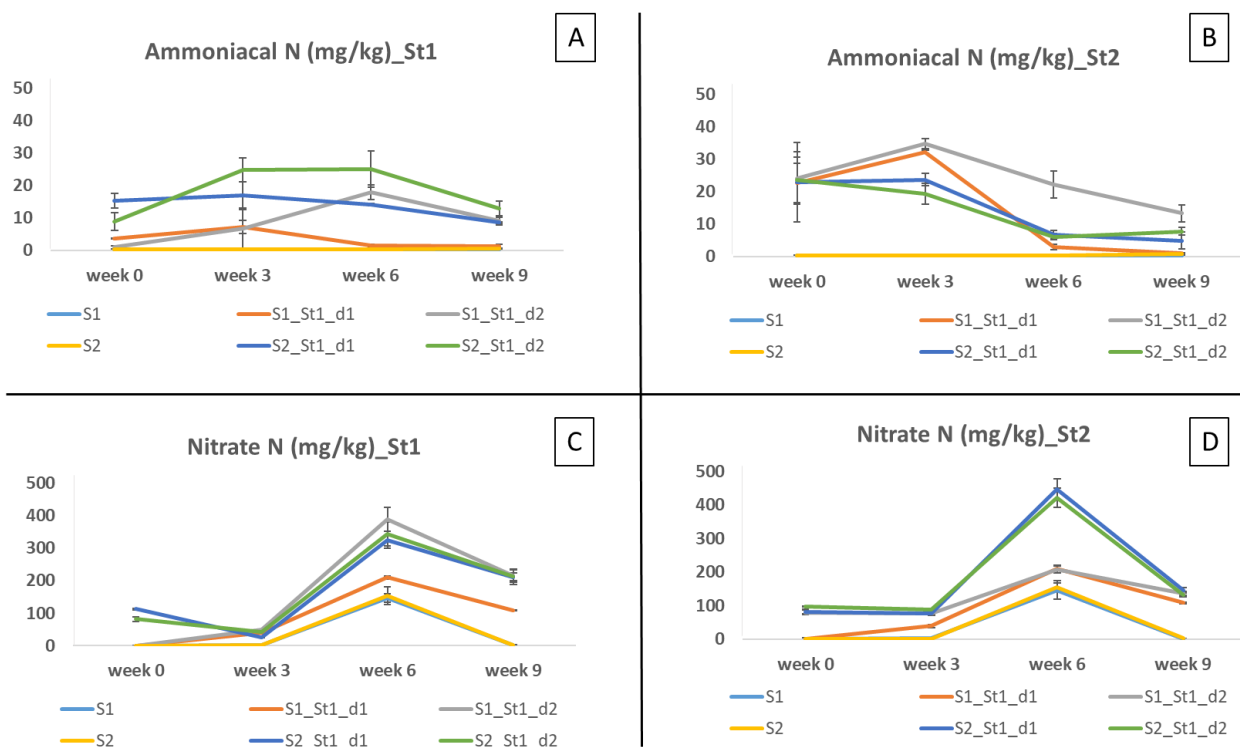
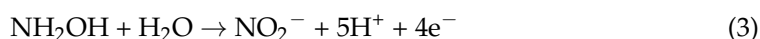
Figure 3C,D show the evolution of EC values during the incubation experiments. The amendments provided soluble salts to the soil which produced a significant increase in EC values over time, and this fact was more evident in the soils that received the highest dose of fertilizer. Statistically significant differences are observed when comparing the EC values at the beginning and at the end of the trials. This parameter should be controlled in the case of continuous applications of the amendments, especially in conditions of poor drainage and/or non-percolating water regime, as it can be a limiting factor in crop development. However, it should be noted that in the incubation experiment, soil drainage has not been allowed. Thus, an increase in the salt content of the samples was expected.

An increase in soil salinity can cause inhibition of plant emergence, decreased size of the plant, a decrease in crop yields, and the death of the plant [41]. Thus, this parameter must be considered in future studies. Even though salinity can be a problem for soil fertility, there are no studies that have investigated the final soil salinity after applying struvite as a fertilizer. The majority of the studies have focused on its potential as a P fertilizer and its relationship with crop yield. Therefore, the implication of the use of struvite fertilizer on soil salinity should be further investigated to help improve its use in agricultural soils. This coincides with the conclusions of other researchers [20] who have emphasized the need to study the effectiveness of this material in different soil types.

Regarding the applied dose, the mixtures with the highest struvite content (50 g of soils + 2 g of struvite; S1 + St1\_d2, S2 + St1\_d2, S1 + St2\_d2, and S2 + St2\_d2) present higher EC values (Figure 3C,D), which demonstrates the importance of adjusting the dose to the needs of the crop to avoid overfertilization. On the other hand, when studying the behavior of soils as a function of their pH, it was observed that mixtures with acid soil (S2 + St1\_d1, S2 + St2\_d2, S2 + St2\_d1, and S2 + St2\_d2) presented slightly higher EC values. These results agreed with previous studies in which acid pH values allowed the solubility of the mineral [3].

### 3.2. Ammonium and Nitrate Values

Figure 4 shows the evolution of ammonium and nitrate concentrations of the mixtures and control soils. The samples showed an evolution consistent with N mineralization associated with ammonification and a subsequent nitrification process. The N cycle is biologically influenced, and soil microorganisms maintain supplies of bioavailable N for plants, whether the inputs are from N fixation, organic manures, or N fertilizers [42]. Ammonification is mediated by various fungi and prokaryotes, which decompose the organic N and release  $\text{NH}_4^+$ , which can then be taken up by plants or converted to  $\text{NO}_3^-$  through nitrification [43]. This last process has two steps. The first step is the oxidation of  $\text{NH}_3$  to nitrite by microbes known as ammonia oxidizers (Equations (2) and (3)). The second step is the oxidation of nitrite to nitrate (Equation (4)) by the nitrite-oxidizing bacteria [43].



**Figure 4.** Results of ammonium and nitrate values (mg/kg). (A): ammoniacal N in the laboratory experiment with St1. (B): ammoniacal N in the laboratory experiment with St2. (C): nitric N results in the experiment with St1. (D): nitric N results in the experiment with St2. Bars indicate the standard deviations of the means of three replicates of each sample.



In the laboratory soil incubations, the accumulation of  $\text{NH}_4^+$  occurred after three weeks of the experiment, and it subsequently decreased in the sixth week. At this moment, an increase in nitrate occurred in all the samples (mixture and control samples). This means that activation of the microorganisms was observed during incubation since mainly microbial processes dominate the N cycle. This fact has a significant impact on soil fertility due to the fact that the N sources taken up by higher plants are mainly ammonium and nitrate [29].

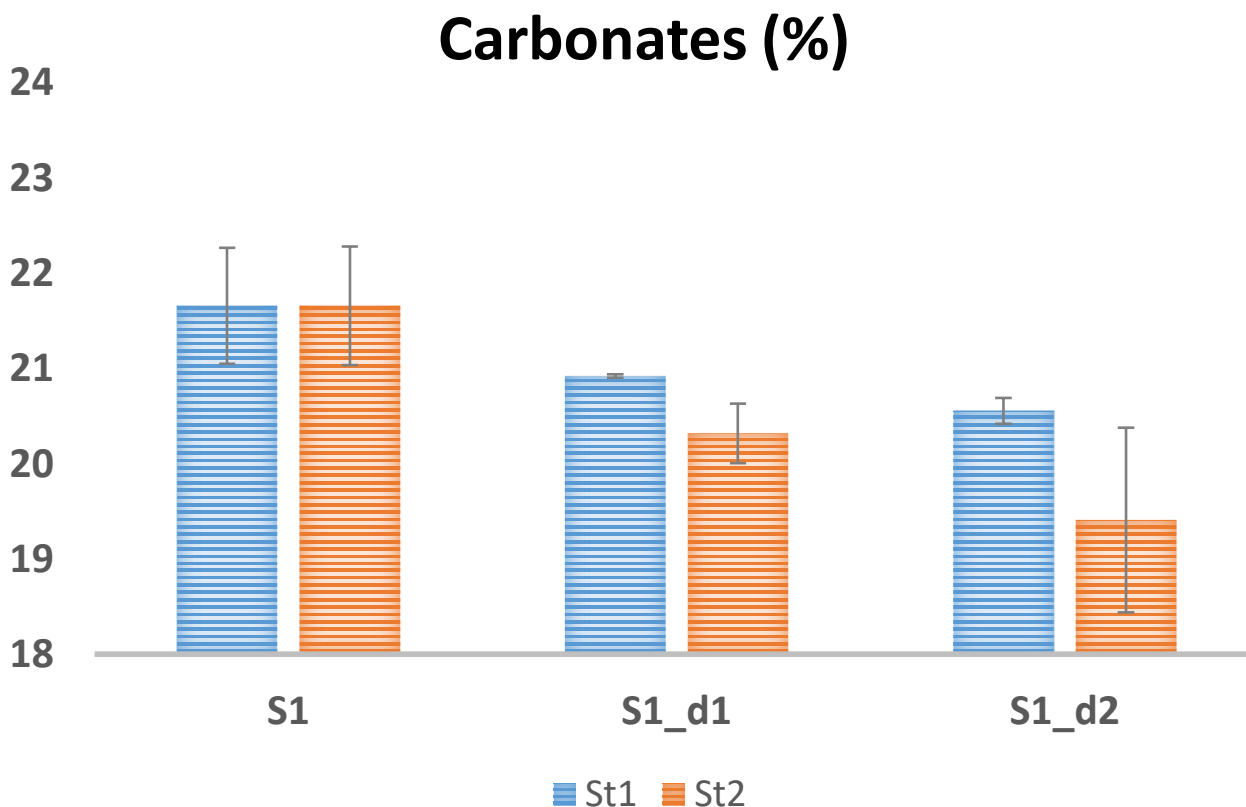
When comparing the mixture samples, it can be observed that these processes were more evident in the mixtures with St2 (Figure 4B,D), since the ammonium peak of the mixtures with St1 was not registered so clearly (Figure 4A,C). However, there are no great differences between the results of St1 and St2 in the incubation experiment. In both cases, the addition of struvite stimulated the mineralization of N by the soil microorganisms. In control soils, these processes have also been observed, but to a lesser magnitude. Thus, the application of struvite in the study soils had an effect on soil fertility, as related to available mineral N forms. The extra mineral N content observed in the mixtures could be due to two non-mutually exclusive causes: First, the dissolution of the mineral ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) and the consequent incorporation of ammonium into the soil solution. Second, an indirect effect related to the activation of the mineralization of the initial organic matter of the soil. This, together with the observation of a much higher peak of  $\text{NH}_4^+$  content in the amended soils than in the controls (Figure 4A,B), supports the hypothesis of struvite being the source of at least some of the  $\text{NH}_4^+$  found in week 3. Therefore, the tests carried out in the laboratory allowed us to observe the positive effect of the application of struvite as an N fertilizer on soil fertility, but due to trial limitations, it was not possible to determine to what extent each of these two processes dominated. This opens a new line of research for future assessments.

Contrary to EC values, the highest concentration values of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were not generally associated with the highest doses (d2). In Figure 4D, it may be clearly observed that the nitrate peak values at week 6 of the experiment with St2 were not dose-dependent, since the same value of  $\text{NO}_3^-$  was detected for both doses in the two tested soils. In the case of the laboratory experiment with St1 (Figure 4C), this fact was observed for the mixtures with the acid soil, but not for the basic soil (S1), where the highest peak of  $\text{NO}_3^-$  was produced in the soil mixtures with the highest dose. Thus, it seems that the dose of struvite was not a determining factor for the nitrification processes to occur, under the conditions of this study. It is noteworthy that the highest  $\text{NO}_3^-$  values were also produced in the mixtures with the acid soil. The fact that higher doses were not associated with the highest concentration values of mineral N should be considered when applying the material as a powder in field conditions to avoid problems associated with overfertilization. Related to application doses in field conditions, the EU-recommended soil application doses should be based on expected crop yields and on the soil availability of P, and not only on total P content. In neutral-to-basic soils, when the application rate is matched to crop demands and soil analysis, the risk is minimized [44].

The control soils presented the same evolution as the mixtures with struvite but to a lesser extent. Keeping the soil samples in the ideal temperature and moisture conditions (25 °C and 60 to 100% of the soil field capacity) resulted in generally increased N availability in the control agricultural soils, very likely because of organic N being transformed into ammonium and nitrate by the soil microorganisms. It must be taken into account that the soils come from real agricultural plots in which conventional fertilizers have been applied for more than 10 years, and organic matter is present at different concentrations (Table 2). In any case, these processes of nitrification seemed to be favored by an acid pH of the soil, which is in agreement with the results of other researchers, who also observed a lower solubility of struvite in alkaline soils [3].

### 3.3. Carbonate Content Values

Despite the fact that these results showed that these materials with struvite could be used as N fertilizer through soil microorganism activation and subsequent organic N mineralization (Figure 4), acidification of the samples was also observed (Figure 3). For this reason, the implication of the acidification process in the carbonate content of the soil was also studied. Figure 5 shows the carbonate content (%) of the basic soil (S1) after the application of St1 and St2 at the end of the laboratory experiments (after 9 weeks).



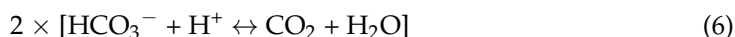
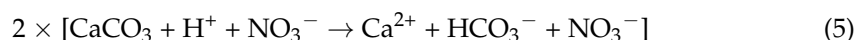
**Figure 5.** Carbonate concentration of the soil–struvite mixtures and the samples of the basic soil after 9 weeks of the experiment. Bars indicate the standard deviations of the means of three replicates of each sample.

Unexpectedly, no significant differences were found in the concentration of total carbonates of S1 after the laboratory experiments due to the acidification of the mixture. Due to the high concentration of carbonates in the study soil (21.6%), changes in the carbonate concentration of the bulk samples were not detected. Similar results have recently been observed by de Soto et al. [45] after 25 years of continuous sludge and mineral fertilizer application on a Mediterranean calcareous soil. This suggests that the initial carbonate content is a key factor for observing and detecting these changes in bulk soil samples with a high content of carbonates.

Although no statistically significant differences were found, a trend is observed in the results of the soils (Figure 5). It seems that the acidification of the mixtures could cause a dissolution of the soil carbonates, and this process could be more important in the test with St2 where the nitrification process was slightly more evident (Figure 4). The tendency of the reduction in carbonate content was greater with increasing dose. Therefore, this process should be taken into account when applying the amendment continuously for a long period of time, especially in soils with low carbonate content, since soil acidification can cause a loss of inorganic carbon in soils [46,47].

Acidity is neutralized by the acceleration of carbonate dissolution. In calcareous soils, such as S1, the  $H^+$  input is balanced by carbonates, leading to the leaching of  $HCO_3^-$ ,

$\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  [47]. The addition of the materials with struvite produces  $\text{H}^+$  and  $\text{NO}_3^-$  release (Equations (1) and (4)) and this has a direct effect on the soil carbonate content by accelerating the dissolution of carbonates (Equations (5) and (6)) [48].



Therefore, the acidification effect due to the application of these materials as N fertilizer should be investigated in future studies because it can affect the C cycle by accelerating the dissolution of carbonates. Long-term mineral N fertilization decreased the soil C stocks mainly through the dissolution of lithogenic carbonates [49], and it has recently been estimated that soil acidification affects up to 40% of arable soils worldwide and more than 70% of potentially arable land [40]. Another recent example is the article by Tao et al. [50], which concluded that Chinese croplands have lost 27–38% of their inorganic carbon density from the 0–40 cm soil layer, and that the soil pH has decreased by 0.53 units over the past 30 years. In that study, N fertilization was one of the major drivers leading to dramatic losses of soil carbonates.

#### 4. Conclusions

The material containing struvite from a WWTP can be a potential N fertilizer for agricultural soils and can promote circular economy opportunities for the wastewater industry. The application of these materials in the ideal temperature (25 °C) and moisture conditions (60 to 100% of the field capacity of the samples) produced an increment in the concentration of  $\text{NH}_4^+$ , which promoted the subsequent transformation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  by soil microorganisms. This extra mineral N content could have two non-mutually exclusive causes: the dissolution of the struvite and an indirect effect related to the activation of the mineralization of the initial organic matter of the soil.

Another positive factor is that this mineral can also be used as a liming agent to enhance productivity and soil fertility of relatively acidic soils, as the pH of the acid soil immediately increased following its application. However, after three weeks of testing, a drop in the pH values was observed due to acidification by nitrification. Although the use of these materials with struvite as N fertilizer seems to be effective in acid and basic agricultural soils, it appears to be more effective in the former, since the acid pH favors the solubility of the mineral.

On the other hand, the application of these materials with struvite in agricultural soils should be further investigated due to the increase in the soil salt content that was observed, which can be a limiting factor for plant development.

Finally, after 3 weeks of the experiment, ammonification and nitrification processes resulted in a decrease in the initial pH values, which can alter the soil C cycle through the dissolution of carbonates. Therefore, future research on the application of these materials as a fertilizer is still needed to explain the real effects of this material on soil and the microbial community, especially in field experiments where its effect on crops under real agricultural conditions could be investigated.

Although this material has not been tested in field conditions, the laboratory results showed that its application as a powder (<2 mm) is adequate. In addition, it is important to take into account the applied doses to avoid overfertilization, which could cause problems of high salt content and soil acidification. The application rate should be based on crop demands, not only on the N and P total content, as recommended by the EU.

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