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► **To cite this version:**

Andrea Danaé Gómez-Suárez, Cécile Nobile, Michel-Pierre Faucon, Olivier Pourret, David Houben. Fertilizer Potential of Struvite as Affected by Nitrogen Form in the Rhizosphere. *Sustainability*, 2020, 12 (6), pp.2212. 10.3390/su12062212 . hal-02571684

HAL Id: hal-02571684

<https://hal.science/hal-02571684>

Submitted on 13 May 2020

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Article

Fertilizer Potential of Struvite as Affected by Nitrogen Form in the Rhizosphere

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Received: 14 February 2020; Accepted: 10 March 2020; Published: 12 March 2020



Abstract: Struvite is increasingly considered a promising alternative to mined phosphorus (P) fertilizer. However, its solubility is very low under neutral to alkaline pH while it increases with acidification. Here, we investigated whether supplying ammonium to stimulate rhizosphere acidification might improve struvite solubility at the vicinity of roots and, ultimately, enhance P uptake by plants. Using a RHIZOtest design, we studied changes in soil pH, P availability and P uptake by ryegrass in the rhizosphere and bulk soil supplied with either ammonium or nitrate under three P treatments: no-P, triple super phosphate and struvite. We found that supplying ammonium decreased rhizosphere pH by more than three units, which in turn increased soluble P concentrations by three times compared with nitrate treatments. However, there was no difference between P treatments, which was attributed to the increase of soluble Al concentration in the rhizosphere, which subsequently controlled P availability by precipitating it under the form of variscite-like minerals (predicted using Visual MINTEQ). Moreover, although ammonium supply increased soluble P concentration, it did not improve P uptake by plants, likely due to the absence of P deficiency. Further studies, especially in low-P soils, are thus needed to elucidate the role of nitrogen form on P uptake in the presence of struvite. More generally, our results highlight the complexity of manipulating rhizosphere processes and stress the need to consider all the components of the soil-plant system.

Keywords: phosphorus management; ammonium; nitrate; recycled phosphorus; RHIZOtest; acidification

1. Introduction

Phosphorus (P) is a major nutrient limiting crop production of many agroecosystems [1]. Currently, P fertilization mainly relies on the use of chemical fertilizers which are derived from phosphate rocks [2]. However, this resource is finite and is located in only a few places on Earth [3]. Developing sustainable fertilization practices based on the reuse of P is thus crucial to achieve the high yields required to feed an ever-increasing human population [4,5]. In this context, it has been increasingly suggested to replace conventional fertilizer with P-rich materials originating from waste materials [6], especially to achieve United Nations Sustainable Development Goals [7].

Considerable interest in the P removal from effluent and recovery in the form of struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$) has arisen in recent years worldwide [8–10]. Struvite production has been considered a promising alternative to conventional P removal technologies (e.g., metal precipitation with Fe or Al salts) in which P precipitates are virtually impossible to recycle in an economical manner [11–13]. Once applied to soil, struvite may act as a

“slow-release fertilizer”, providing a longer-term source of P for crop growth than readily soluble forms of P while preventing P from sorption on soil constituents or loss by leaching or runoff [14,15]. However, the use of struvite might also result in an insufficient supply of P to crops, especially at the early stage of growth, if the release is slower than the plant requirements for P [15–17]. Struvite solubility is predominantly controlled by pH [9]. High pH favors the formation of struvite crystals (pH range of 7 to 11), whereas low pH favors its solubilization [18]. As a result, unlike the highly soluble commercial P fertilizers such as potassium phosphate, which are bioavailable over a broad pH range, uptake of P from struvite can be low at neutral to alkaline pH [19].

Rhizosphere processes such as root-induced changes in pH or redox potential and root exudate release play a key role in nutrient acquisition [20]. It has long been known that rhizosphere chemistry can be significantly changed according to the form of N taken up. Ammonium (NH_4^+) supply may decrease rhizosphere pH by promoting H^+ release, whereas nitrate (NO_3^-) supply may increase rhizosphere pH through releasing OH^- [21], which can in turn affect the availability of sparingly soluble P compounds [22]. For instance, supplying plants with $\text{NH}_4\text{-N}$ could increase the solubility of sparingly soluble P compounds such as apatite, resulting in higher P availability compared with the supply of $\text{NO}_3\text{-N}$ [23,24]. Since struvite solubility is strongly dependent on pH, such observation raises the question of whether manipulation of rhizosphere processes by stimulating rhizosphere acidification through $\text{NH}_4\text{-N}$ supply might be an effective approach to improve struvite solubility at the vicinity of roots. On the other hand, root-induced acidification in the rhizosphere of $\text{NH}_4\text{-fed}$ plants may increase the concentration of Al in solution [25], potentially resulting in toxicity for plants [26] and P precipitation as variscite, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ [27].

In order to optimize the use of more sustainable P sources, the objective of this study was therefore to gain a better insight on how the N form affects P availability in the presence of struvite. We hypothesize that adding $\text{NH}_4\text{-N}$ would acidify the rhizosphere, resulting in higher P uptake as compared to the supply of $\text{NO}_3\text{-N}$.

2. Materials and Methods

2.1. Experimental Design

The studied soil was sampled in Beauvais (Northern France; Figure 1) and was classified as a Haplic Luvisol [28]. A total mass of 100 kg was obtained by composite sampling (0–10 cm depth; five random samplings) in a long-term (>20 years) cropland field with an oilseed rape–winter wheat–winter barley rotation and organic and mineral fertilization based on soil tests, crop requirements and timed to crop uptake [5,29].



Figure 1. Location of the sampling site.

After sampling, the soil was air-dried, crushed and sieved at 2 mm for further use at the laboratory. Particle size analysis using the pipette method revealed that the soil was a silt loam (USDA classification) with 16% sand, 67% silt, and 17% clay. Organic C, total N, available concentrations as assessed using the acetate ammonium-ethylenediamine tetraacetic acid (AA-EDTA), pH and cation exchange capacity (CEC) are presented in Table 1.

Table 1. Soil characteristics.

Organic C (%)	Total N (%)	Ca _{AA-EDTA} (mg kg ⁻¹)	Mg _{AA-EDTA} (mg kg ⁻¹)	K _{AA-EDTA} (mg kg ⁻¹)	P _{AA-EDTA} (mg kg ⁻¹)	pH	CEC (cmol _c kg ⁻¹)
1.54	0.18	3869	101	292	72	7.8	12.5

At the laboratory, the soil was amended with an appropriate amount of powder of struvite or triple superphosphate (TSP) corresponding to 50 mg P kg⁻¹ soil, as recommended by Bonvin et al. [16]. Struvite was produced from wastewater and provided by a French fertilizer company. Struvite was crushed to reach a particle size <250 µm prior to use. Untreated (hereafter called “0P”) soil was also part of the experimental design. Amended soils were thoroughly homogenized in large plastic containers and individually prepared immediately prior to use. The mixtures were then placed in a climate-controlled dark room and equilibrated during two weeks at field capacity.

We used the RHIZOtest device (MetRHIZlab, France) described in Bravin et al. [30]. The principle of this device consists in separating plant roots from soil with a 30-µm polyamide mesh to facilitate the collection of roots and rhizosphere [31,32]. In a first step, 0.27 g of ryegrass (*Lolium multiflorum*) was grown (preculture period) for 14 days in hydroponics in a cylinder closed at the bottom with a 30 µm polyamide mesh allowing the development of a dense, planar root mat with nutrient solution: Ca(NO₃)₂ (2 mmol L⁻¹), MgSO₄ (0.5 mmol L⁻¹), K₂SO₄ (0.7 mmol L⁻¹), KCl (0.1 mmol L⁻¹), KH₂PO₄ (0.1 mmol L⁻¹), MnSO₄ (0.5 µmol L⁻¹), CuSO₄ (0.5 µmol L⁻¹), ZnSO₄ (0.5 µmol L⁻¹), (NH₄)₆Mo₇O₂₄ (0.01 µmol L⁻¹) and Fe-EDTA (100 µmol L⁻¹). In a second step (culture period), the plants were pressed down firmly onto a thin layer (2-mm thick) of equilibrated soil for a period of 12 days. Soil layers were connected to 1-dm³ of nutrient solution with a filter paper wick. The composition of this nutrient solution was the same as that used for the preculture period except that P was not added and N was added as either Ca(NO₃)₂ (2 mmol L⁻¹) or (NH₄)₂SO₄ (2 mmol L⁻¹). To make the amounts of Ca equal between the treatments of NO₃-N and NH₄-N, CaCl₂ was supplemented to the NH₄-N treatment. Similarly to Houben and Sonnet [31], unplanted control treatments, in which the soil had been incubated in similar devices without plants (thereafter called bulk soil), were carried out. In total, 48 such devices were implemented: 3 P treatments (0P, TSP and struvite) × 2 N forms (NO₃-N and NH₄-N) × 2 crop conditions (ryegrass and bulk soil) × 4 replicates.

2.2. Plant and Soil Analyses

At harvest, shoots and roots were separated and roots were gently rinsed with deionized water. Shoots and roots were then dried at 60 °C, weighed and crushed. The concentration of P in shoots and roots was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Scientific XSERIES 2) after mineralization by HNO₃ and aqua regia digestion. As described in Lange et al. [33], quantitative analyses were carried out by external calibration (eight points) by using a mono-element standard solution (Accu Trace Reference, USA). Indium was used as an internal standard at a concentration of 100 µg.L⁻¹ in order to correct for instrumental drift and matrix effects. Total P uptake by plants was calculated by summing P uptake by roots (i.e., P concentration in roots multiplied by root dry mass) and P uptake by shoots (i.e., P concentration in shoots multiplied by shoot dry mass).

At the completion of the RHIZOtest experiment, cropped soils (rhizosphere) and uncropped soils (bulk soil) were collected and dried at ambient temperature. According to the scheme proposed by DeLuca et al. [34], each sample of soil was subjected to a CaCl₂ (0.01 mol L⁻¹) extraction which

extracts soluble and weakly adsorbed inorganic P and emulates P accessed by root interception and diffusion. One g of soil was transferred to a polypropylene centrifugation tube in which 20 mL of $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$ was added and then shaken for 3 h in a reciprocal shaker at 200 rev min^{-1} at 20°C . After shaking, the pH (pH- CaCl_2) was measured in the suspension and the extract was separated from the solid residue by centrifugation at $3000g$ for 15 min. In the extract, P concentrations were analyzed colorimetrically [35] using a spectrophotometer (712 nm). As an indicator of potential Al toxicity [36], Al concentration in $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$ extracts was also measured, using ICP-MS.

2.3. Modeling

Equilibrium modeling was performed with Visual MINTEQ 3.1 software to identify possible precipitates that may control P solubility [37]. The input data included pH and concentration of P and Al in the $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$ extract. The saturation index (SI) representing the degree of saturation with respect to a specific P solid phase is defined as

$$\text{SI} = \log \text{IAP} - \log K_{\text{sp}}$$

where IAP is the ion activity product and K_{sp} is the solubility product constant.

If $\text{SI} > 0$, the solution is supersaturated with respect to the mineral phase; if $\text{SI} < 0$, the solution is undersaturated; if SI is near zero, this suggests that saturation is reached and that equilibrium exists between the mineral and the aqueous solution.

2.4. Statistical Analyses

All recorded data were analyzed using descriptive statistics (mean \pm standard error) and normality was determined using the Shapiro-Wilk test. The data were then subjected to one-way ANOVA and Tukey's post-hoc test to compare treatments. To determine the effect of each variable as well as the interaction between P treatments (OP, TSP and struvite), N forms ($\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$) and the presence of plants (planted vs. unplanted), a two-way ANOVA (P treatment \times N form) and a three-way ANOVA (P treatment \times N form \times Planted/Unplanted) was conducted. As recommended by Schabenberger and Pierce [38], the results of ANOVA were presented by showing the degree of freedom (Df), F-ratio (F, i.e., the between-group variance divided by the within-group variance) and p-value (i.e., the lowest probability level at which the means are considered significant). All statistical analyses were performed using R software version 3.5.0 [39] and the package Rcmdr [40].

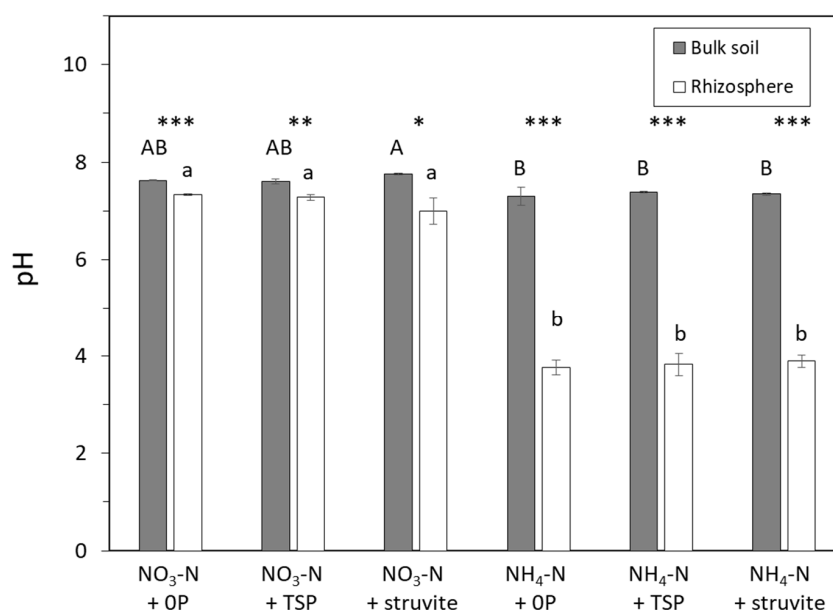
3. Results and Discussion

3.1. Bulk Soil and Rhizosphere pH

It has been long known that plants may significantly affect soil pH, especially due to nutrient uptake in the rhizosphere [21]. Here, unlike the P treatment, the N form, the presence of plants and their interaction had a significant effect on soil pH (Table 2), confirming that the effect of plants on soil pH is impacted by the form of N supplied to plants. In the bulk soil, except for the struvite treatment in which pH was slightly increased in the presence of $\text{NO}_3\text{-N}$, which is due to struvite dissolution [14], the N form had no significant effect soil pH (Figure 2). Therefore, changes in the rhizosphere pH between N treatments can be predominantly attributed to root activity. As expected, supplying $\text{NH}_4\text{-N}$ to plants lowered rhizosphere pH compared to the treatments supplied with $\text{NO}_3\text{-N}$, which is predominantly due to the release of H^+ by roots to compensate for the excess of positive charges following NH_4^+ absorption [21,22]. The range of the pH drop following $\text{NH}_4\text{-N}$ supply was similar [25,41] or higher [42] than that reported for ryegrass by other authors, which is likely due to the differences of pH buffering capacity between the studied soils [31,43,44].

Table 2. Three-way ANOVA results testing the effects of P treatment (No-P, triple superphosphate (TSP) or struvite), N form ($\text{NO}_3\text{-N}$ or $\text{NH}_4\text{-N}$) and plant (unplanted or planted) on pH and CaCl_2 -extractable P.

	pH			P_{CaCl_2}		
	Df	F	p-Value	Df	F	p-Value
P treatment	2	0.04	0.96	2	3.99	<0.05
N form	1	594.6	<0.001	1	26.48	<0.001
Planted/Unplanted	1	694.8	<0.001	1	40.88	<0.001
P treatment \times N form	2	0.62	0.54	2	1.73	0.19
P treatment \times Plant	2	0.64	0.53	2	1.39	0.26
N form \times Plant	1	403.3	<0.001	1	68.30	<0.001
P treatment \times N form \times Plant	2	1.49	0.24	2	1.54	0.23

**Figure 2.** pH in bulk soil and rhizosphere. Uppercase letters indicate significant differences between treatments in the bulk soil and lowercase letters indicate significant differences between treatments in the rhizosphere ($p < 0.05$). Asterisks indicate significant differences between bulk soil and rhizosphere for each treatment (*, ** and ***: $p < 0.05$, 0.01 and 0.001, respectively). Error bars indicate standard error.

3.2. Root-induced Mobilization of P

Concomitantly with the decrease of rhizosphere pH, P_{CaCl_2} concentration significantly increased in the NH_4 -supplied rhizosphere (Figure 3). Concentrations of P_{CaCl_2} were predominantly impacted by the presence of plant, the N form and their interactions while P treatment had surprisingly only a minor effect (Table 2). In the bulk soil, struvite was as efficient as TSP to increase P_{CaCl_2} concentration. Compared with the $\text{NO}_3\text{-N}$ treatment, the $\text{NH}_4\text{-N}$ treatment had lower P_{CaCl_2} concentration. As shown by Talboys et al. [14], this is likely due to the counter-ion effect of NH_4^+ in the nutrient solution which had a negative effect on the equilibrium P concentration. In the rhizosphere, although P_{CaCl_2} concentrations were higher with $\text{NH}_4\text{-N}$ than with $\text{NO}_3\text{-N}$, there was no difference among the P treatments for a given N form. This suggests that P solubility was primarily controlled by root-induced changes in the rhizosphere while P treatment played a minor role. As found by many studies [23,24,26], acidification of the rhizosphere of the NH_4 -fed plants increased P solubility. However, in the present study, P_{CaCl_2} concentration in the OP control was as high as those in the TSP or struvite treatments, which suggests that root-induced acidification increased solubility of legacy soil P, likely due to desorption of (hydr)oxide surfaces and weathering [27]. As shown in Figure 4, the pH decrease in the NH_4 -supplied rhizospheres led to an increase of soluble Al concentration which is consistent with

previous findings (e.g., review by Zhao et al. [45]). As reported by other researches [27,46], the release of Al into the soil solution may promote the precipitation of variscite, $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$, especially in P-fertilized agricultural soils. In the present study, irrespective of the P treatment, NH_4 -supplied rhizospheres were saturated with variscite (SI was very close to zero; Table 3). This suggests that variscite, or most likely a precursor metastable amorphous phase (amorphous AlPO_4) since the rate of variscite formation is known to be very slow [47], controlled the equilibrium level of Al and P in solution. Thus, by increasing soluble Al concentration, root-induced acidification in NH_4 -supplied rhizosphere promoted the formation of amorphous AlPO_4 phase (i.e., variscite-like phase), thereby hindering the effect of P fertilizer on the soluble P concentration. This is consistent with previous studies [48,49] which demonstrated a predominant role of Al phosphates on P solubility in acidic fertilized soils.

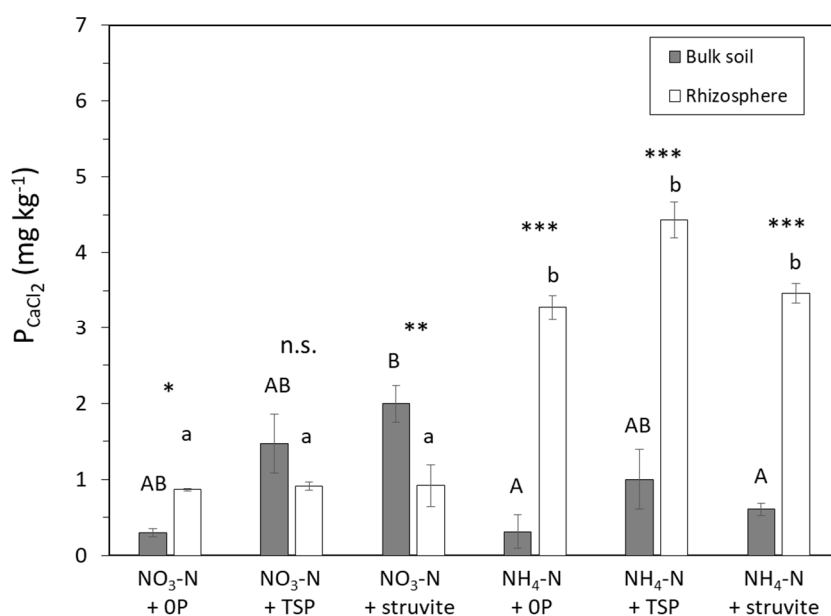


Figure 3. CaCl_2 -extractable P concentration in bulk soil and rhizosphere. Uppercase letters indicate significant differences between treatments in the bulk soil and lowercase letters indicate significant differences between treatments in the rhizosphere ($p < 0.05$). Asterisks indicate significant differences between bulk soil and rhizosphere for each treatment (*, ** and ***: $p < 0.05$, 0.01 and 0.001, respectively). Error bars indicate standard error.

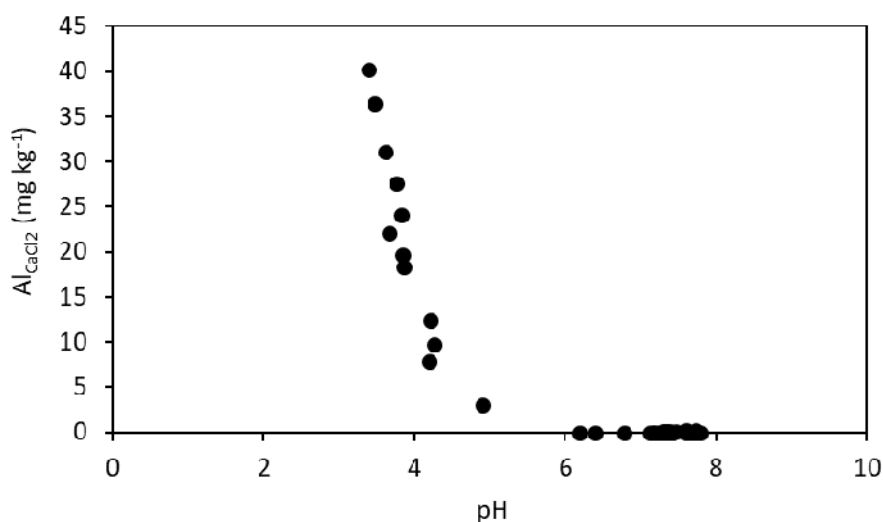


Figure 4. Relationship between pH (pH- CaCl_2) and soluble ($0.01 \text{ mol L}^{-1} \text{ CaCl}_2$) concentration of Al.

Table 3. Saturation Index of variscite in bulk soil and rhizosphere. Results are mean \pm standard error.

	Saturation Index of Variscite	
	Bulk Soil	Rhizosphere
NO ₃ -N + 0P	-9.46 \pm 2.26	-11.46 \pm 0.07
NO ₃ -N + TSP	-9.71 \pm 2.46	-11.30 \pm 0.12
NO ₃ -N + struvite	-9.80 \pm 2.46	-10.80 \pm 0.53
NH ₄ -N + 0P	-12.28 \pm 3.98	0.02 \pm 0.06
NH ₄ -N + TSP	-9.48 \pm 2.55	0.34 \pm 0.12
NH ₄ -N + struvite	-1.89 \pm 0.36	0.33 \pm 0.20

3.3. Effect of N Forms on P Uptake

Similar to soluble P concentration in the rhizosphere, total P uptake by plants was primarily controlled by N forms whereas P treatments had no significant effect (Table 4). Overall, the average total P uptake was slightly higher ($p < 0.01$) in plants supplied with NH₄-N than with NO₃-N (2.53 ± 0.06 mg kg⁻¹ and 2.26 ± 0.06 mg kg⁻¹, respectively; $p < 0.01$), which can be related to the higher P solubility. However, in the presence of NH₄-N, there was no significant difference between P treatments (Figure 5). As for soluble P concentration in the rhizosphere, this is most likely due to the precipitation of an amorphous AlPO₄ phase (i.e., variscite-like phase) under low pH which in turn controlled P influx towards the roots [46,50], thereby hindering the effect of P fertilizer. It is also likely that the increased soluble Al concentration brought about by root-induced acidification restricted P uptake by plants grown under NH₄-N supply due to Al toxicity [51]. The lower root biomass under NH₄-N supply (Table 5; Table 6) is consistent with the well-reported inhibition effect of aluminum toxicity on root growth [52] and may in turn impair P uptake by plants. For instance, in the rhizosphere of NH₄-N fed maize, Bradáčová et al. [43] found that the pH decrease from 6.1 to 4.6 resulted in a 60% reduction in root growth, which in turn limited P uptake by plants.

Table 4. Two-way ANOVA results testing the effects of P treatment (No-P, TSP or struvite) and N form (NO₃-N or NH₄-N) on total P uptake by plant (i.e., P uptake by root + P uptake by shoot).

	P uptake by the Whole Plant		
	Df	F	p-Value
P treatment	2	1.24	0.32
N form	1	13.84	<0.01
P treatment \times N form	2	5.57	<0.05

Table 5. Two-way ANOVA results testing the effects of P treatment (No-P, TSP or struvite) and N form (NO₃-N or NH₄-N) on root and shoot biomass.

	Root Biomass			Shoot Biomass		
	Df	F	p-Value	Df	F	p-Value
P treatment	2	0.76	0.48	2	1.66	0.22
N form	1	38.06	<0.001	1	6.65	<0.05
P treatment \times N form	2	3.00	0.08	2	0.50	0.61

Table 6. Biomass of root, shoot and the whole plant (root + shoot biomasses). Different letters indicate significant differences between treatments ($p < 0.05$). Results are mean \pm standard error.

	Root Biomass (g)	Shoot Biomass (g)	Total Biomass (g)
NO ₃ -N + 0P	0.36 \pm 0.01 b	0.96 \pm 0.04 a	1.32 \pm 0.05 a
NO ₃ -N + TSP	0.34 \pm 0.02 ab	1.08 \pm 0.06 a	1.42 \pm 0.07 a
NO ₃ -N + struvite	0.40 \pm 0.02 b	1.06 \pm 0.05 a	1.46 \pm 0.04 a
NH ₄ -N + 0P	0.30 \pm 0.01 a	1.11 \pm 0.02 a	1.41 \pm 0.01 a
NH ₄ -N + TSP	0.30 \pm 0.02 a	1.16 \pm 0.06 a	1.46 \pm 0.05 a
NH ₄ -N + struvite	0.29 \pm 0.01 a	1.08 \pm 0.04 a	1.37 \pm 0.05 a

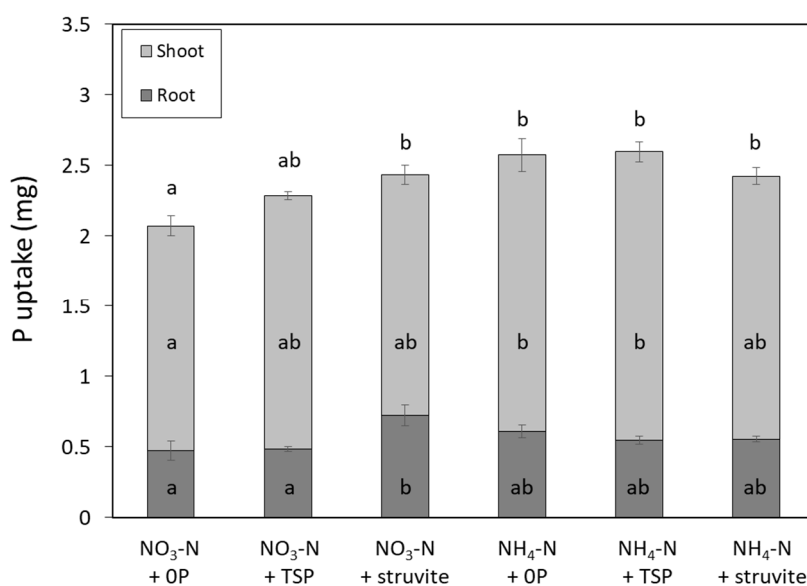


Figure 5. Phosphorus uptake by root and shoot. Different letters indicate significant differences between treatments for P uptake by root, shoot and the whole plant ($p < 0.05$). Error bars indicate standard error.

For the struvite treatment, P uptake was similar regardless of the N form ($p > 0.05$), which might reflect that P uptake was not dependent on soil pH. In a previous study [31], we have shown that ryegrass might release significant amounts of carboxylates into the rhizosphere. As suggested by Robles-Aguilar et al. [53], these exudates can promote the release of P from struvite in either NH₄-N or NO₃-N supplied rhizosphere, which could therefore explain the lack of P uptake improvement in the presence of NH₄-N. Interestingly, in the presence of NO₃-N, struvite was more efficient than TSP to improve P uptake by roots compared to the 0P control. This is consistent with Robles-Aguilar et al. [53] who found that P uptake by maize under NO₃-N supply was greater in the presence of struvite than TSP as a result of the slow-release fertilizing effect of struvite. In addition, it is likely that the lack of significant impact of N form and P treatment on P uptake by plants was partially related to the absence of P deficiency in soil (AA-EDTA extractable P = 72 mg kg⁻¹; Table 1), as reported by other authors for e.g., ryegrass and oat [54,55]. According to Robles-Aguilar et al. [56], the response of plants with high needs for P (e.g., legume and some brassicaceae species) to N form and P treatment could be more sensitive in such a P-rich context.

4. Concluding Remarks

Moving toward more sustainable sources for managing the P nutrition in agroecosystems, struvite is increasingly considered a promising alternative to mineral P fertilizers on a worldwide scale. In the present study, we investigated whether the manipulation of rhizosphere processes by stimulating rhizosphere acidification through NH₄-N supply might be an effective approach to improve struvite solubility at the vicinity of roots and, ultimately, enhance P uptake by plants. Our findings showed that despite increasing soluble P concentrations in the rhizosphere, supplying NH₄-N did not improve P uptake by plants. This was partially attributed to the increase of soluble Al concentration in the rhizosphere, which subsequently controlled P availability by precipitating it under the form of an amorphous AlPO₄ phase (i.e., variscite-like phase). Thus, our results did not support our hypothesis that root-induced acidification of the rhizosphere by supplying NH₄-N instead of NO₃-N would result in higher P uptake. More generally, they highlight the complexity of manipulating rhizosphere processes and stress the need to consider all the components of the soil-plant system. The perspectives of this work are (1) to test a partial substitution of NO₃-N by NH₄-N in order to acidify rhizosphere but

without reaching pH values at which Al^{3+} is soluble (i.e., $\text{pH} < 5.5$), and (2) to investigate the ability of plants with contrasted P mobilization/acquisition traits to mobilize and uptake P from struvite.

Author Contributions: Conceptualization, D.H., O.P. and M.-P.F.; methodology, A.D.G.-S., D.H. and C.N.; investigation, A.D.G.-S.; writing—original draft preparation, D.H. and A.D.G.-S.; review and editing, O.P. and M.-P.F.; supervision, D.H.; funding acquisition, D.H., O.P., M.-P.F. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the GoLaSalle 2019 program (UniLaSalle).

Acknowledgments: We thank Laure Lemal (MetRHIZlab) for providing the RHIZOtest devices.

Conflicts of Interest: The authors declare no conflict of interest.

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