

Circular economy approach in phosphorus fertilization based on vivianite must be tailored to soil properties

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10 **Abstract.** Although there is relevant knowledge based on the effect of soil properties on the efficiency of common commercial fertilizers, this effect remains poorly understood for the use of vivianite from water purification as an innovative P fertilizer meeting a circular economy approach. This study aimed to evaluate the effect of soil properties on the efficiency of vivianite recovered from water purification as a P fertilizer and to provide practical recommendations for its effective use. Vivianite and a soluble mineral P fertilizer (superphosphate) were compared at two P application rates (50 and 100 mg P kg⁻¹) in soils ranging
15 widely in properties in a pot experiment using wheat. Soluble P fertilizer provided the best results in terms of dry matter (DM) yield, P uptake, and Olsen P in soils, while vivianite led to the best results of DTPA extractable Fe in soils after crop harvest. The application of vivianite as a P fertilizer was more efficient in acidic soils (pH < 6.6). The effect of vivianite on dry matter (DM) yield was equivalent on average to 26 or 40 %, depending on the rate, of the same amount of soluble fertilizer in these acidic soils (i.e., P fertilizer replacement value –PFRV– on DM basis), it being around 50 % in some cases. The effect on
20 Olsen P in soil was equivalent, on average, to 49 or 61 %, depending on the rate, of the same amount applied as soluble mineral fertilizer in acidic soils. This can be explained by the increased solubility of this fertilizer product under acidic conditions, supported by the highest increase in DTPA extractable Fe in these soils. Acidic soils were those with initial Olsen P below the threshold value for fertilizer response (TV). However, PFRV on different approaches (DM, P uptake, and Olsen P) decreased more consistently with increased values of the difference between initial Olsen P and TV (46 to 87 % of the variance explained)
25 than with increased pH. This reveals that besides soil pH, a low P availability to plants can trigger plant and microbial mobilization mechanisms, leading to increased efficiency of vivianite as a P fertilizer. Further studies are needed to assess the residual effect of vivianite and its effectiveness under field conditions, particularly in soils with low P availability status and an acidic pH.

Phosphorus (P) is an essential nutrient required for optimal crop production (Balemi and Negisho, 2012; Sharma et al., 2013; Recena et al., 2017). Phosphorus fertilizers are majorly derived from phosphate rock (PR), which is a non-renewable and strategic resource (Recena et al., 2022; Ayeyemi et al., 2023; 2024). Currently, 82% of PR is used for manufacturing phosphate fertilizers (Heckenmüller et al., 2014; Schröder et al., 2011). Phosphate rock production is expected to peak in the current century (Cordell et al., 2009; Keyzer, 2010), posing a serious constraint to global food security. The recent discovery of huge PR deposits in Norway (The Economist, 10 June 2023; Hernández-Mora et al., 2024) would allow us to think about a change in the situation concerning the use of P resources. However, new industrial uses (e.g. production of batteries) would lead to an increase in consumption of this non-renewable resource, with expected constraints for agricultural production (García-López et al., 2025). Thus, ensuring food security for an increasing world population, with an estimated rise to nine billion by 2050 (United Nations, 2017), makes it crucial to explore alternative sources of P fertilizers aside from PR to support crop production.

The productivity of soils is dependent on their physical, chemical, and biological properties (Delgado and Gómez, 2024; Bibi et al., 2023). These properties and their interactions govern the availability of nutrients in the soil rhizosphere (Jiang et al., 2009), including P. Several studies have revealed that the P adsorption and desorption capacities of soils are strongly dependent on their chemical properties, such as soil pH, iron (Fe) and aluminium (Al) oxides, and carbonates (Pizzeghello et al., 2016; Zhang et al., 2019; Sun et al., 2022). Physical properties such as soil texture and aggregate stability are also closely related to these chemical properties (Zhang et al., 2019). Organic matter, as a biological factor, also plays a major role in P availability in soils, decreasing its adsorption and precipitation in non-available forms (Delgado et al., 2002; Delgado and Scalenghe, 2008). The organic fraction of soil is a direct source of available P through its mineralization and the turnover of microbial biomass (Recena et al., 2015; 2018; Bueis et al., 2019).

The properties of soils are widely different globally due to soil-forming factors and processes (Mahdi and Uygur, 2018). Soils of the humid tropics, for example, are known to have a high P-sorption capacity because of their highly weathered nature and low organic matter content (de Campos et al., 2016). The sorption of P on Fe and Al oxides is predominant in these soils (Bortoluzzi et al., 2015). Consequently, most soils of the humid tropics are deficient in P (Tiessen, 2015; Hanyabui et al., 2020). The situation is different in Mediterranean soils where the dominant parent material could be limestone, dolomite, or marl, with limited weathering, explaining some key characteristics: pH frequently ranging from slightly acid to alkaline, accumulation of carbonates, and low contents of Fe and Al oxides (Hillel and Hatfield, 2005; Torrent et al., 2017; Torrent, 2005). The introduction of new and alternative P fertilizer products into crop production systems should consider the significant role that soil properties play in the reactions of P and, consequently, in the availability of native and applied P in soils.

A sustainable strategy to manage P resources is through the recycling of P from all current waste streams throughout the whole food system, including production, processing and consumption (Cordell et al., 2009; Recena et al., 2022). Vivianite, a Fe^{2+} phosphate mineral ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), is a P-removal product that is obtained from wastewater treatment plants (Wilfert

et al., 2018). It is produced by adding Fe^{2+} salts under anaerobic conditions and is easily separated based on its magnetic properties (Zhang et al., 2022).

Synthetic vivianite has proved to be an effective Fe fertilizer for overcoming Fe chlorosis in calcareous soils (Eynard et al., 1992; Rombolà et al., 2003; de Santiago et al., 2010). It is now gaining attention as a potential P fertilizer (Yaya et al., 2015; Wu et al., 2019). A recent study by Ayeyemi et al. (2023) revealed that industrially produced vivianite has a replacement value, i.e. an equivalence in dry matter production, to 50-75% of the same amount of superphosphate. Eshun et al. (2024) demonstrated that vivianite produced with the use of Fe-reductant microorganisms was an efficient P fertilizer. In addition to the little information available on vivianite as a P fertilizer, it is unknown how soil properties affect the effectiveness of this product as a fertilizer. This is crucial information for practical recommendations and efficient use. Therefore, the objective of this study was to assess the impact of soil properties on the effectiveness of vivianite obtained from water purification as a P fertilizer. This will allow us to demonstrate the possible use of vivianite as a P fertilizer under different soil conditions leading to proper recommendations of its usage depending on soil properties.

2 Material and Methods

2.1 Soils

Twelve soil samples were collected from the surface horizon of typical soils developed under the Mediterranean. Soils were classified according to the Soil Taxonomy (Soil Survey Staff, 2014), i.e. Inceptisols, Alfisols, Vertisols, and Mollisols, including calcareous and non-calcareous soils. In each selected location, a square with homogeneous soil considered location, color, texture, and structure in the surface horizon in the soil was defined. Then, subsamples of the surface layer (0–20 cm) of the soil were randomly taken in 10–12 sampling points. To this end, in each sampling point (1 m^2), eight soil cores (50 mm diameter) were taken to obtain a subsample, and after that, all the subsamples from each sampling point were mixed to obtain a composite sample.

The soils were air-dried, clods and lumps broken, and thereafter passed through a 2 mm sieve for laboratory analysis and sieved to $<4 \text{ mm}$ for pot experiment to avoid excessive destruction of soil structure that may affect crop performance in pots.

Soils were analyzed for particle size distribution according to (Gee and Bauder, 1986), organic C by the oxidation method of (Walkley and Black, 1934), total CaCO_3 equivalent (CCE) by the calcimeter method, pH, and electrical conductivity in water at a soil: extractant ratio of 1:2.5, and the cation exchange capacity (CEC) by using 1 M NH_4OAc buffered at pH 7 (Sumner and Miller, 1996). Extraction was performed to determine Fe present in Fe oxides: oxalate to release Fe in poorly crystalline Fe oxides (Fe_{ox}), and citrate-bicarbonate-dithionite to release Fe in crystalline oxides (Fe_d) according to Recena et al. (2015).

Olsen P was determined by weighing two grams of soil into 50 mL falcon tubes, after which 40 mL of 0.5M NaHCO_3 at pH 8.5 was added. The mixture was shaken in a mechanical end-over-end shaker for 30 mins at 180 rpm. Subsequently, the suspension was centrifuged for 10 min at 900 g. The P concentration of the extract was determined by the colorimetric method of Murphy and Riley (1962) using a spectrophotometer at 882 nm. The DTPA (Diethylenetriaminepentaacetic acid) extractable

Fe determination was carried out according to Lindsay and Norvell (1978) with slight modifications as Fe availability index.

95 To this end, five grams of soil were weighed into 50 mL falcon tubes, and 20 mL of DTPA/CaCl₂ TEA (triethanolamine) was added and stirred for 2 h at 160 rpm. The suspension was then placed in the centrifuge for 15 min at 900 g. The Fe concentration of the extract was determined by atomic absorption spectrometry. Since the soils have very different properties, it is expected that the Olsen P threshold value (TV), i.e., the value above which no response in yield is expected with P fertilization, ranges widely between soils (Recena et al., 2016). This TV was calculated according to the model proposed by (Recena et al., 2022).

100 The equation of the model is $Y = 43.7 - 0.016 \text{ Clay} - 3.81 \text{ pH}$. To assess the available P status of soils, the Olsen P value was compared with the specific TV for each soil. The more negative this difference between current Olsen P in soil and TV (Olsen P – TV) is, the more deficient the soil is in P. The detailed properties of the soils used in this experiment are shown in Table 1.

2.2 Fertilizers

105 Two fertilizer products were studied in this experiment: (i) Water Purification Vivianite (WPV) obtained from Wetsus (European Centre of Excellence for Sustainable Water Technology) from Leeuwarden, the Netherlands, and (ii) Superphosphate as a reference P fertilizer: $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

The elemental composition of the WPV (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 Fe^{2+} to Fe^{3+} ratio was determined by Mossbauer spectroscopy and X-ray photoelectron spectroscopy (XPS). This ratio is relevant since Fe^{3+} compounds are less soluble and contribute little to nutrient supply to crops (Ayeyemi et al., 2023).

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2.3 Experimental Design

The experiment was conducted using wheat (*Triticum durum* L. cv. Amilcar) and was arranged in a Randomized Complete Block Design (RCBD) with three replicates. Each replicate was a pot with one wheat plant. Two factors were involved in the experiment: Soil type (12) and P fertilizer treatment, involving the two fertilizers described above, at two rates (50 and 100 mg P kg⁻¹) and a non-fertilized control. The lowest P rate was selected since it is generally believed that plants respond to fertilizer application at this rate in P-poor growing media in pot experiments (García-López et al., 2016). The highest rate was chosen to check the impact of a high rate on P absorption and availability in the growing medium.

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The growing media was prepared by mixing fertilizer products with 300 g of soil and placed in cylindrical polyethylene pots with a volume of 350 mL (height 150 mm, diameter 55 mm). The mixing of fertilizer products (in powder form) with soil was carried out three days before transplanting the wheat seedlings. Wheat seeds were pregerminated by sowing in a nursery for 15 days, after which they were transplanted into already prepared growing assays. 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 by 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 type) was applied on a regular basis. The composition of this

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Soil	Clay	Silt	Sand	CCE	Organic C	pH	EC	CEC	Fe _{ox}	Fe _d	Olsen P	TV*	Olsen T
		g kg ⁻¹					µS/cm ⁻¹	cmolc kg ⁻¹				mg kg ⁻¹	mg kg ⁻¹
Soil 1	362	140	180	330	6.2	8.30	284	34.3	0.68	5.8	17.0	6.3	10.3
Soil 2	245	126	488	140	8.8	8.50	134	17.0	0.30	10.5	14.4	7.4	7.4
Soil 3	228	164	463	139	8.4	8.70	201	13.0	0.36	14.5	14.5	6.9	7.4
Soil 4	168	158	480	184	7.3	8.80	157	9.7	0.24	12.0	8.9	7.5	13.4
Soil 5	222			212	9.7	8.10	278	16.3	0.66	6.7	16.3	9.3	7.4
Soil 6	120	150	630	43	12.0	8.26	173	28.5	1.55	8.4	16.9	10.3	6.3
Calcareous Mean±SD	224±81.8 (362-120)	147±15.06 (164-126)	448±164.16 (630-180)	175±95.31 (330-43)	8.73±2.01 (12.0-6.2)	8.44±0.27 (8.8-8.1)	204±63.17 (284-134)	19.8±9.53 (34.3-9.7)	0.63±0.49 (1.55-0.24)	9.65±3.31 (14.5-5.8)	14.67±3.05 (17.0-8.9)	7.95±1.53 (10.3-6.3)	6.74±1.53 (10.3-6.3)
Soil 7	92	150	769	0	4.1	6.44	45	7.3	1.47	6.7	16.4	17.7	-3.4
Soil 8	62	170	771	0	13.2	6.60	30	11.1	0.90	13.5	8.4	17.6	-5.4
Soil 9	155	212	632	0	8.8	5.84	40	12.1	1.74	17.4	7.3	19.0	-1.4
Soil 10	130	180	690	0	5.8	5.76	84	10.8	1.40	13.0	12.0	19.7	-5.4
Soil 11	388	156	443	0	15.6	7.86	138	58.6	2.59	17.5	20.7	7.5	13.4
Soil 12	274			0	6.4	7.90	224	15.4	0.74	17.1	13.8	9.2	4.4
Non-calcareous Mean±SD	183±123.9 (388-62)	173±24.47 (212-150)	661±135.06 (769-443)	0 (0-0)	8.98±4.52 (15.6-4.1)	6.73±0.94 (7.90-5.84)	93.5 ±75.30 (224-30)	19.2±19.47 (58.6-7.3)	1.47±0.66 (2.59-0.74)	14.2±4.18 (17.5-6.7)	13.1±5.02 (20.7-7.3)	15.12±5.33 (19.7-7.5)	3.34±1.53 (13.4-6.3)

Table 2. Elemental composition of the vivianite used in the experiment and percentage of total Fe as Fe²⁺ and Fe³⁺ according to Mossbauer spectroscopy and X-ray photoelectron spectroscopy (XPS)

C	N	P	K	Ca	Mg	Fe	Zn	Mn	Cu	Mossbauer		XPS	
										Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺
g kg ⁻¹										%			
nd	nd	108	0.25	8.9	9.2	280	0.16	1.14	0.04	75	25	41	59

nd = not detectable; XPS. X-ray Photoelectron Spectroscopy

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 58 days after transplanting at the ripening stage.

2.3 Collection of Soil and Plant Samples

At the end of the experiment, bulk soil samples (the entire soil samples in the pots) were collected for Olsen P and DTPA Fe analyses as described above. These samples were dried and milled to pass through a 2 mm screen. The roots and shoots of the wheat plants were also 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.

2.3.1 Plant Samples Analysis

Root and shoot wheat samples were ground. Subsequently, wet acid digestion was carried out. To this end, 50 mg of plant materials were placed in glass test tubes, and 1 mL HNO₃ was added. The mixture was left to stand overnight. This was placed in an open block digest the next morning and allowed to heat to temperatures of 120°C -130°C until the plant materials were fully digested and clear. 10 mL of Milli-Q water was added and allowed to stand overnight, after which P concentration in the digest was determined by ICP-OES. 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 Phosphorus fertilizer replacement value (PFRV) of vivianite was adapted from (Hijbeek et al., 2018) as the amount of commercial mineral P fertilizer (superphosphate) saved or replaced when using an alternative fertilizer (in this case, vivianite) while attaining the same yield, P uptake, or Olsen P in soils. This gives an idea of equivalence if expressed on a percentage basis. It is expressed as 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 fertilizers that can be replaced by alternative fertilizers. It was estimated on a DM basis for each P rate following Eq. (1):

$$PFRV_{DM} = \frac{DM_v - DM_c}{DM_s - DM_c} \quad (1)$$

where DM_v is the DM yield with vivianite, DM_c is the average DM in the non-fertilized control, and DM_s, the average DM in the superphosphate treatment at the same P rate as vivianite.

The PFRV was estimated on a P uptake basis for each P rate following Eq. (2):

$$PFRV_{P \text{ Uptake}} = \frac{P_{\text{uptake}_v} - P_{\text{uptake}_c}}{P_{\text{uptake}_s} - P_{\text{uptake}_c}} \quad (2)$$

Where P_{uptake_v} is the P uptake by crop with vivianite, P_{uptake_c} is the average P uptake in the non-fertilized control, and P_{uptake_s}, the average P uptake in the superphosphate treatment at the same P rate as vivianite.

The PFRV was also estimated on an Olsen P basis following Eq. (3):

$$160 \quad \text{PFRV}_{\text{Olsen P}} = \frac{\text{Olsen P}_v - \text{Olsen P}_c}{\text{Olsen P}_s - \text{Olsen P}_c} \quad (3)$$

where Olsen P_v is the Olsen P with vivianite, Olsen P_c is the average Olsen P of the non-fertilized control and Olsen P_s, the average bioavailable P in the superphosphate treatment at the same rate as vivianite

2.4 Statistical Analysis

Statistical analysis was performed with Statgraphics Centurion 18 (Statgraphics Technologies, 2018). The effect of factors (P
165 fertilizer treatment and soils as fixed factors) on DM yield and P uptake was assessed by means of a two-way analysis of variance (ANOVA). To assess the effect of soil on the different PFRV indices studied and in the increase of DTPA extractable Fe, one-way ANOVA was performed for each P rate independently. Before ANOVA, normality and homogeneity of variance were assessed with the use of the Smirnov–Kolmogorov and Levene tests, respectively. Power transformations were performed when one or both tests were not passed. Mean separation was conducted using the Tukey Honest Significant Difference (HSD)
170 test at P < 0.05. If the interaction between factors was significant, the effects of the main factors were not discussed since the effect of one factor depends on the level of the other. To assess the differences in PFRV indices and increase in DTPA extractable Fe between calcareous and non-calcareous soils, an ANOVA with the factor soil type (i.e. calcareous or non-calcareous) was performed and means compared according to the Tukey test as above. To assess the differences between soils with pH < 6.6 (n = 4) and those with pH > 7.86 (n = 8), the non-parametric Kruskal-Wallis test was performed. In this case,
175 medians were compared according to the procedure of Bonferroni. Regression and correlation analysis were performed using the same software to see relationships between different soil properties.

3 Results

3.1 Soil Properties

There was wide variation in the properties of the set of soils used in this experiment (Table 1), especially clay content and
180 calcium carbonate equivalent (CCE), which are relevant properties affecting P dynamics in soils. The 12 soils used were grouped into two broad categories: six calcareous and six non-calcareous. The pH of the non-calcareous soils varied from 5.76 to 7.90, while in the calcareous soils, it ranged from 8.10 to 8.80. The DTPA extractable Fe content of the calcareous soils ranged from 5.0 to 9.8 mg kg⁻¹, while those of non-calcareous soils were higher, ranging from 17.8 to 83.0 mg kg⁻¹. The organic matter content of all soils varied from 4.1 to 12.0 g kg⁻¹, while the clay content of all soils varied from 62 to 388 g kg⁻¹. There
185 was also wide variation in the Olsen P value of the soils from 7.3 to 20.7 mg kg⁻¹. The Olsen P – TV of the calcareous soils ranged from 1.4 to 10.7, while those of non-calcareous soils ranged from -11.7 to 13.2. The Olsen P – TV values were positively correlated with pH (r = 0.83; P < 0.001) and clay content (r = 0.77; P < 0.01). The four non-calcareous soils with pH lower

than 6.6 were the soils with negative values of Olsen P – TV. The oxalate and dithionite extractable Fe were negatively correlated with carbonate content ($r = -0.62$ and -0.59 , respectively; $P < 0.05$ in both cases).

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3.2 Effect of Soils and Fertilizer Treatments on Crops and Soil

The dry matter (DM) yield, total P uptake by plants, and Olsen P and DTPA extractable Fe in the soil after crop were significantly affected by the interaction between both factors, soil and fertilizer treatment ($P < 0.001$ in all the cases; Table 3). This means that the effect of fertilizer treatments depends on soil. Overall, soluble mineral fertilizer (superphosphate) provided the best results in terms of DM, P uptake, and Olsen P, meanwhile vivianite led to the best results of DTPA extractable Fe in soil after crop (Table 3). The vivianite treatments led to increased DM yield relative to non-fertilized control in soils 8, 4, 9 and 10 (Table S1). In these soils and in soil 3, vivianite treatments slightly increased P uptake when compared with the control (Table S1). In soils 8, 4, 7, 9 and 10, vivianite led to higher Olsen P after crop than control, and in soils 9 and 10, the highest rate of vivianite promoted higher Olsen P than the lowest rate of mineral soluble P fertilizer (Table S1). The increase of DTPA extractable Fe with vivianite relative to superphosphate and control was particularly evident in soils 8, 9, and 10 (Table S1).

With vivianite at 50 mg P kg^{-1} , the effect of soil was not significant for the P fertilizer replacement value on a DM basis (PFRV_{DM}). Soil had a significant effect on PFRV on a P uptake basis ($\text{PFRV}_{\text{P Uptake}}$, $P < 0.001$) and on an Olsen P basis ($\text{PFRV}_{\text{Olsen P}}$, $P < 0.001$) at this lowest vivianite rate. At the highest rate (100 mg P kg^{-1}), PFRV_{DM} , $\text{PFRV}_{\text{P Uptake}}$, and $\text{PFRV}_{\text{Olsen P}}$ of vivianite were significantly affected by soil ($P < 0.05$, 0.01 and 0.001 , respectively) (Table S2). In order to better understand the effect of soils on the different PFRV indices used, the relationships of these variables with soil properties were studied. These PFRV indices provide a relative comparison of efficiency with the mineral soluble P fertilizer.

3.3 Phosphorus Fertilizer Replacement Value on a Dry Matter Basis

When soils were discriminated by carbonate content, differences in this index were not significant. Meanwhile, soils with pH lower than 6.6 showed PFRV_{DM} at the highest P rate, significantly higher than those with $\text{pH} > 7.86$ (Table 4). However, PFRV_{DM} at both rates was not correlated with pH. It was negatively correlated with clay content ($r = -0.79$; $P < 0.01$) and the value of the difference between soil Olsen P and its threshold value (Olsen P – TV; $r = -0.71$; $P < 0.05$) at the lowest P fertilizer rate (50 mg P kg^{-1}) (in both cases an outlier with $\text{PFRV}_{\text{DM}} > 540$ was excluded), meanwhile it was negatively correlated only with Olsen P – TV ($r = -0.68$; $P < 0.05$) at the highest P fertilizer rate (100 mg P kg^{-1}). Thus, Olsen P – TV was the only variable that was correlated with PFRV_{DM} at both P fertilizer rates, and PFRV_{DM} decreased significantly with increased values of the difference (Olsen P – TV; Figure 1). It was observed that for soils with Olsen P-TV less than 0 (which were also the soils with $\text{pH} < 6.6$), PFRV_{DM} was always positive at both P fertilizer rates, with average values of 26 and 40 % at the lowest and the highest P fertilizer rates, respectively. However, for soils with Olsen P – TV higher than 0, most of the soils showed negative PFRV_{DM} at the lowest P rate and three soils at the highest rate (Figure 1). At the lowest P fertilizer rate, the soil with an Olsen P – TV of -9.2 resulted in a PFRV_{DM} of 54%. At the highest rate of P fertilizer application, soils with Olsen P – TV < -5 showed PFRV_{DM} of around 50 % (Figure 1).

Table 3. Effect of fertilizer treatments and soil on dry matter yield (DM) and P uptake by crop. and Olsen P and DTPA extractable Fe after crop

Factor	n	DM	P uptake	Olsen P	DTPA Fe
		g plant ⁻¹	mg plant ⁻¹	mg kg ⁻¹	
Fertilizer treatment					
Control	36	1.21 ± 0.07	1.64 ± 0.15	14.7 ± 1.3	14.7 ± 1.3
Superphosphate 100	36	1.74 ± 0.08	4.67 ± 0.27	48.1 ± 3.0	48.1 ± 3.0
Superphosphate 50	36	1.67 ± 0.07	3.46 ± 0.24	28.3 ± 1.8	28.3 ± 1.8
Vivianite 100	36	1.28 ± 0.06	1.63 ± 0.10	17.7 ± 1.1	17.7 ± 1.1
Vivianite 50	36	1.27 ± 0.06	1.67 ± 0.12	15.8 ± 1.0	15.8 ± 1.0
Soil					
Soil 1	15	0.52 ± 0.03	0.53 ± 0.10	29.0 ± 4.6	5.9 ± 0.2
Soil 2	15	1.29 ± 0.10	2.18 ± 0.41	26.6 ± 5.1	4.3 ± 0.3
Soil 3	15	1.24 ± 0.10	2.33 ± 0.34	20.9 ± 4.5	5.1 ± 0.2
Soil 4	15	1.36 ± 0.11	2.64 ± 0.36	20.5 ± 4.5	3.8 ± 0.1
Soil 5	15	1.65 ± 0.06	3.51 ± 0.33	44.8 ± 4.9	9.4 ± 0.2
Soil 6	15	1.91 ± 0.10	3.62 ± 0.38	26.1 ± 3.6	7.3 ± 0.2
Soil 7	15	1.43 ± 0.07	2.63 ± 0.40	21.9 ± 2.4	49.1 ± 1.7
Soil 8	15	1.42 ± 0.14	2.31 ± 0.43	21.0 ± 2.7	32.7 ± 4.3
Soil 9	15	1.42 ± 0.09	2.13 ± 0.29	15.3 ± 1.8	52.6 ± 3.4
Soil 10	15	1.60 ± 0.08	3.26 ± 0.62	19.6 ± 1.9	49.9 ± 3.4
Soil 11	15	1.83 ± 0.08	3.26 ± 0.44	20.3 ± 3.2	14.9 ± 0.4
Soil 12	15	1.53 ± 0.06	2.97 ± 0.43	32.8 ± 5.2	5.6 ± 0.1
ANOVA					
		P value			
Fertilizer treatment (A)		< 0.001	< 0.001	< 0.001	< 0.001
Soil (B)		< 0.001	< 0.001	< 0.001	< 0.001
A x B		< 0.001	< 0.001	< 0.001	< 0.001

Mean ± standard error

Number after fertilizer indicates the P rate in mg kg⁻¹ of soil

Mean comparison is not performed since the interaction of both factors is significant. In that case, the effect of one factor depends on the other and an analysis of the effect of main factor cannot be performed

Table 4. Effect of soils on the mineral P fertilizer replacement value (PFRV) expressed in % estimated based on different approaches (DM yield, P uptake, Olsen P) and on the DTPA extractable Fe after crop for both P fertilizer rates (50 and 100 mg P kg⁻¹ soil)

Soil type	n	PFRV _{DM}		PFRV _{Puptake}		PFRV _{OlsenP}		Increase in DTPA extractable Fe
		50 mg kg ⁻¹	100 mg kg ⁻¹	50 mg kg ⁻¹	100 mg kg ⁻¹	50 mg kg ⁻¹	100 mg kg ⁻¹	50 mg kg ⁻¹
Non-calcareous	6	0 ± 20	13 ± 25	9.3 ± 7	7.6 ± 3	33 ± 21	30 ± 33	10 ± 4.2
Calcareous	6	2.2 ± 12	-41 ± 27	- 22 ± 21	-4.2 ± 14	-3.6 ± 7.8	0 ± 3.6	0 ± 0.1
ANOVA P value								
		NS	NS	NS	NS	NS	NS	p < 0.01
Soil pH								
< 6.6	4	26 ± 11	40 ± 6	16 ± 6	11 ± 3.1	61 ± 16	49 ± 12	15 ± 4.8
> 7.86	8	-13 ± 15	-41 ± 23	-18 ± 16	-2.8 ± 10	-8.5 ± 7.5	-2.1 ± 2	0.2 ± 0.2
Kruskall-Wallis P value								
		NS	<0.05	NS	NS	<0.01	<0.01	<0.01

Mean ± standard error

NS, not significant

Means followed by the same letter are not significantly different according to the Tukey test at P < 0.05

The subindices for the P fertilizer replacement value abbreviation (PFRV) indicates: DM, on a dry matter basis. Puptake, on a P uptake basis, and OlsenP on a Olsen P after crop basis

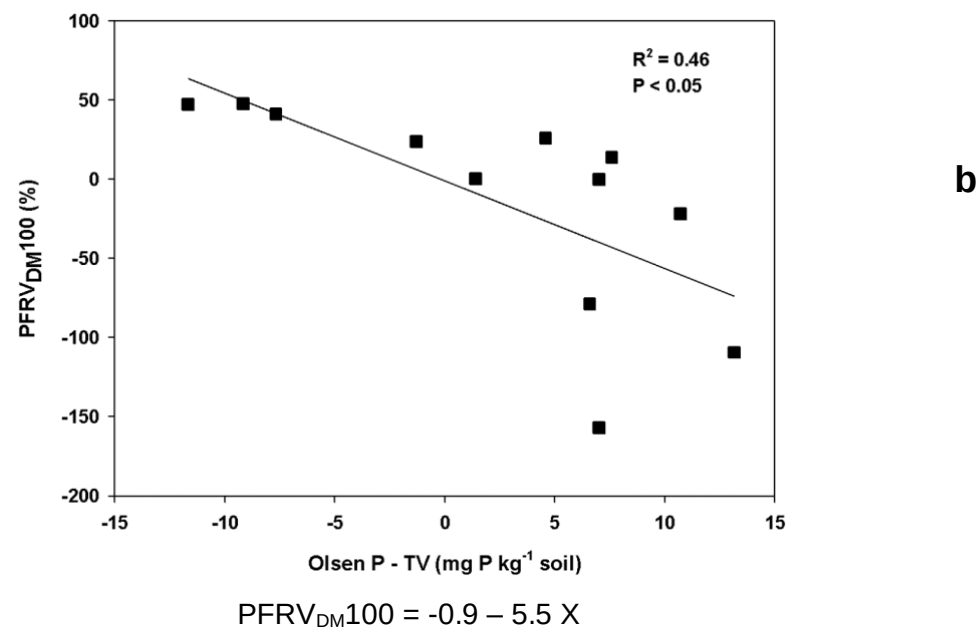
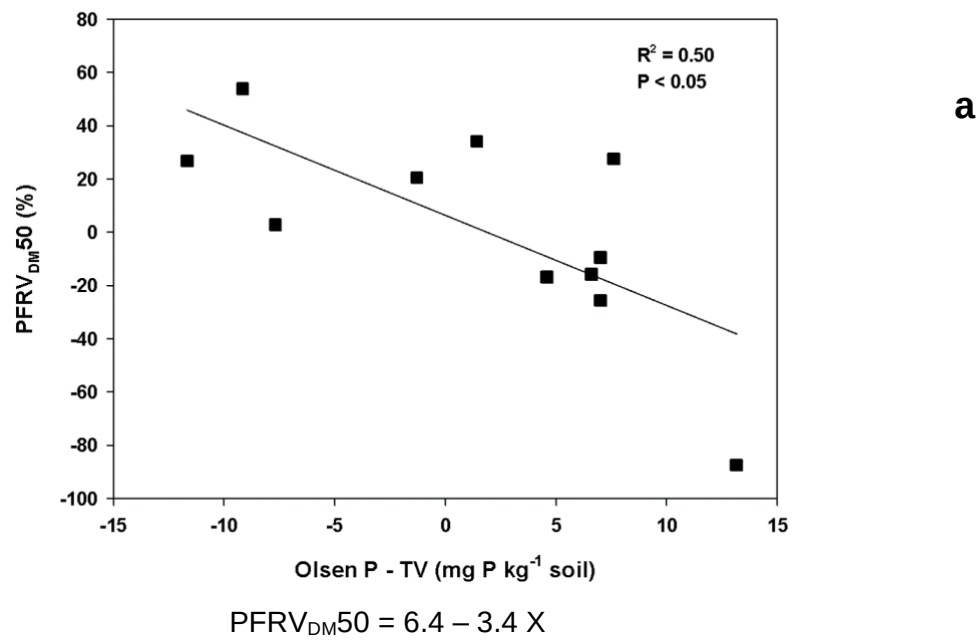
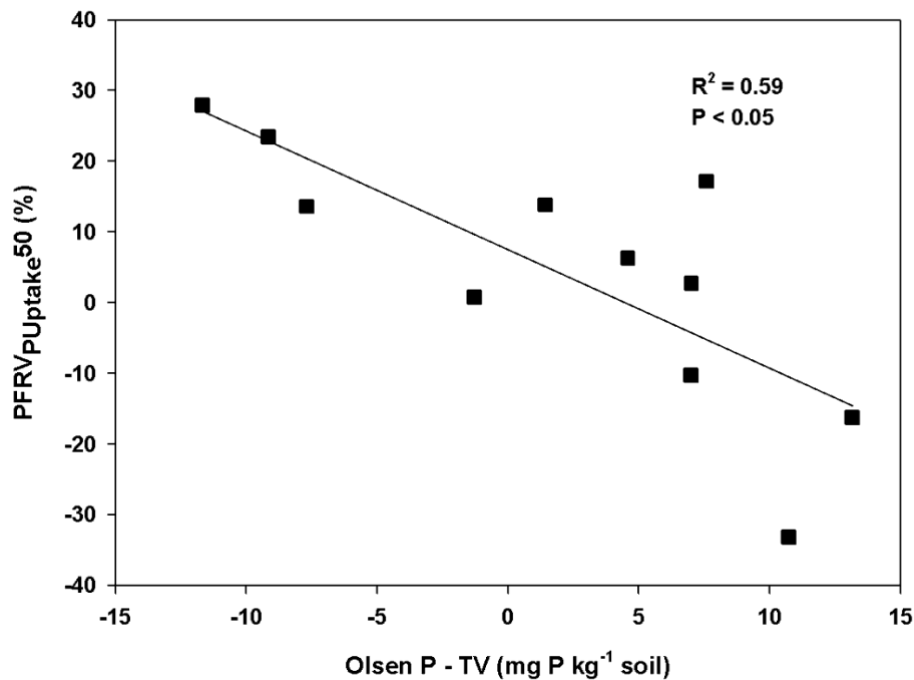


Figure 1. Relationship between the P fertilizer replacement value on a dry matter basis at 50 (PFRV_{DM50}) (a) and at 100 mg P kg⁻¹ (PFRV_{DM100}) (b) and the difference between the initial Olsen P in soil and the estimated threshold value (Olsen P – TV).

3.4 Phosphorus Fertilizer Replacement Value on a P Uptake Basis

235 The P fertilizer replacement value on a P uptake basis ($PFRV_{P\ Uptake}$) was significantly affected by soil (Table S2). However, when soils were grouped by carbonate content or pH, the effect of soil type was not significant (Table 4). At the lowest P fertilizer rate, the relationship between $PFRV_{P\ Uptake}$ and soil properties was similar to that observed for $PFRV_{DM}$: it was negatively correlated with clay content and Olsen P – TV ($r = -0.76$ and -0.77 , respectively, $P < 0.01$ in both cases; an outlier with $PFRV_{P\ Uptake} < -130$ excluded). The values of $PFRV_{P\ Uptake}$ for the lowest P fertilizer rate were in most of the cases above 0, with an average of 16 % for Olsen P – TV less than 0 and -18 % for Olsen P – TV higher than 0 (Figure 2). At the highest P fertilizer rate, $PFRV_{P\ Uptake}$ was not related to any soil property, and its values ranged between -50 and 50, with an average of 11 % and -3 % for soils with Olsen P – TV less and higher than 0, respectively. When clay content and Olsen P – TV were considered in a multiple regression, both explained 53 % of the variance in $PFRV_{P\ Uptake}$ at the highest rate ($Y = -40.8 - 2,9$ (Olsen P – TV) + 0,24 Clay²; $R^2 = 0.53$; $P < 0.05$).

245



$$PFRV_{P\ Uptake\ 50} = -0.7 - 2.4 X$$

250 Figure 2. Relationship between the P fertilizer replacement value on a P uptake basis at 50 mg P kg⁻¹ ($PFRV_{P\ Uptake\ 50}$) and the difference between the initial Olsen P in soil and the estimated threshold value (Olsen P – TV).

3.5 Phosphorus Fertilizer Replacement Value on an Olsen P Basis

255 The P fertilizer replacement value on an Olsen P basis ($PFRV_{P\ Olsen P}$) was also significantly affected by soil (Table S2). When
soils were differentiated between calcareous and non-calcareous, differences in this index between both types of soil were not
significant at both P fertilizer rates (Table 4). However, when discrimination was done on a pH basis, soils with $pH < 6.6$ had
significantly higher $PFRV_{P\ Olsen P}$ than those with $pH > 7.86$ at both P fertilizer rates (Table 4). The $PFRV_{Olsen P}$ at the lowest P
fertilizer rate was negatively correlated with clay content ($r = -0.73$; $P < 0.01$), pH ($r = -0.80$; $P < 0.01$), and Olsen P – TV (r
260 $= -0.83$; $P < 0.001$). Correlations were similar for $PFRV_{Olsen P}$ at the highest P fertilizer rate: clay content ($r = -0.65$; $P < 0.05$),
pH ($r = -0.86$; $P < 0.001$), and Olsen P – TV ($r = -0.93$; $P < 0.001$). Overall, the highest correlation coefficients were observed
for Olsen P – TV, which explained 69 and 87 % of the variance at the lowest and the highest P fertilizer rate, respectively
(Figure 3). For Olsen P – TV less than 0, the average $PFRV_{Olsen P}$ for the lowest and the highest fertilizer rate was 61 and 49
%, respectively; meanwhile, for Olsen P – TV higher than 0, it was –8.5 and –2.1 %, respectively.

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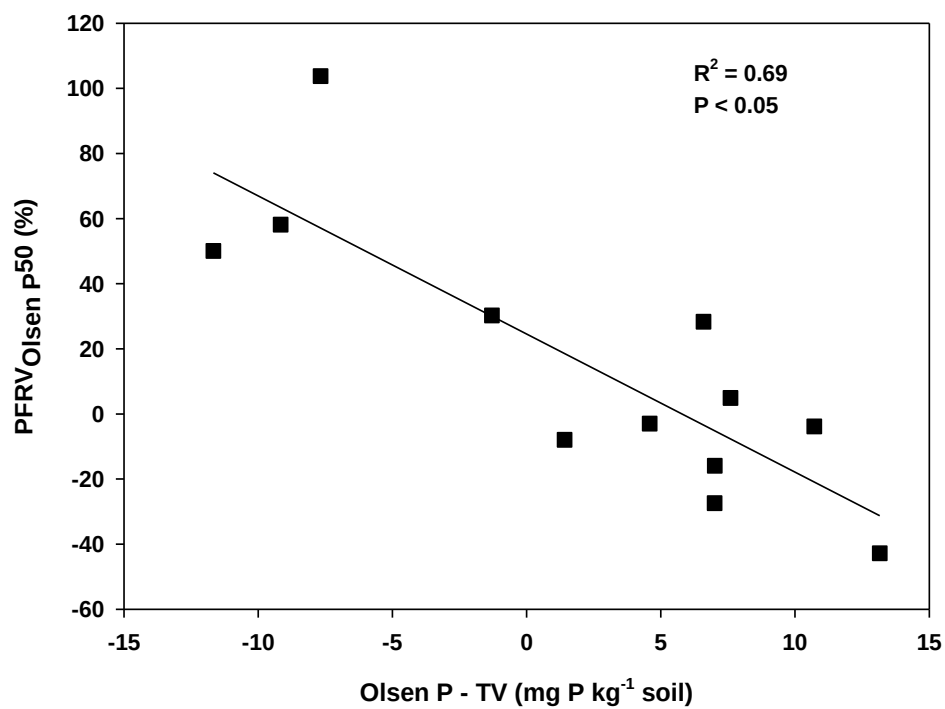
3.6. Increment in DTPA Extractable Fe

The effect of soil on the increment in DTPA extractable Fe with vivianite application relative to the control without fertilizer
application was very significant (Table S2). While the increase was negligible in calcareous soils or in soil with $pH > 7.86$, this
increase was significant in non-calcareous or in soils with $pH < 6.6$ (Table 4). The increase in DTPA extractable Fe was
270 negatively correlated with pH, clay, and Olsen P – TV. At the lowest P rate, the correlation coefficients were –0.58 ($P < 0.05$)
for clay, –0.76 ($P < 0.01$) for pH, and –0.81 ($P < 0.01$) for Olsen P – TV. At the highest rate, correlation coefficients were –
0.84 for pH and –0.9 for Olsen P – TV ($P < 0.001$ in both cases). At both vivianite rates, DTPA extractable Fe was significantly
increased at Olsen P – TV less than 0 (Figure 4).

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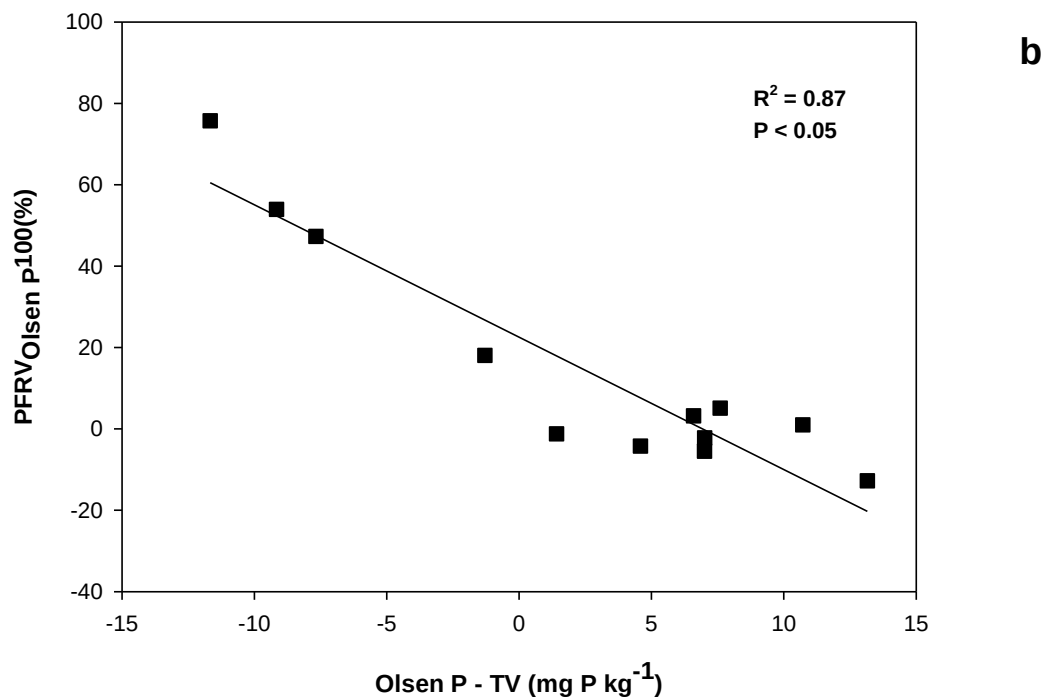
280

285



a

$$PFRV_{Olsen P} 50 = 24.5 - 4.2 X$$



295

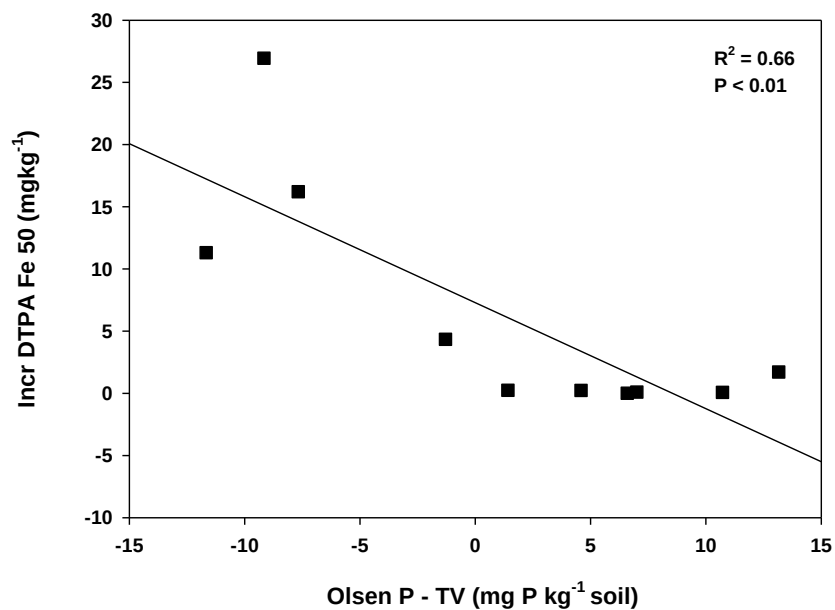
$$\text{PFRV}_{\text{Olsen P } 100} = 22.5 - 3.2 X$$

300

Figure 3. Relationship between the P fertilizer replacement value on an Olsen P basis at 50 (PFRV_{Olsen P} 50) (a) and 100 mg P kg⁻¹ (PFRV_{Olsen P} 100) (b) and the difference between initial Olsen P in soil and the estimated threshold value (Olsen P – TV).

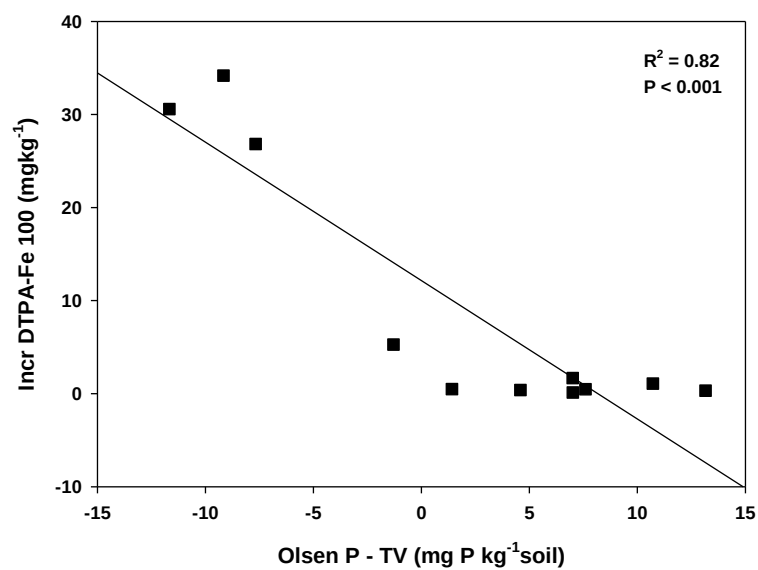
305

310



a

$$\text{Incr DTPA Fe 50} = 7.1 - 0.87 X$$



b

$$\text{Incr DTPA Fe 100} = 11.9 - 1.5 X$$

Figure 4. Relationship between the increase of DTPA extractable Fe at 50 (PFRV_{DM50}) (a) and 100 mg P kg⁻¹ (PFRV_{DM100}) (b) and the difference between the initial Olsen P in soil and the estimated threshold value (Olsen P – TV)

4. Discussion

Soil properties determine the reactions of applied fertilizers depending on their chemical form and, consequently, the response of crops to their application (Bindraban et al., 2015). Hence, crops grown on different soils respond differently to fertilizer application (Olaniyan et al., 2011). With respect to P fertilizer application, the definition of threshold values for soil P test, such as Olsen P, is necessary to predict the crop response in yield to the application of P fertilizers (Recena et al., 2016; 2022). The threshold value is the limit of the soil P test above which soils are not responsive to P fertilizer application (Syers et al., 2008). This is sometimes referred to as P-critical value. An efficient use of P from an agronomic and environmental standpoint can be achieved if the P threshold value is taken into account in P fertilizer strategies and management (Syers et al., 2008).

Overall, the effect of the mineral soluble fertilizer on DM yield, P uptake, and Olsen P outperformed that of vivianite, which did not always provide increased values relative to non-fertilized control (Table 3). However, this effect was dependent on the soil, and the four soils with acidic pH (< 6.6) and two calcareous soils (Soil 3 and 4) provided better results than the non-fertilized control (Table S2). The highest increase of DTPA Fe with vivianite relative to control and mineral soluble fertilizer was observed in three acidic soils. This reveals that conditions prone to vivianite dissolution, i.e., acidic pH in soils, determine its efficiency as a P and Fe fertilizer.

Since soil properties affect the fate of both soluble mineral P fertilizer and vivianite, a more accurate assessment of the efficiency of vivianite relative to mineral fertilizer can be done based on the P fertilizer replacement value (PFRV). The PFRV estimated with the three approaches (DM, P uptake, and Olsen P) ranged widely between soils. When the P fertilizer replacement value was estimated on a DM basis, values around 50 % were feasible in some soils. This means that in some soils, a relatively acceptable result can be achieved in terms of replacing at least part of the soluble mineral P fertilizer. Overall, results were lower when the PFRV was estimated on a P uptake basis, and only values above 20 % were found in two soils at the lowest P fertilizer rate (Figure 2). Lower PFRV values on a P uptake basis can be expected since, with the P rates applied, particularly the highest P rate, a luxury consumption can be promoted, i.e., P accumulation in plants exceeding the minimal for maximum DM yield (Penn et al., 2023). On the other hand, negative values are expected when the P supply capacity of soils is high enough to cover crop needs, and this explains that frequently, PFRV values were negative when Olsen P – TV was higher than 0, that is, when soil P is expected to cover crop needs. According to Johnston (2001), an increase in Olsen P above the P threshold value did not result in a further increase in crop yield. Hence, maintaining soils well above the P threshold value is not economical for farmers and often leads to an increased loss of P from soils, resulting in environmental problems such as eutrophication (Johnston, 2005; Tandy et al., 2021). This could partly explain why soils with an already high P status in the current study did not lead to an increased PFRV.

An analysis of the PFRV on an Olsen P basis allows one to think that results could even be more positive with the application of vivianite as P fertilizer since average values were 49 and 61 % at the highest and lowest P rate, respectively, when the soil Olsen P was below the threshold value which corresponded with soils with pH lower than 6.6 (Table 4). This is much higher than PFRV on a DM or P uptake basis and reveals that the long-term effect of vivianite, beyond the studied crop cycle, could be very interesting in acidic soils with P levels below the threshold value. Thus, one short-term growing cycle probably does

not reflect the full potential of vivianite as a P fertilizer, which can have a relevant residual effect according to the effect on the soil P test in soils with low P status.

It can be supposed that PFRV was determined by the solubility of the fertilizer product, with a crop response above the threshold values not being expected. However, the values of the PFRV on an Olsen P basis reveal that there is limited solubilization when the soil Olsen P value is above the threshold value (PFRV_{Olsen P} around 0). Theoretically, for soluble fertilizers such as superphosphate, solubilization is not necessarily limited in soils with Olsen P above the threshold value. These results with Olsen P after harvesting agree with the observed increase in DTPA extractable Fe. This increased DTPA extractable Fe comes from the dissolution of vivianite (de Santiago & Delgado, 2010). This increase was negligible when the soil Olsen P was above the threshold value. Thus, it seems that fertilizer dissolution determined the response of crops to applied vivianite, and this dissolution was expected to be increased at acidic pH (pH < 6.6), which corresponded to soils with Olsen P values below the threshold value for fertilizer response. In fact, the highest PFRV on Olsen P basis (around 100 %) was found in the more acidic soil. Metz et al. (2023) found that the dissolution rate of vivianite under anoxic conditions increased strongly with a decreasing pH, and at pH 5, all solid materials of vivianite were found to have completely dissolved. This observation was similar when a vivianite dissolution experiment was conducted under oxic conditions (personal communication with Rouven Metz). This could invariably mean that an acidic pH favours the dissolution of vivianite, leading to the release of P from vivianite, thereby making P available in the soil solution where plants can take up P. This situation seems to be different in alkaline calcareous soils (the other eight soils with pH > 7.86) because of a lower rate of dissolution (Metz et al., 2023). However, pH should not be the only factor affecting P recovery from vivianite. In fact, soil 4 was calcareous and showed a PFRVDM of 34 % at the lowest fertilizer rate. This was also the only calcareous soil in which vivianite at both rates increased DM yield relative to control (Table S1). In addition, PFRV on a DM and P uptake basis was related to Olsen P – TV but not to pH. However, pH was negatively correlated with PFRV on an Olsen P basis. Thus, it seems that soil pH may have a crucial role in the dissolution of vivianite, as mentioned above, but there are other factors contributing to its use as fertilizer by crops, in particular the available P status of soil (reflected in the Olsen P – TV values). This difference between Olsen P and threshold value explained more variance in the PFRV on DM and P uptake basis than pH. In any case, it is not easy to separate the effect of soil pH from that of low P availability since pH and Olsen P – TV were positively correlated.

According to Schütze et al. (2020), organic ligands released by roots, such as citrate, enhance the dissolution of vivianite. The exudation of organic ligands is a mechanism for mobilizing poorly soluble P from soil (Kpombrekou-A & Tabatabai, 2003; Johnson & Loeppert, 2006). In P-limiting soils, mechanisms to obtain adequate P for growth are triggered (Raghothama & Karthikeyan, 2005; Balemi & Negisho, 2012). This involves the modification of the plant root system (Lynch, 2011; López-Arredondo et al., 2014) and the increased exudation of organic acids (Neumann & Römheld, 1999; Dechassa & Schenk, 2004). These mechanisms contribute to mobilizing and solubilizing P from soils, eventually leading to increased P use efficiency. Talboys et al. (2016) observed an increased organic acid concentration in the rhizosphere when struvite, a poorly soluble P compound, was supplied as a P fertilizer instead of soluble fertilizers. Thus, when a poorly soluble fertilizer is applied, an

increased expression of P mobilizing mechanisms in P-poor soils can be expected. This contributes to explaining the decrease in PFRV with increased Olsen P – TV values.

The role of soil microorganisms in the rhizosphere cannot be discarded (Richardson, 2007). They play an important role in the solubilization and mobilization of P (García-López et al., 2018; 2021), thus increasing the bioavailability of P (Deubel & Merbach, 2005), especially in P-poor soils. In P-deficient soils, microbial communities are often dominated by phosphate-solubilizing bacteria and fungi, capable of producing organic acids and enzymes that solubilize P, thus making it available for plant uptake (Weigh et al., 2023). This is not always the case under P-abundant conditions (R. Sun et al., 2022; Yadav & Yadav, 2024).

The negative correlation observed between replacement values and clay content in some cases can be determined by the correlation between this soil property and the Olsen P – TV values. In addition, the soils with pH above neutrality had the highest clay content. Furthermore, clay is a soil property usually positively correlated with P buffer capacity and P adsorption, thus affecting P dynamics and availability to plants (Recena et al., 2015; 2016).

In the current study, the DTPA extractable Fe supports the increased dissolution of vivianite under acidic conditions, which were also the soils with the lowest P availability to plants. Vivianite has a considerable content of Fe (Eynard et al., 1992), and the release of Fe is expected following its dissolution. A study conducted by Thinnappan et al. (2008) revealed that there was a preferential release of P over Fe at alkaline pH, leading to the structural oxidation of Fe and the subsequent formation of a Fe(III)-bearing phosphate phase. In fact, the efficiency of synthetic vivianite as a source of Fe for plant nutrition, especially in calcareous soils (Rombolà et al., 2003; Díaz et al., 2009), has been ascribed to the formation of poorly crystalline hydroxide phases such as ferrihydrite and lepidocrocite (Eynard et al., 1992; Roldán et al., 2002). These oxides have a high specific surface and high P adsorption capacity. Thus, reaction products of vivianite dissolution in alkaline soils can contribute to a decreased PFRV in these soils.

5. Conclusions

Overall, vivianite was not as efficient as P fertilizer as a soluble mineral fertilizer. The application of vivianite as a P fertilizer was more effective in acidic soils with soil P tests below the threshold value for fertilizer response. The effect of vivianite on dry matter yield could be equivalent, on average, to 40 % of the same amount applied as mineral soluble fertilizer in these soils (P fertilizer replacement value). The effect on Olsen P in soil could be equivalent, on average, to 61 % of the same amount applied as soluble mineral fertilizer. This is explained not only by the increased solubility of this fertilizer under acidic conditions but also by a low P availability to plants, which can trigger plant and microbial mobilization mechanisms, leading to increased efficiency of this product as a P fertilizer. Further studies are required to assess its residual P fertilizer effect and its effectiveness under field conditions in soils with low P status and acidic pH.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author Contributions

Conceptualization, T.A., R.R. and A.D.; data curation, T.A.; formal analysis, T.A, J.M.Q. and A.D; investigation, T.A., R.R.,
425 J.M.Q., A.M.G.-L. and A.D.; methodology, T.A., R.R. and A.M.G.-L.; supervision, A.D. and M.C.d.C.; writing—original
draft, T.A., M.C.d.C. and A.D.; writing—review and editing, T.A., M.C.d.C. and A.D. All authors have read and agreed to the
published version of the manuscript.

Conflicts of Interest

430 The authors declare no conflicts of interest.

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Figure captions

Figure 1. Relationship between the P fertilizer replacement value on a dry matter basis at 50 ($\text{PFRV}_{\text{DM50}}$) (a) and 100 mg P kg^{-1} ($\text{PFRV}_{\text{DM100}}$) (b) and the difference between the initial Olsen P in soil and the estimated threshold value ($\text{Olsen P} - \text{TV}$).

675 Figure 2. Relationship between the P fertilizer replacement value on a P uptake basis at 50 mg P kg^{-1} ($\text{PFRV}_{\text{P Uptake50}}$) and the difference between the initial Olsen P in soil and the estimated threshold value ($\text{Olsen P} - \text{TV}$).

Figure 3. Relationship between the P fertilizer replacement value on an Olsen P basis at 50 ($\text{PFRV}_{\text{Olsen P 50}}$) (a) and 100 mg P kg^{-1} ($\text{PFRV}_{\text{Olsen P 100}}$) (b) and the difference between initial Olsen P in soil and the estimated threshold value ($\text{Olsen P} - \text{TV}$).

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Figure 4. Relationship between the increase of DTPA extractable Fe at 50 ($\text{PFRV}_{\text{DM50}}$) (a) and 100 mg P kg^{-1} ($\text{PFRV}_{\text{DM100}}$) (b) and the difference between the initial Olsen P in soil and the estimated threshold value ($\text{Olsen P} - \text{TV}$).