

Article

Circular Economy Approach to Enhance Soil Fertility Based on Recovering Phosphorus from Wastewater

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Abstract: Phosphorus (P) is a non-renewable resource whose future scarcity will constrain agricultural sustainability. Thus, to ensure this sustainability, a circular economy approach involving the use of recycled P sources is needed. The objective of this study was to assess the fertilizer effect of two recycled P products that can be obtained from water purification: vivianites and struvites. Five vivianites (one synthetic, one obtained from industrial process, and three from water purification) and two struvites (named A and B) from diverse origins were compared with soluble mineral P fertilizer (superphosphate) in a pot experiment using wheat at two P rates (50 and 100 mg P kg⁻¹) in two Mediterranean soils. Struvites performed similarly to superphosphate and outperformed all types of vivianites in terms of dry matter (DM) yield and P uptake. Industrial and synthetic vivianites, led to higher DM yield and P uptake by plants than vivianites from water purification. Synthetic and industrial process vivianites increased Olsen P in soils after harvesting, relative to non-fertilized soils. Differences between vivianites can be explained by the different Fe²⁺ to Fe³⁺ ratios, the different crystal sizes, and morphology. Struvite B can replace 65–92% superphosphate on a P uptake basis, and 94–154% on a DM yield basis (the range depends on the P rate). Vivianite from industrial process can replace 54–75% of superphosphate on a DM basis, depending on the P rate. Thus, struvites were as efficient as superphosphate as P fertilizer. However, the results obtained with industrial process vivianite are promising with a view to its potential use in agriculture.

Keywords: biobased fertilizer; vivianite; struvite; water purification



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1. Introduction

Phosphorus (P) is considered a critical raw material since it is a non-renewable and strategic resource that is essential for agriculture [1,2]. This is particularly relevant in Europe [3], where P is essentially an imported resource [4]. The production of P fertilizers from phosphate rock is expected to peak in the current century [5,6], and the offer and demand for P fertilizers are highly concentrated [7]. All these will contribute to future volatility in the P market, which is bound to affect agricultural sustainability. In this regard, P is still a factor contributing to crop-yield gaps in nearly 30% of agricultural lands in the world, mostly in developing countries [8].

The use of phosphorus is particularly inefficient [9–11]. There is an assumption that only 15% of P applied to agricultural soil goes into the food chain [5,12] due to P reactions in soil [10,13,14]. In addition, the supply of P in human diets is high but the capability for assimilation is limited [15]. P losses from human consumption in the European Union amount to around 50% of the P fertilizer applied in agriculture, excluding recycled manure (around 650 Gg of P per year) [16]. These authors considered that the main losses from consumption can be ascribed to wastewater treatment and untreated residual water, amounting to around 600 Gg y⁻¹, 54% of total P losses. Under an expected panorama of future scarcity and increased prices, which will negatively affect agricultural sustainability, it is mandatory to have a more efficient use of P on a societal scale. This should involve a

circular economy approach with the use of recycled P sources in agriculture, the so-called bio-based fertilizers, and better allocation of the resources in P-responsive soils [4,17]. To bring about this approach, P recycling from wastewater is essential.

The removal of P from wastewater or water purification for drinking water can be performed by chemical removal, advanced biological treatment, or a combination of both [18,19]. Chemical removal usually involves the addition of salts for precipitating insoluble metal phosphates (Ca, Mg, Fe, Al) or the use of P sinks, such as resins, biochar, or Fe-oxide sludge [19–22]. Iron oxides have also been used in the removal of P from drainage and runoff water from agricultural lands [23,24] and for water purification for drinking water [25]. However, for practical P recycling, a high P concentration in the resulting byproducts is necessary for facilitating transport and field application as fertilizers. This requirement reduces the interest in the use of Fe-oxide sludge as biofertilizers. Products resulting from metal–phosphate precipitation have a higher P concentration. However, in these cases, low solubility and the difficult recovery of these materials constrain their practical use as bio-based fertilizers or raw materials for the fertilizer industry [19,26].

Struvite, an ammonium–magnesium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), spontaneously precipitates in wastewater treatment plants. Under controlled conditions, its precipitation may be an effective method for P removal from wastewater [27,28]. Struvite is usually produced by adding magnesium (Mg) to wastewater with ammonium (NH_4^+) and P, followed by further concentration using different methods, such as cathode electrodeposition [29]. Although struvite is poorly soluble in water, there is evidence of its usefulness as a P fertilizer; this potential use, however, should be checked under different soil conditions [30]. The precipitation of vivianite, an Fe^{2+} phosphate mineral ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) is also gaining attention as a P-removal product [2,27]. It precipitates under anoxic conditions [31] but it is a metastable compound that quickly oxidizes under aerobic conditions. It can be produced from wastewater by adding Fe^{2+} salts under anaerobic conditions and easily separated due to its magnetism [32]. The quick oxidation of vivianite under oxic conditions leads to the precipitation of poorly crystalline Fe oxides and may affect the potential bioavailability of P [33] and consequently its potential use as bio-based fertilizer. Vivianite has proved to be an efficient Fe fertilizer for overcoming Fe-deficiency chlorosis in calcareous soils [34]. However, there is little or no information about its efficacy as a P fertilizer.

Struvite and vivianite precipitation are two promising methods for wastewater purification [29,32]. Both compounds have a relatively high P content and low solubility [29,32], and consequently, a slow-release fertilizer effect may be anticipated. This can be of interest for reducing P loss from soils, thus decreasing the environmental risks related to P fertilization. While there are some promising results using struvite as a P source for plants [35,36], there is no evidence regarding the use of vivianite. Vivianite can be produced not only from wastewater treatment plants but also from industrial process, as well as synthetically, according to De Santiago et al. [34]. The molar ratio of Fe or Mg and PO_4 , and other ions present in the effluents used for the precipitation of vivianites or struvites, and microbial activity, can affect the crystallinity, elemental composition, and recovery of these products [29,32,37]. This can affect the solubility and consequently the fertilizer effect of struvites and vivianites. However, despite this practical relevance, the consequences of the origin of these products on their fertilizer effect remains unclear.

This study aimed to evaluate struvites and vivianites of diverse origins as P fertilizers in two different soils. This will allow us to provide evidence of their potential use as bio-based fertilizers under different soil conditions and how the chemical and mineralogical properties of these compounds may affect their efficiency as P fertilizers.

2. Materials and Methods

2.1. Soils

Two Mediterranean soil samples were collected and prepared for the experiment. The soils were air-dried, clods and lumps broken and passed through a 2 mm sieve for laboratory analyses and a 6 mm sieve for pot experiments. These soils were chosen because

of their low Olsen P content, while one of them (TRQ4), in particular, was chosen because of its carbonate content. The soil TRQ4 was classified as a Calcixerollic Xerochrepts, and the soil MSQ1 as a Calcic Haploxeralf, according to the Soil Taxonomy of USDA. The Properties of soils used in this experiment are shown in Table 1.

Table 1. Soil properties.

Soil	Clay	Silt	Sand	CCE	ACCE	Organic C	pH	EC	CEC	Ca	Mg	K	Na	Olsen P	Fe	Mn	Zn	Cu
				g kg ⁻¹				μS/cm ⁻¹	cmolc kg ⁻¹				mg kg ⁻¹					
TQR4	225	547	228	472	96	6.8	8.51	139	9.64	8.34	0.79	0.43	0.09	6.40	9.0	8.9	3.3	26.6
MSQ1	154	191	655	33	12	4.5	8.34	126	10.45	9.42	0.53	0.42	0.07	3.50	10.7	13.4	0.4	19.8

CCE, Ca carbonate equivalent; ACCE, active Ca carbonate equivalent; EC, electrical conductivity; CEC, cation exchange capacity; Ca, Mg, K, and Na, exchangeable cations; Fe, Mn, Zn, and Cu extracted with DTPA.

2.2. Fertilizers

The fertilizer products studied in this experiment were:

1. Three different types of vivianite from water purification (WP1 Vivianite, WP2 Vivianite, and WP3 Vivianite) were provided by Wetsus (European Centre of Excellence for Sustainable Water Technology) from Leeuwarden, the Netherlands. These three vivianites were selected because they were produced in different batches of water purification and had gone through different cleaning methods. In addition, the three vivianites had different levels of purity;
2. One vivianite obtained from industrial process provided by Fertiberia fertilizer company (Seville, Spain);
3. Synthetic vivianite was produced by mixing FeSO₄ and (NH₄)₃PO₄ in the laboratory according to De Santiago [34];
4. Two types of struvite obtained from Municipal Wastewater Treatment Plant and were provided by Aquaminerals (Nieuwegein, Netherlands). These two struvites (Struvite A and B) were selected because they were produced from different locations (Struvite A from Apeldoorn and Struvite B from Amsterdam West);
5. Superphosphate as reference P fertilizer: Ca(H₂PO₄)₂ H₂O.

The elemental composition of fertilizers (Table 2) was determined by ICP-OES after acid digestion except for C and N; these two elements were determined in an elemental analyzer. The Fe²⁺ to Fe³⁺ ratio was determined by Mossbauer spectroscopy and X-ray photoelectron spectroscopy (XPS). This ratio is relevant since Fe³⁺ compounds are assumed to be insoluble and contribute little to nutrient supply to crops. Scanning electron microscope images were acquired using a JEOL JSM 6300 microscope at the SCAI-University of Cordoba (Spain) facilities.

2.3. Plant Material

Wheat was chosen for this experiment because of its global importance as an agricultural crop. Wheat seeds were germinated by seeding in a nursery for 15 days, after which they were transplanted into pots containing soil already mixed with fertilizer products.

2.4. Experimental Design

The experiment was designed as a Randomized Complete Block Design (RCBD) experiment with three replications for each treatment. Each replicate corresponded to a pot with one wheat plant. The experiment with this setup was repeated twice in order to improve the consistency of the results. Thus, in total, there were six replicates per treatment, in two different batches. Since differences can exist between batches, variation ascribed to batches was considered in the statistical analysis. Two factors were involved in the experiment: soil type (2), P fertilizer treatments (fertilizer products mentioned above plus a non-fertilized control applied at two P rates (50 and 100 mg P kg⁻¹). P rate could not be considered an additional factor since there was a control without fertilization. The lowest P rate was selected since it is known that this is a rate at which plants respond to fertilizer

supply in growing media poor in P [38]. The highest was selected to check the effect of a very high rate on P uptake and availability in the growing medium.

Table 2. Elemental composition and properties of studied fertilizers and percentage of Fe²⁺ and Fe³⁺ in the products.

Fertilizer	C	N	P	K	Ca	Mg	Fe	Zn	Mn	Cu	Mossbauer		XPS		
											Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺	
	g kg ⁻¹										%				
Vivianites															
Synthetic Vivianite	nd	nd	116.3	nd	nd	nd	314	nd	nd	nd					
WP1 Vivianite	nd	nd	108	0.25	8.9	9.2	280	0.16	1.14	0.04	75	25	41	59	
WP2 Vivianite	nd	nd	106.4	0.21	17.4	13.9	267.3	0.17	1.11	0.08			78	22	
WP3 Vivianite	100	11	97.9	0.72	22.2	10.1	232.4	0.45	1.02	0.15	84	16	89	11	
Industrial Process Vivianite	nd	nd	105.4	1	0.13	2.6	263	nd	0.92	0.1			81	19	
Struvites															
Struvite A	75.5	55	114	0.65	0.35	95	12.5	0.11	0.6	0.31					
Struvite B	85	50	199	1.3	2.1	152	0.67	<0.01	0.2	<0.01					

nd = not detectable; WP, vivianites obtained from water purification; XPS, X-ray photoelectron spectroscopy.

2.5. Experimental Setup

The growing media was prepared by mixing fertilizer products with 300 g of soil and placed in cylindrical polyethylene pots with a capacity of 350 mL (height 150 mm, diameter 55 mm). The mixing of fertilizer products (in powder form) with soil was carried out four days before transplanting the wheat seedlings. The assay was placed in the growing chamber with temperatures of 25 °C/16 °C day/night and irrigation till 70% of the water holding capacity of the soils, with replenishment of weight loss. Within the first two days of transplanting the wheat seedlings, irrigation was conducted only with water, after which a P-free nutrient solution (Hoagland Solution) was applied on a regular basis. The composition of this nutrient solution was (all concentrations in mmol L⁻¹): MgSO₄ (2), Ca(NO₃)₂ (5), KNO₃ (5), KCl (0.05), Fe-EDDHA (0.02), H₃BO₃ (0.024), MnCl₂ (0.0023), CuSO₄ (0.0005), ZnSO₄ (0.006), and H₂MoO₄ (0.0005). The wheat plants were harvested at the ripening stage, 51 days after transplanting.

2.6. Collection of Soil and Plant Samples

Rhizospheric soil samples were collected at the end of the experiment by shaking off soils from wheat roots [14] for microbial biomass analyses. These samples were maintained at 4 °C until analysis. Bulk soil samples were also collected for Olsen P and DTPA Fe analyses. These samples were dried and milled to pass through a 2 mm screen. At the end of the experiment, the roots and shoots of the wheat plants were collected separately. Wheat root and shoot plant samples were placed in a forced-air oven dryer at 65 °C for 72 h after which the dry matter (DM) in each organ was determined.

2.7. Plant Analysis at the End of the Experiment

Root and shoot samples were ground. Subsequently, the ground plant materials (0.25 g) were mineralized in porcelain crucibles in a muffle furnace at 550 °C for 8 h. Subsequently, acid digestion (1 M HCl) of the ashes was performed at 100 °C on a hotplate for 15 min. The concentration of P was determined by the colorimetric method according to Murphy and Riley [39] with subsequent measurement in the spectrophotometer at 882 nm. Fe, Zn, Cu and Mn were determined by atomic absorption spectrophotometry (AAS). The total P uptake by plants was determined as the sum of the product of the dry weight of each organ and its P concentration. The replacement value (RV) of fertilizer products (struvites and vivianites) was adapted from [40] as the amount of commercial mineral P fertilizer saved or replaced when using an alternative fertilizer (in this case, vivianites or struvites), while attaining the same P uptake or yield. This provides an idea of equivalence: if expressed on

a % basis, it means the kg of commercial mineral fertilizer that provides the same effect as 100 kg of alternative fertilizer. Thus, it can be interpreted as the percentage of commercial mineral fertilizer that can be replaced by alternative fertilizers. It was estimated on a P uptake basis for each P rate as:

$$RV_P = \frac{P_{uptake_i} - P_{uptake_c}}{P_{uptake_s} - P_{uptake_c}}$$

where, P_{uptake_i} is the P uptake by the crop in the treatment with alternative fertilizer i , P_{uptake_c} is the average P uptake in the control treatment, and P_{uptake_s} is the average P uptake in the superphosphate treatment at the same P rate as i .

The RV was also estimated on a total dry matter basis as:

$$RV_{DM} = \frac{DM_i - DM_c}{DM_s - DM_c}$$

where, DM_i is the DM of the crop in the treatment with alternative fertilizer i , DM_c is the average DM of the control treatment and DM_s , the average DM of the superphosphate treatment at the same P rate as i .

2.8. Soil Samples Analysis at the End of the Experiment

For Olsen P determination, 2 g of soil were weighed into 50 mL falcon tubes, and 40 mL of 0.5 M NaHCO_3 at pH 8.5 was added and stirred for 30 min at 180 rpm. Subsequently, the suspension was placed in the centrifuge for 10 min at 2500 rpm. The P content of the extract was determined by the colorimetric method according to Murphy and Riley [39] using a spectrophotometer at 882 nm. The DTPA (Diethylenetriaminepentaacetic acid) extractable Fe determination was carried out according to Lindsay and Norvell [41]. Five grams of soil were weighed into 50 mL falcon tubes, and 20 mL of DTPA/ CaCl_2 TEA (triethanolamine) was added and stirred for 2 h at 160 rpm. The suspension was then placed in the centrifuge for 15 min at 2500 rpm. The Fe content of the extract was determined by AAS.

Total microbial biomass (TMB) and main microbial groups (bacteria, fungi) and microfauna were assessed using the ester-linked fatty acid profile (ELFAs) after extraction in mild alkaline methanol, which is known to extract ester-linked fatty acids, but not free fatty acids, as described by Schutter and Dick [42] and García-López et al. [43]. First, 15 mL of 0.2 M KOH in methanol was added to 3 g of soil and incubated at 37 °C for 1 h. Tubes were vortexed every 10 min during the incubation. After that, the pH of the suspension was neutralized by adding 3 mL of 1 M acetic acid. ELFAs were separated into an organic phase by adding 10 mL of hexane followed by centrifugation at $480 \times g$ for 10 min. After that, the hexane layer was transferred to a clean glass test tube and the hexane evaporated with rotavapor at 30 °C for 20 min. Finally, ELFAs were dissolved in 0.5 mL of 1:1 hexane:methyltertbutylether and transferred to a gas chromatograph vial for analysis.

2.9. Statistical Analysis

Statistical analysis was performed with Statgraphics Centurion XVI. The effect of factors (soil and fertilizer treatment as fixed factors) was assessed by means of a two-way analysis of variance (ANOVA). Previously, normality and homogeneity of variance were assessed with the use of the Smirnov–Kolmogorov and Levene test, respectively. Data of both replications of the experiments were jointly analyzed, considering the replication of the experiment as an additional influencing factor in the ANOVA. Mean separation was conducted using the Tukey Honest Significant Difference (HSD) test at $p < 0.05$. If the interaction between factors was significant, the effects of the main factors were not discussed.

3. Results

3.1. Fertilizer Properties

Vivianites from water purification (WP) and industrial process had a slightly lower P and Fe concentrations than synthetic vivianite. This latter had values closer to the theoretical values of the pure compound. Since the synthetic vivianite was precipitated from analytical grade reagents, other elements besides P and Fe were not detectable. (Table 2). The vivianites from water purification and struvites showed some carbon (C) and nitrogen (N) content. The Fe²⁺ to Fe³⁺ ratio in vivianites ranged widely, according to XPS. These ratios were not fully consistent with those obtained by Mossbauer spectroscopy in two of the products (Table 2). The crystal size and morphology were different between vivianites from water purification and vivianites from industrial process (Figure S1). Figure 1 shows the higher heterogeneity in crystallinity and the overall larger crystal size in the WP3 vivianite compared to the industrial process vivianite.

3.2. Effect of Fertilizers on Plant Development and Nutrition

Although the effect of soil was significant on all the studied properties, the interaction between both factors (fertilizer and soil) was not significant (Tables 3 and 4). This means that the effect of the fertilizers was independent of soil. This allowed us to make a joint analysis of the effect of fertilizer treatments on both soils.

Table 3. Effect of different fertilizer treatments (mean \pm standard deviation) on dry matter yield and nutrient content in plants.

Fertilizer	P Rate	Dry Matter Aerial Part	Dry Matter Roots	P Concentration Aerial Part	P Concentration Roots	Fe Uptake	DTPA Extractable Fe
		g plant ⁻¹		g kg ⁻¹		mg plant ⁻¹	mg kg ⁻¹
Control Superphosphate	0	0.55 \pm 0.12 g	0.10 \pm 0.03 d	1.74 \pm 0.42 bc	0.64 \pm 0.31 bc	0.33 \pm 0.21 B	4.3 \pm 0.6 e
	100	1.10 \pm 0.40 cde	0.35 \pm 0.26 ab	3.36 \pm 1.48 a	0.97 \pm 0.27 a	1.40 \pm 1.33 A	4.6 \pm 0.7 cde
	50	1.23 \pm 0.46 abcd	0.25 \pm 0.16 abc	2.32 \pm 1.22 abc	0.69 \pm 0.18 bc	0.99 \pm 1.33 Ab	4.5 \pm 0.7 de
Struvites A	100	1.43 \pm 0.15 ab	0.27 \pm 0.15 ab	2.17 \pm 0.84 ab	0.80 \pm 0.24 ab	1.08 \pm 1.43 ab	4.8 \pm 1.0 cde
	50	1.17 \pm 0.18 bcd	0.24 \pm 0.16 abc	1.95 \pm 0.53 bc	0.71 \pm 0.27 abc	1.03 \pm 1.26 ab	4.6 \pm 0.8 cde
	100	1.56 \pm 0.33 a	0.32 \pm 0.20 a	2.49 \pm 1.27 ab	0.77 \pm 0.28 abc	1.24 \pm 1.35 a	4.4 \pm 1.3 e
B	100	1.29 \pm 0.12 abc	0.27 \pm 0.16 ab	1.86 \pm 0.44 bc	0.73 \pm 0.25 abc	1.30 \pm 1.38 ab	4.4 \pm 1.1 e
	50						
Vivianites Synthetic Vivianite	100	1.01 \pm 0.21 cde	0.16 \pm 0.10 bcd	1.57 \pm 0.39 bc	0.68 \pm 0.42 bc	0.51 \pm 0.40 ab	6.5 \pm 1.6 ab
	50	0.84 \pm 0.24 ef	0.12 \pm 0.08 cd	1.72 \pm 0.42 bc	0.71 \pm 0.33 abc	0.57 \pm 0.56 ab	5.6 \pm 1.4 cde
WP1 Vivianite	100	0.79 \pm 0.26 efg	0.13 \pm 0.06 bcd	1.60 \pm 0.71 c	0.59 \pm 0.28 bc	0.60 \pm 0.38 ab	4.8 \pm 0.6 cde
	50	0.66 \pm 0.13 fg	0.12 \pm 0.04 bcd	1.62 \pm 0.50 bc	0.65 \pm 0.20 bc	0.50 \pm 0.26 ab	4.6 \pm 0.7 cde
WP2 Vivianite	100	0.92 \pm 0.23 def	0.15 \pm 0.08 bcd	1.42 \pm 0.29 c	0.59 \pm 0.22 bc	0.64 \pm 0.44 ab	5.3 \pm 0.8 cde
	50	0.79 \pm 0.19 efg	0.15 \pm 0.04 abcd	1.77 \pm 0.87 bc	0.62 \pm 0.30 bc	0.51 \pm 0.32 ab	4.8 \pm 0.8 cde
WP3 Vivianite	100	0.91 \pm 0.22 def	0.14 \pm 0.06 bcd	1.58 \pm 0.41 bc	0.64 \pm 0.32 bc	0.57 \pm 0.45 ab	5.3 \pm 1.0 cde
	50	0.83 \pm 0.17 ef	0.12 \pm 0.03 bcd	1.62 \pm 0.47 bc	0.52 \pm 0.16 c	0.43 \pm 0.32 ab	5.4 \pm 1.1 bcd
Industrial Process Vivianite	100	1.06 \pm 0.21 cde	0.19 \pm 0.09 abcd	1.60 \pm 0.56 bc	0.59 \pm 0.21 bc	0.88 \pm 0.73 ab	6.7 \pm 1.5 a
	50	0.93 \pm 0.23 def	0.17 \pm 0.10 abcd	1.63 \pm 0.54 bc	0.55 \pm 0.23 bc	0.70 \pm 0.90 ab	5.5 \pm 1.4 bcd
ANOVA		<i>p</i> values					
Treatment		0	0	0	0	0.0056	0
Soil		0	0	0.061	0	0.0008	0.5033
Treatment x Soil		0.0635	0.934	0.3546	0.0547	0.9753	0.4336

Means followed by different letter are significantly different according to the Tukey test ($p < 0.05$); WP, water purification.

The two P rates did not lead to significant differences in dry matter (DM) yield and P uptake for all fertilizer products studied (Figures 2 and 3). Overall, differences in DM yield and P uptake were not significantly different between superphosphate and struvites (Figures 2 and 3). The highest DM yield was promoted by struvite B at the highest P rate. In general terms, vivianites sustained less biomass growth than superphosphate and struvites at both rates. However, industrial process-vivianite and synthetic vivianite at the highest rate did not lead to significantly different DM yield from that obtained with superphosphate at both rates and with struvites at the lowest P rate (Figure 2). The DM in aerial parts was very similar for superphosphate and vivianite obtained from industrial process at the highest P rate (Table 3). The dry matter yield with vivianites WP2 and WP3 at the highest rate was not significantly different to that obtained with superphosphate at

both rates. Vivianite WP1 was the only fertilizer that did not lead to increased total DM yield compared to control. The differences between vivianite WP3 and vivianites obtained from industrial process with superphosphate were less evident for DM yield in the aerial part than for the total DM (Table 3).

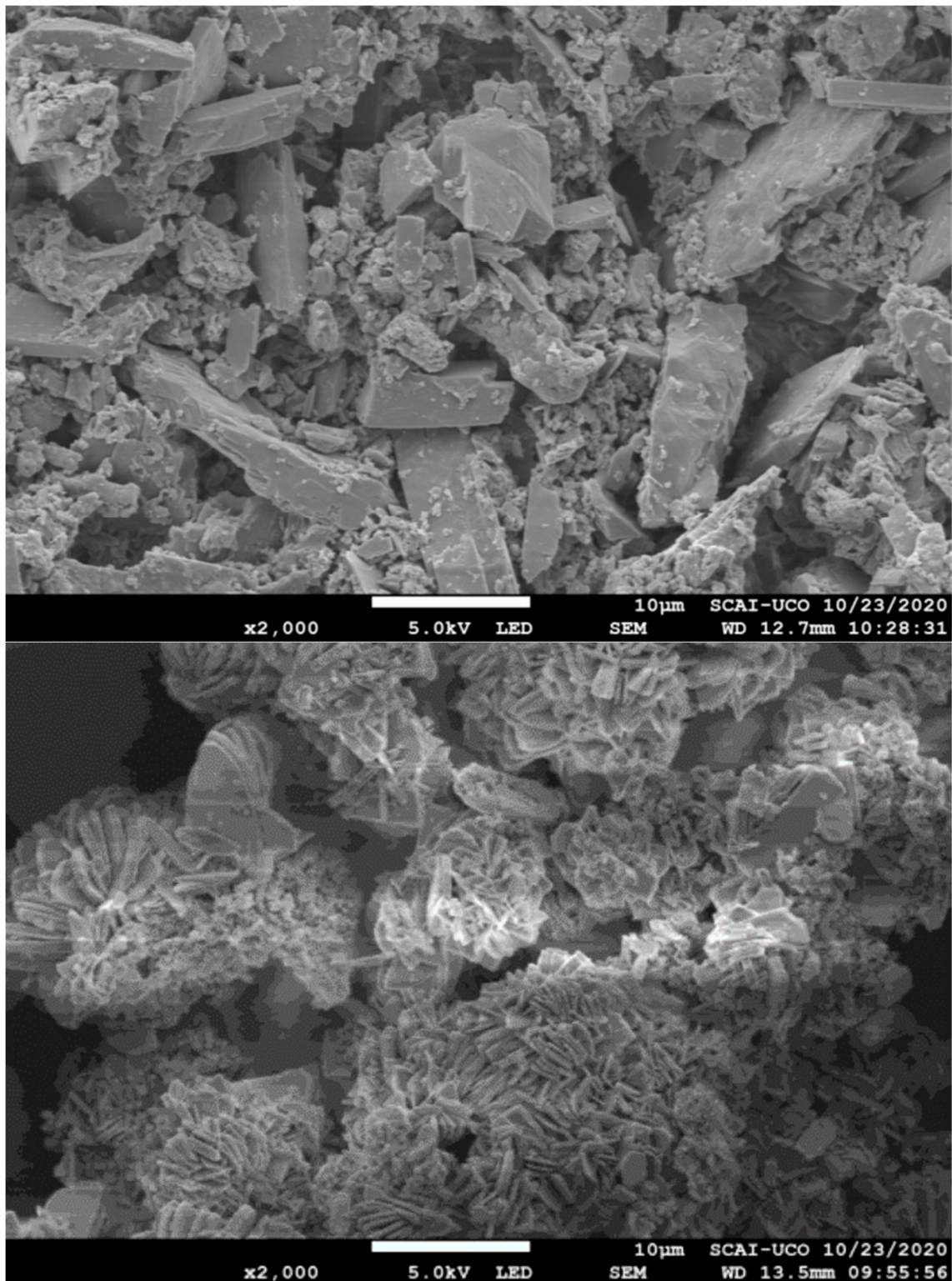


Figure 1. Scanning electron microscope images of vivianite from water purification (WP3 vivianite, upper image), and vivianite obtained from an industrial process (lower image).

Table 4. Effect (Mean ± standard deviation) of fertilizer treatments (control and the highest P rate of each fertilizer –100 mg P kg⁻¹–) on microbial community in plant rhizosphere.

Fertilizer Treatment	Microbial Biomass	Bacteria	Gram+	Gram–	Gram+/Gram–	Fungi	Bacteria/Fungi Ratio	Microfauna
				nmol g ⁻¹				
Control	257 ± 31	47.4 ± 9.4	11.8 ± 3.3	29.7 ± 6.6 ab	0.41 ± 0.10 c	8.7 ± 2.5	5.9 ± 1.9 ab	2.2 ± 1.0
Superphosphate	472 ± 258	42.3 ± 14.0	14.7 ± 4.9	15.6 ± 6.0 b	0.98 ± 0.23 a	9.0 ± 1.6	4.6 ± 1.0 ab	3.6 ± 2.1
Struvite A	361 ± 140	34.2 ± 5.5	11.4 ± 3.1	13.8 ± 1.9 b	0.82 ± 0.17 ab	10.2 ± 2.1	3.4 ± 0.7 b	2.9 ± 0.6
Synthetic Vivianite	373 ± 95	49.3 ± 23.5	14.6 ± 8.6	24.2 ± 12.6 ab	0.63 ± 0.22 bc	11.4 ± 4.1	4.3 ± 0.9 ab	3.3 ± 1.4
Industrial Process Vivianite	228 ± 38	49.1 ± 6.2	14.9 ± 1.6	25.3 ± 7.0 ab	0.63 ± 0.20 bc	8.4 ± 1.3	6.0 ± 1.6 a	2.8 ± 0.5
WP1 Vivianite	609 ± 673	57.6 ± 24.2	13.4 ± 4.6	35.4 ± 14.8 a	0.40 ± 0.09 c	12.1 ± 11	6.0 ± 2.4 a	3.4 ± 2.7
ANOVA	<i>p</i> value							
Treatment	0.3381	0.3088	0.7150	0.0094	0	0.6529	0.0182	0.8101
Soil	0.3287	0.1308	0.0344	0.7353	0.0047	0.1097	0.2709	0.6691
Treatment x soil	0.6619	0.7258	0.7948	0.7599	0.183	0.235	0.1510	0.3497

Means followed by different letter are significantly different according to the Tukey test (*p* < 0.05); WP, water purification.

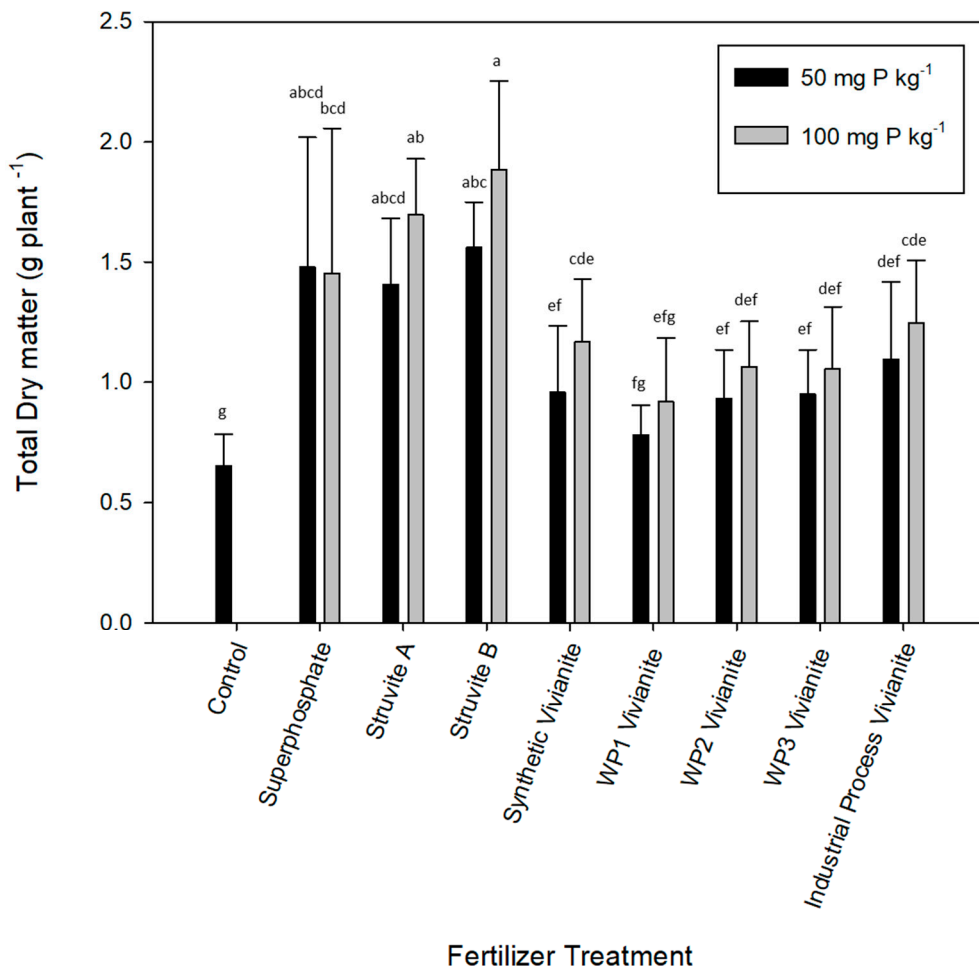


Figure 2. Effect of fertilizer treatments on total dry matter yield of wheat plants; WP (water purification) vivianites. Means with the same letter were not significantly different according to the Tukey test (*p* < 0.05). Error bars represent the standard deviation for each treatment.

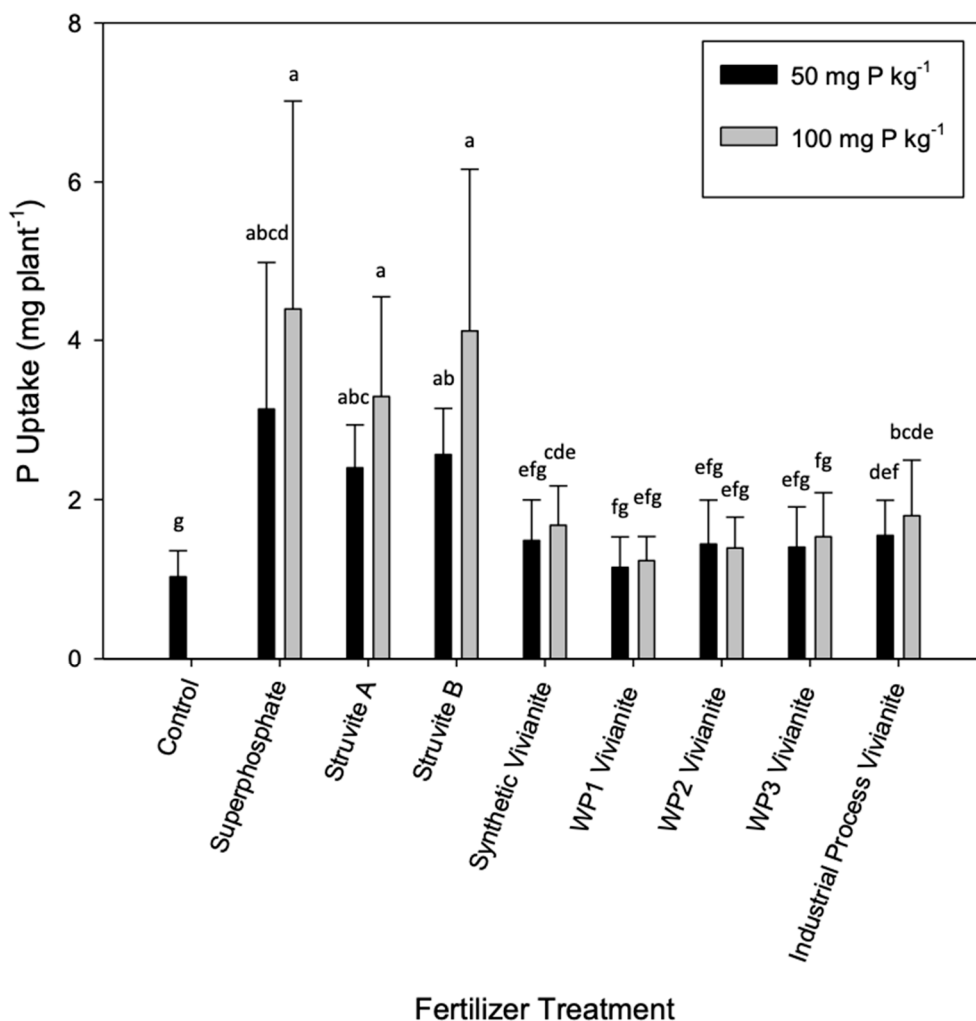


Figure 3. Effect of fertilizer treatments on P uptake of wheat plants; WP (water purification) vivianites. Means with the same letter were not significantly different according to the Tukey test ($p < 0.05$). Error bars represent the standard deviation for each treatment.

At the highest P rate, both struvites and superphosphate led to significantly higher P uptake than all the studied vivianites (Figure 3). Vivianites WP1 and WP2 at both rates, and synthetic vivianite and vivianite WP3 at the lowest rate, did not significantly increase P uptake when compared with the control. In terms of P uptake, the best results among vivianites was obtained from the vivianite from industrial process. At the highest rate, this vivianite did not lead to significantly different results from that obtained with superphosphate or struvites at the lowest rate (Figure 3). Overall, P concentrations in aerial parts and roots were not significantly different among most of the treatments (Table 3). Only superphosphate and struvite B increased Fe uptake significantly relative to the non-fertilized control (Table 3).

3.3. P Fertilizer Replacement Value

The replacement value on a P uptake basis (RV_P) was overall similar at both P fertilizer rates. Struvite A had an RV_P of 65 and 67%, while struvite type B had a RV_P of 73 and 92% for the low and high P rate, respectively (Figure 4). The RV_P of struvites were significantly higher than those of vivianites. The RV_P of vivianites ranged between 5 and 25% depending on the product and P rate (Figure 4). The vivianite from industrial process had the highest RV_P (25 and 23%, for the low and high P rate, respectively) while vivianite WP1 had the lowest (5 and 6% for the low and the high P rate, respectively).

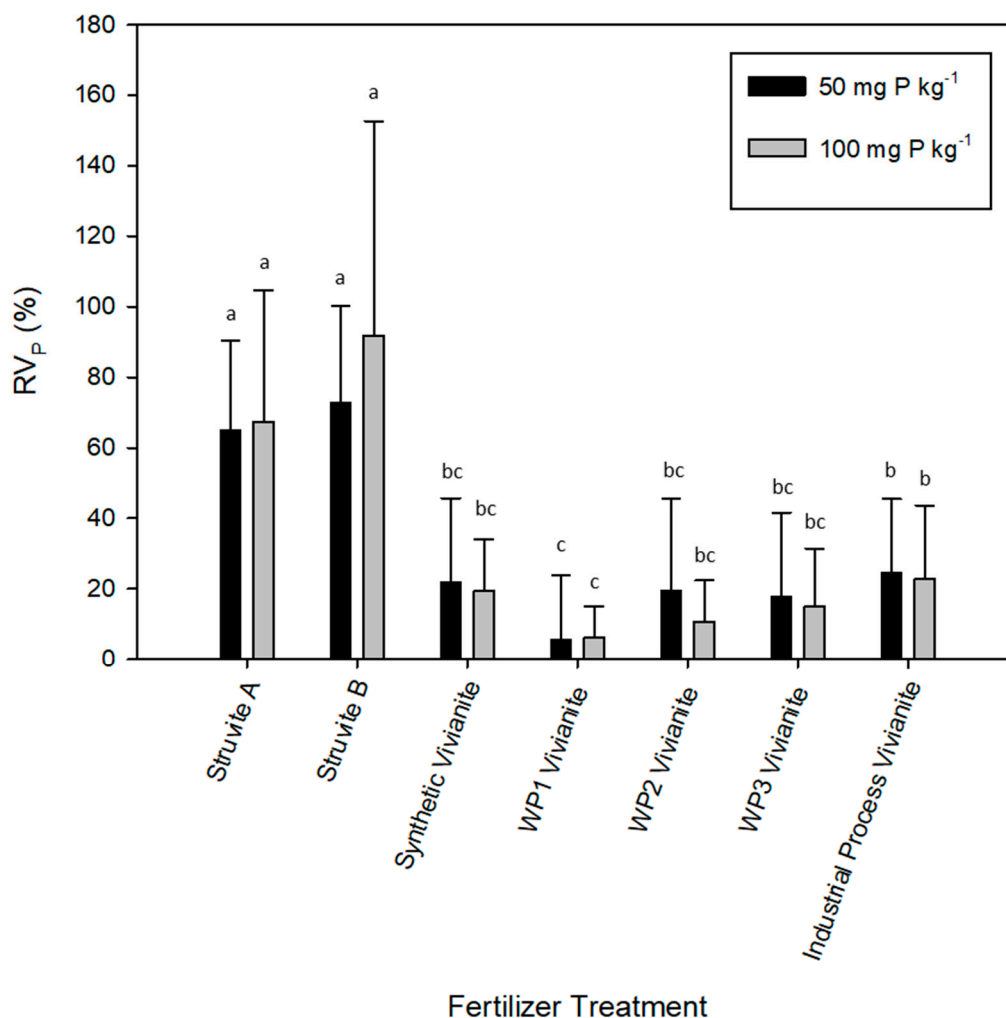


Figure 4. Phosphorus fertilizer replacement value on a P uptake basis for the different P fertilizers. Means with the same letter were not significantly different according to the Tukey test ($p < 0.05$). Error bars represent the standard deviation for each treatment.

Regarding RV_{DM} , struvites also performed better than vivianites (Figure 5). However, values were generally higher than those of RV_P . Overall, the RV_{DM} was lower at the lowest P rate. However, except for struvite A at the lowest P rate, the RV_{DM} of struvites were higher than 100%. The best performance between vivianites was achieved with the vivianite obtained from industrial process, with an RV_{DM} of 54 and 75% for the low and the high P rate, respectively (Figure 5).

3.4. Effect of Fertilizers on Soil Phosphate, Fe Availability Indexes, and Microorganisms

Overall, superphosphate and struvites outperformed vivianites in increasing Olsen P in soils after crop harvesting. However, at the high P rate, synthetic vivianites did not lead to significantly lower Olsen P than superphosphate and struvites at the lowest P rate (Figure 6). Among vivianites, synthetic vivianite and industrial-process vivianite at both rates significantly increased Olsen P in soil when compared with the non-fertilized control. These two fertilizer types, applied at the highest rate, increased the DTPA extractable Fe in soil relative to all other treatments (Table 3).

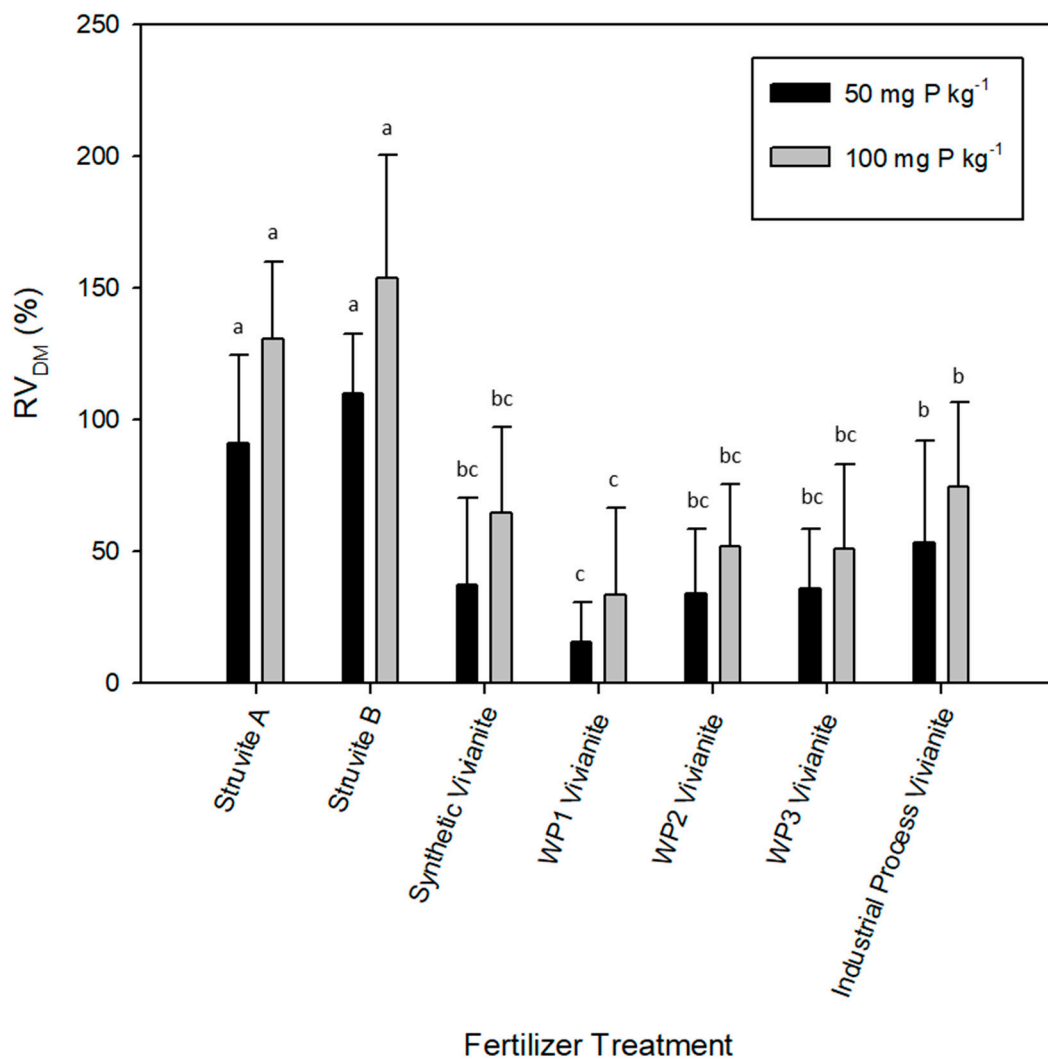


Figure 5. Phosphorus fertilizer replacement value on a total dry matter basis for the different P fertilizers. Means with the same letter were not significantly different according to the Tukey test ($p < 0.05$). Error bars represent the standard deviation for each treatment.

Fertilizers also affected the biological properties of the soils. Although the total microbial biomass was not affected, the population of Gram –ve bacteria, the ratio of Gram +ve to Gram –ve bacteria, and the bacteria to fungi ratio was significantly affected (Table 4 shows results for some treatments with fertilizers applied at the highest P rate). Vivianites showed a lower Gram +ve to Gram –ve ratio than superphosphate and a higher bacteria-to-fungi ratio than struvite A.

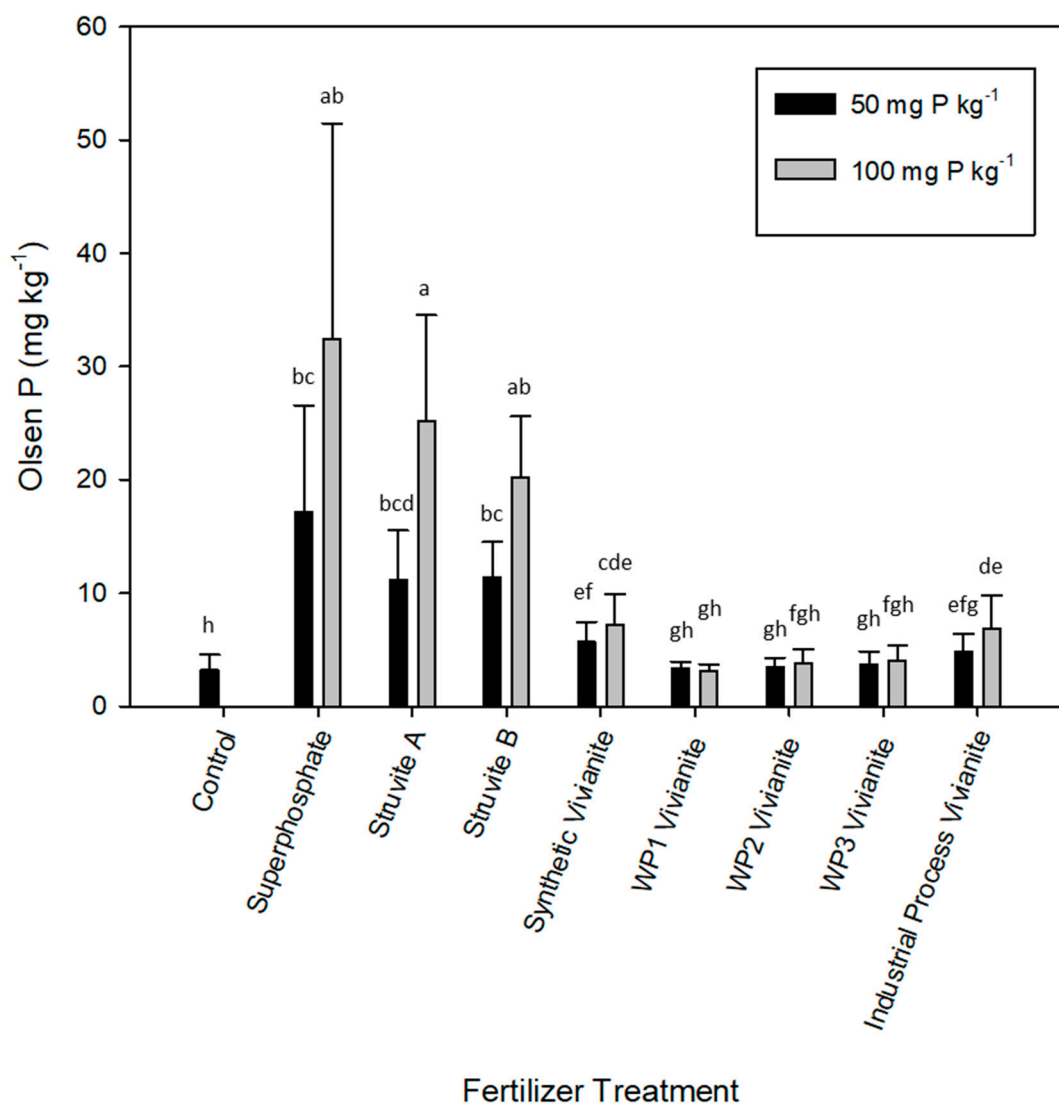


Figure 6. Effect of the different fertilizer treatments on Olsen P in soil after harvesting. Means with the same letter were not significantly different according to the Tukey test ($p < 0.05$). Error bars represent the standard deviation for each treatment.

4. Discussion

4.1. Efficiency of Fertilizer Products as P Source for Plants

In general, struvites were a more effective source of P for crops than vivianites, independent of the soil. In terms of DM yield, P uptake, and residual effect estimated from the Olsen P values in soils after crop harvest, the results obtained with struvites were similar to those of soluble mineral fertilizer (superphosphate). This agrees with previous studies [35,44]. According to Talboys et al., [36], the slower rate of P release from struvite granules during the early stage of plant growth did not have a detrimental effect on the final yield. Therefore, despite the low solubility of struvite, it can be considered a useful substitute for soluble mineral P fertilizers. It can be assumed that there is no need for an additional transformation for its agronomic efficiency to be increased before it can be used in agriculture. Struvite can perform even better than soluble mineral fertilizer in terms of DM yield at the highest rate, with an RV_{DM} higher than 100% in three of the four struvite-based treatments. This can be explained because, in addition to P supply, other factors can affect their effects on crop yield. In this sense, the potential supply of Mg by struvite can overcome the risk of nutritional antagonism between Ca and Mg in these soils, where the Ca to Mg ratio is higher than 10 [45]. Although all the essential

nutrients except P were applied with a nutrient solution, both soils were prone to Mg deficiency due to antagonism. Thus, counterions in fertilizers may be interesting to supply additional nutrients to crops. Furthermore, the higher values of RV_{DM} (overall > 100%) than RV_P (65 to 92%) with struvite may indicate that there is a luxury consumption of P with soluble mineral P fertilizer, i.e., absorption of P that does not lead to an increase in biomass production [46].

4.2. Vivianites as P Fertilizers

The replacement value for P fertilizers in terms of P uptake (RV_P) was quite low in the case of all vivianites. Best results were obtained with the vivianite obtained from industrial process. In fact, DM yield with this vivianite at the highest rate was not significantly different from that obtained with superphosphate at the same rate. However, P uptake with this vivianite was significantly lower than that with superphosphate. This perhaps reveals some luxury consumption with the most soluble fertilizers, as mentioned above. Vivianite can replace, in terms of DM yield, 75% of superphosphate at the highest P rate. Thus, despite the lower equivalence in terms of P uptake, this vivianite can provide enough P to achieve yields that are not far from those obtained with more soluble sources. Perhaps the limited availability of P in this fertilizer product can be offset by increased application rates, or by a combination with more soluble P sources.

Vivianite was also a source of available Fe [47]. Differences in Fe uptake were not observed since wheat is efficient in mobilizing and absorbing soil Fe [48]. However, synthetic, and industrial-process vivianite significantly increased Fe availability in soil relative to the control or fertilizer without Fe. Furthermore, these two vivianites increased Fe availability at the highest rate in comparison to other vivianites. The better performance as a P fertilizer of vivianite obtained from industrial process, when compared with other vivianites, can thus be related to its effect on the content of more readily extractable Fe forms in soil. The overall worse results with vivianite from water purification than the results with industrial process or synthetic vivianite can be explained, at least in part, by the composition of vivianites. It is assumed that synthetic vivianite has Fe mostly as Fe^{2+} since it is precipitated just before the application, and the vivianite from industrial process has a high Fe^{2+} to Fe^{3+} ratio in comparison to the other vivianites used in the study (Table 2). Thus, it seems that this ratio is a crucial factor explaining the efficiency of vivianites as P fertilizers. However, the highest Fe^{2+} to Fe^{3+} ratio was observed in vivianite WP3, which did not promote the best result. An additional factor that can explain the different performance of vivianites can be their crystallinity (Figures 1 and S1). The crystal morphology in vivianite from industrial process was similar to that expected in this type of compound, a monoclinic system with a layered structure in which stacking occurs along the b-axis of the unit cell [37]. However, in vivianites from water purification, and in particular WP3 Vivianite, the pattern was more irregular, with alteration of the cell parameters and irregular particle sizes (Figures S2–S4). Overall, the particle size was greater in vivianites from water purification than in vivianite obtained from industrial process. According to Kubeneck et al. [37], crystal morphology greatly affects the reactivity of vivianite in oxidizing environments, thus impacting the potential bioavailability of nutrients contained in the mineral. These authors observed that the incorporation of Mg and Mn in vivianite promoted different crystal morphology and size. In our case, vivianites from water purification and industrial process had a similar Mn content, and perhaps the differences in crystal size and morphology can be explained by Mg, whose content in vivianite obtained from industrial process was lower than in vivianites from water purification. This requires further research to check if vivianites with low Mg content could be more interesting fertilizer products.

4.3. Effect of P Recycled Source on Soil-Quality Indicators

As mentioned above, all the fertilizers tested were effective in increasing available P to plants, to a different extent depending on the specific product. In addition, some vivianites

were effective in increasing Fe availability index in soils. However, it is interesting to assess, as a crucial factor affecting soil functions, the effect on soil biological properties. In the short term of this study, total microbial biomass was not affected. However, there was a change in the composition of microbial populations. Industrial process and WP1 vivianites increased the bacteria-to-fungi ratio relative to more efficient P fertilizers (superphosphate, struvite A; Table 4). This can probably be explained by the different availability of P with different fertilizers and agrees with [49], who observed that the application of P decreased the bacteria-to-fungi ratio in nutrient-poor soils. This may have consequences on soil functioning. The soil bacterial-to-fungal ratio is related to C cycling in soils and a decreased bacteria-to-fungi ratio has been associated with increased C storage in soils [50,51].

5. Conclusions

Struvites were effective in supplying P to plants and increasing the availability of P in soil. The efficiency of vivianites was determined by their Fe^{2+} to Fe^{3+} ratio, crystal size, and morphology. Crystal properties seemed to be controlled by the presence of other cations, such as Mg, in the mineral composition. Vivianite can replace, in terms of DM yield, 75% of superphosphate at the highest P rate. Thus, although not as efficient as soluble P fertilizers and struvite, results are promising with a view to its potential agricultural use. Mixing with soluble P fertilizers or banding applications may be considered in fertilizer strategies for the practical use of vivianite. This requires further research for solid practical recommendations. The effect of fertilizers on microbial communities should be further investigated to assess their consequences for soil functioning.

Supplementary Materials: The supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/agronomy13061513/s1>, Figure S1: Scanning electron microscope image of the WP1 vivianite; Figure S2: Scanning electron microscope image of the WP2 vivianite; Figure S3: Scanning electron microscope image of the WP3 vivianite; Figure S4: Scanning electron microscope image of the vivianite from industrial process.

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