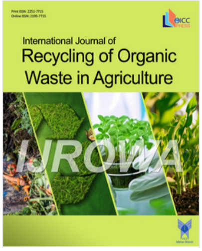

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Soil phosphorus mobilization as affected by long-term organic fertilization in a tropical Regosol

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Original Research

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Abstract:

Purpose: Phosphorus mobilization (PM) in tropical Regosols may be harmful to the environment and water quality. It is expected that high contents of soluble phosphorus in sandy soils may promote the *P* leaching through the transport of the available phosphorus from the soil surface to deeper layers. This study aimed to evaluate the PM in a tropical Regosol by using soil columns (10 cm depth) during steady saturated water flow and PM was correlated with Fe and Al oxides.
Method: Soil samples were collected in four sites characterized as smallholder farming systems that shared the same land uses and soil type with each other. *P* content was estimated by using water, Melich-1, and resin extraction protocols. We estimated the contents of Fe and Al oxides with high and low crystallinity. The miscible displacement technique was used to simulate *P* leaching in soil columns, and the leached *P* was quantified by colorimetry.
Results: Soil *P* loss showed a significant coefficient of determination ($r^2 > 0.80$) with *P* content. We found the highest values of Fe oxalate (0.30 mg/g), and Al oxalate (0.53 mg/g) in the long-term organic fertilization, while the highest values of Fe dithionite and Al dithionite were found with the non-fertilization system.
Conclusion: The highest soil pH (8.01), soil *P* content by different extractors (*P* mehlich-1, *P* water, and *P* resin were 54.45, 14.36, and, 38.70 mg/kg, respectively), and soil *P* loss (128.83 mg/kg) were observed with the long-term non-fertilization system.

Keywords: Farmyard manure; Phosphorus leaching; Organic fertilization; Smallholder farming system; Tropical Regosol

1. Introduction

Phosphorus (*P*) loss by leaching from sandy soils during the rainy season has been considered a major environmental concern for semiarid regions in Brazil (Azevedo et al., 2018). Rainfall varies greatly throughout the year in the Brazilian semiarid. It has a significant influence on annual crop yield, soil *P* leaching, groundwater quality, and water eutrophication (Fischer et al., 2018). Tropical Regosol is commonly used in the bean–maize–fennel rotation system from the Brazilian semiarid (Song and Burgin, 2017). However, the interaction between this rotation system, the continuous use of farmyards, and their associated natural environment remains unclear. In particular, organic fertilization influences soil *P* mobilization with a direct impact on ecoregional agriculture (Galvão and Salcedo, 2009).
In this context, *P* leaching to groundwater is likely to take place in sandy soils, but such a problem has not been conveniently studied in smallholder farming systems from tropical soils in northeastern Brazil. Continuous use of farmyard manure at high rates (i.e., up to 20 T/ha) may exceed the removal of *P* by crops leading to a gradual build-up of *P*

in sandy soils. Soil *P* losses are expected due to the low adsorption capacity of these (Silva and Menezes, 2007). Some studies have shown that organic fertilization using farmyard manure, under high rainfall may increase the rate of *P* loss and decrease the *P* adsorption capacity of the soil (Nziguheba et al., 2016; Spain et al., 2018).
Soil chemical and physical properties of Regosols play an important role in soil *P* leaching. Azevedo et al. (2018) have shown that the *P* flow in macropores depends on such soil properties. The higher the aluminium oxide, clay, and very fine sand contents, the lower the *P* leaching, which is often better correlated with water-soluble content in sandy soils. Several studies have pointed out the importance of assessing *P* leaching in sandy soil from semiarid ecoregions (Tarkalson and Leytem, 2009; Ojekami et al., 2011; Kang et al., 2011; Hariharan et al., 2013).
Sandy soils from semiarid ecoregions have been considered subject to *P* loss by erosion (Galvão and Salcedo, 2009), overland flow (Toor and Sims, 2015), and subsurface flow. The *P* loss to the soil subsurface is reported to mainly occur in sandy soils with low organic matter content (Galvão and Salcedo, 2009), and the continuous use of organic fertilizers under such conditions may increase *P* loss (Oliveira et al., 2011). Agricultural soils with low contents of aluminium and iron oxides and low contents of fine sand and very fine sand are positively correlated with high *P* loss (Sims et al., 1988).
The present study was carried out on soil cores to answer the following question: Does the continuous use of farmyard manure promote *P* leaching in sandy soils? Based on the results from Azevedo et al. (2018), we expected to find high *P* leaching in sites with long-term use of farmyard manure. We also hypothesize that the *P* leaching in the fertilized sites is positively correlated with the soil *P* content according to results observed by Galvão and Salcedo (2009). To accomplish with, we performed both, field sampling in four sites to characterize the soil's chemical and physical properties, and a bioassay with repacked soil columns. The aim was to understand *P* mobilization in sandy soils with low organic matter content and high farmyard manure inputs.

2. Material and methods

Site description and sampling

The soil sampling was performed in four sites with similar smallholder farming systems, soil types, and climatic traits in Esperança, Paraiba, Brazil (Site 1: 06°59′08.6″ S, 35°52′36.2″ W; Site 2: 06°58′03.7″ S; 35°51′31.8″ W; Site 3: 06°59′09.8″ S; 35°52′35.6″ W; and Site 4: 06°58′07.9″ S; 35°51′30.3″ W). Into these sites, the maize (*Zea mays* L.) - common bean (*Phaseolus vulgaris* L.) – and fennel (*Foeniculum vulgare* Mill.) following rotation was selected as our model agricultural system. The climate is classified as "As" type according to the Köppen-Geiger classification, i.e., tropical wet and dry climate with pronounced dry season. The historical mean of annual precipitation and average air temperature are 941 mm and +25° C, respectively. Data on the climate of this area were also obtained from January to April 2016 at the website: http://www.inmet.gov.br. Monthly rainfall and mean temperatures were considered and reported for downtown Esperança, Paraiba, Brazil (Fig. 1). The soil at the experimental sites was classified as Regosol. Soil samples were collected at the beginning of January 2016, during the dry season in each studied site. The soil was prepared for maize–common bean–fennel–fallow rotation through animal traction. No liming was used in the studied sites. Despite the characterization of each studied site, we can describe each one as follows:
Sites with long-term fertilization using organic residues:
Site 1: It receives long-term fertilization with 12 T/ha/year of farmyard manure consecutively during the 5 years until the beginning of the experiment. During the field experiment, the amount of farmyard manure of reduced by 50% (6 T/ha).
Site 2: It receives long-term fertilization with 12 T/ha/year of farmyard manure consecutively during the 5 years until the beginning of the experiment. During the field experiment, this site did not receive any amount of farmyard manure. Thus, it was unfertilized during the field experiment.
Site with short-term fertilization using organic residues:
Site 3: It did not receive any organic fertilization during the 5 years until the beginning of the experiment. However, during the field experiment, it received 12 T/ha of farmyard manure to assess the short-term influence of organic fertilization.
Control treatment:
Site 4: It did not receive any amount of farmyard as organic residue. Thus, by considering the long- and short-term fertilization, it was unfertilized for both conditions.
The farmyard manure was incorporated into the soil profile 2 months before planting. To access more details about the harvest yield of fennel, common bean, and maize during the past 5 years see the electronic supplementary material (Fig. 2). In each site, four blocks were delimited following a randomized block design. We tested two treatments (organic fertilization vs. control–non-fertilization). Ten plots of 10 m^2 were considered in each block (5 fertilized

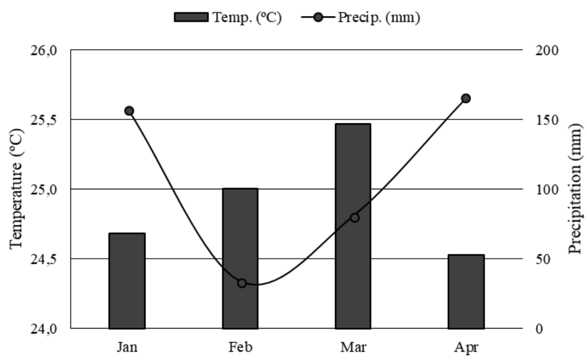

Figure 1. Mean temperature (° C, Black bars) and accumulated precipitation (mm, black line) in the studied site near to downtown Esperança, Paraiba, Brazil from January to April 2016; data were obtained from the website: http://www.inmet.gov.br.

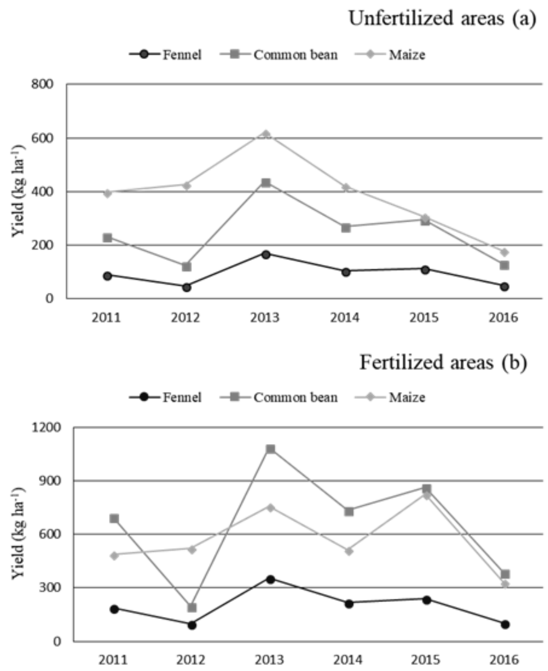

Figure 2. Harvest yield of fennel, common bean and maize during the past 5 years (2011 – 2015) and the studied year (2016) of the experiment in the unfertilized (a) and fertilized areas (b). Values are given as mean.

plots and 5 unfertilized plots), according to Fortin and Dale (2005). We collected in each plot 10 samples at the soil surface (0 to 10 cm deep). After homogenization, aliquots of each sample were prepared for analysis and submitted to a steady saturated water flow bioassay in soil columns.

Chemical analyses of the soil samples included pH, available phosphorus (Mehlich-1, resin, and water), and exchangeable Al, ($N = 400$ per site). Soil pH was determined in a 1:2.5 soil: distilled water suspension (Black, 1965). Soil phosphorus was determined by colorimetry of the phospho-molibidic complex at 882 nm wavelength after extraction by (i) Mehlich-1 method M-1 (0.05 mol/L HCl + 0.025 mol/L H_2SO_4) (P_{ext}) (Galvão and Salcedo, 2009); (ii) deionized water (P_W) (Damon et al., 2014); and (iii) ion exchange resin (P_{resin}) (Murphy and Riley, 1962) protocols. The 1 mol/L potassium chloride solution was used to extract the exchangeable Al^{3+} (Page et al., 1982), which was determined by titration with 1 mol/L NaOH. Poorly crystalline Fe and Al (Fe_{ox} and Al_{ox}) were extracted with ammonium oxalate (Jackson et al., 1986), while the total amounts of Fe (hydr)oxides were extracted by dithionite-citrate-bicarbonate (Fe_{di} and Al_{di}) according to Mehra and Jackson (1960).

We also collected undisturbed soil samples using volumetric rings with 100 cm^3 to physically characterize the soil from each studied site. We analyzed bulk density, and soil texture (sand, clay, and silt contents). Soil bulk density was calculated by the ratio between the soil dry weight and the cylinder volume. Soil texture was determined by a particle size analysis of the dispersed soil (Galvão and Salcedo, 2009). The clay was flocculated by adding NaCl solution as a chemical dispersing agent, the sand was quantified by sieving, and the silt by the difference between the other estimated particles (Black, 1965).

Two months before sowing, 20 T/ha of farmyard manure (Table 1) was applied on the soil surface and later incorporated in the 0 – 20 cm soil layer. To better simulate the smallholder farming system commonly used in Esperança, Paraiba, Brazil, no dolomitic limestone was added to the plots. The N, P, and K contents were measured by H_2O_2 and H_2SO_4 digestion. The carbon content in the farmyard manure was determined by the rapid dichromate oxidation method following the protocol described by Black (1965).

Bioassay with re-packed soil columns

Rigid polyvinyl chloride columns (10 cm long and 2.56 cm internal diameter) with 2 mm (diameter) outlet ports were used to evaluate the *P* leaching. Rubber stoppers were used to keep the outlets firmly closed. The columns were filled with soil cores, which were prepared for carefully packing the soil samples into the columns. An average of 82 g of sieved soil (2 mm) per column was packed into the columns, yielding a soil bulk density (dry weight) of 1.60 g cm^{-3}. A small plug of nylon was attached to the bottom of the column to prevent soil leakage. The soil cores were kept at 25° C throughout all experiments. 0.001 M Calcium chloride and 0.001 M potassium chloride solutions were pumped into the columns at a flow rate of 2.9 cm^3 mm^{-1} in the center of the soil surface. The soil cores were brought to 100% of the moisture-holding capacity during 24 h with saline solutions, which were slowly percolated during the next day at 42.98 cm/h. Effluents of the columns were collected from the beginning of drainage and the *P* concentration of the leachates was deter-mined according to Murphy and Riley (1962).

Statistical analyses

The Shapiro-Wilk test and linear equations were applied to test the normality of the data distribution and to evaluate the relationships between the soil *P* losses and *P* content by different extractors, respectively. One-way ANOVA was used to evaluate the influence of the continuous use of high rates of farmyard manure on *P* leaching, and soil chemical properties. Data sets were transformed, but the results are presented in their original scale for measurement (means with standard deviation). When

Table 1. Chemical composition of the farmyard manure used in the experiment. Values are given as mean.

Moisture (%)	N (g/kg)	K (g/kg)	C (g/kg)	P (g/kg)	C/P (g/kg)
20.53	4.78	48.03	67.39	1.04	65.11

Table 2. Linear equations of different *P* extractors used to obtain soil *P* loss ($N = 1600$).

Model	F value	*P* value	Adj-R-Squared
$P_{loss} = 2.1877P_{ext} - 5.9632$	$F_{1,38} = 234.5$	$P < 0.001$	0.86
$P_{loss} = 10.6423P_{w} - 31.7812$	$F_{1,38} = 626.2$	$P < 0.001$	0.94
$P_{loss} = 2.9359P_{res} + 11.3653$	$F_{1,38} = 210.1$	$P < 0.001$	0.84

necessary, Bonferroni's test was conducted to assess the differences among the studied treatments. To evaluate the relationships between soil properties and *P* leaching a principal component analysis (PCA) was performed. All statistical analyses were conducted using *R*.

3. Results and discussion

Estimating soil P loss through linear regression as a function of soil P contents obtained by different P extractors

Soil *P* loss showed a significant correlation with the soil *P* content obtained by different extractors in a Regosol from a semiarid region in Brazil. The coefficient of determination was higher for soluble soil *P* content, extracted by deionized water *l* ($r^2 = 0.94$) than for *P* extracted by Mehlich-1 ($r^2 = 0.86$) or resin protocols ($r^2 = 0.84$). Overall, *P* loss presented a linear increment due to the increase in soil *P* content. It is worthy of note that the range of concentrations covered in this research (from 6.5 to 14.4 mg/kg of soluble *P*) (Table 2) represents very rich *P* soils. Such *P* contents in soils can be also considered a high risk for surface water eutrophication (Chen et al., 2022). Some studies have reported that Regosols with significative content of sandy and low clay content have a high potential for *P* loss through run-off and soil *P* leaching (Neto et al., 2023). On one hand, we did not analyze soil *P* loss by run-off, but on the other hand, the soil *P* loss by leaching was intensively analyzed under the hypothesis that the continuous use of farmyard manure can promote *P* leaching in sandy soils (Simansky et al., 2022) by using a bioassay with re-packed soil columns. Our findings supported this hypothesis, and other studies have reported soil *P* loss in sandy soils with the continuous input of organic residues ranging from 24 to 56% (Raguet et al., 2023; Sarti et al., 2022).

Our results emphasize the influence of the continuous use of higher rates of farmyard manure on soil *P* loss considering different *P* extractors. We have confirmed a positive correlation between soil *P* content (estimated by Melich-1, water, and resin extractors) and soil *P* loss in sandy soils with continuous input of farmyard manure. Other studies have reported the same findings regarding the correlation between soil *P* content and *P* loss in sandy soils (Saentho et al., 2022; Chardon et al., 2022). Essentially, we aimed to understand how the continuous use of farmyard manure (more than 5 years) changes the soil *P* content, soil chemical properties, and soil *P* loss. The vertical *P* mobilization (soil *P* leaching) generally was higher in the following soil conditions: i) areas with long-term use of an average rate of farmyard manure (Rinasoa et al., 2023); and ii) areas with the addition of high rates of farmyard manure in short-term (Selmy et al., 2022). These results support the hypothesis that continuous use of high rates of farmyard manure may promote *P* loss in sandy soils. Accordingly, to the study done by Chen et al. (2022), the two main factors associated with *P* loss in tropical soils are (i) the low content of soil particles with high adsorption rate of *P* (e.g., clay, organic matter in high levels of decomposition, and organic acids released by root systems); and (ii) the critic *P* content in the soil system that defines the rate of adsorption, sorption, uptake, release on soil solution, and loss.

Effects of long-term farmyard manure utilization on soil acidity, *P* content, iron, and aluminium oxide-hydroxides

The long-term effects of farmyard manure on Regosol

Table 3. Soil chemical properties for each studied site. Values are given as mean ± SE ($N = 1600$).

Properties	Site 1 -Fertilized	Site 2 – Unfertilized	Site3 - Fertilized	Site 4 -Unfertilized
Soil pH (1:2.5)	8.01 ± 0.11 a	8.02 ± 0.01 a	7.91 ± 0.01 b	7.78 ± 0.03 c
P mehlich-1 (mg/kg)	49.58 ± 0.65 b	54.45 ± 0.61 a	45.32 ± 0.54 c	19.95 ± 0.19 d
P water (mg/kg)	12.00 ± 0.02 b	14.36 ± 0.23 a	11.58 ± 0.71 b	6.55 ± 0.02 c
P resin (mg/kg)	30.19 ± 0.51 b	38.70 ± 0.33 a	21.8 ± 0.93 c	12.35 ± 0.12 d
Al^{+3} ($cmol_c$/kg)	0.08 ± 0.01 c	0.10 ± 0.01 c	1.05 ± 0.06 b	1.45 ± 0.01 a
Fe oxalate (mg/g)	0.30 ± 0.01 a	0.17 ± 0.01 c	0.26 ± 0.04 b	0.27 ± 0.01 b
Al oxalate (mg/g)	0.53 ± 0.01 a	0.32 ± 0.01 b	0.32 ± 0.01 b	0.06 ± 0.01 c
Fe dithionite (mg/g)	0.51 ± 0.01 c	0.49 ± 0.02 c	0.78 ± 0.03 b	1.34 ± 0.04 a
Al dithionite (mg/g)	0.31 ± 0.04 c	0.31 ± 0.01 c	0.49 ± 0.04 b	0.74 ± 0.01 a
P loss (mg/kg)	85.71 ± 0.51 c	128.83 ± 0.64 a	91.69 ± 1.73 b	40.38 ± 0.58 d

Different letters represent statistically significant differences ($P < 0.05$) among studied sites, after one-way ANOVA and Bonferroni's test for overall comparisons.

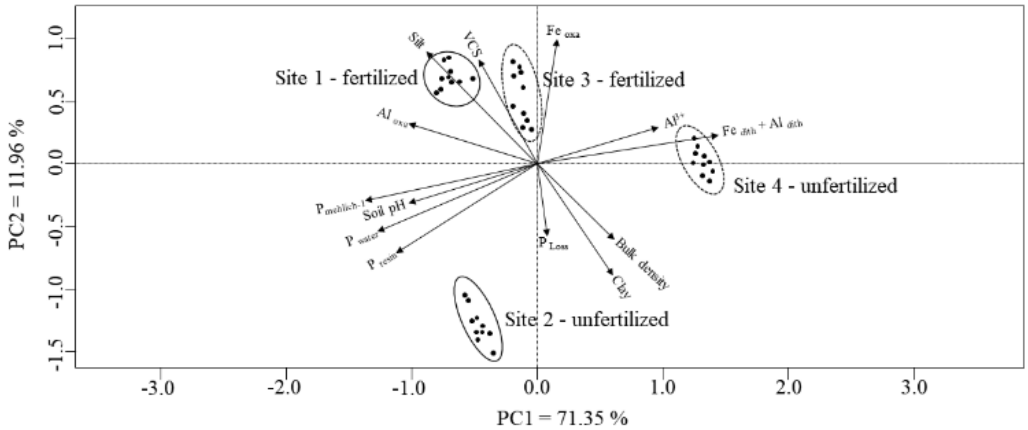

Figure 3. PCA score plot of soil physical and chemical properties for the four studied sites.
Site 1 - fertilized; Site 2 - unfertilized; Site 3 – fertilized; and Site 4 - unfertilized. Points represent samples from each plot by studied sites.

chemical properties were significant ($P < 0.01$). The one-way ANOVA showed a significant effect of the treatments on soil pH ($F_{1,38} = 31.35$, $P < 0.001$), soil P content extracted by Mehlich-1 ($F_{1,38} = 24.01$, $P < 0.001$), water ($F_{1,38} = 32.96$, $P < 0.001$) and resin ($F_{1,38} = 23.73$, $P < 0.001$), soil exchangeable aluminium ($F_{1,38} = 31.35$, $P < 0.001$), oxalate extractable Fe ($F_{1,38} = 39.71$, $P < 0.001$) and Al ($F_{1,38} = 24.10$, $P < 0.001$), dithionite extractable Fe ($F_{1,38} = 23.12$, $P < 0.001$) and Al ($F_{1,38} = 12.16$, $P < 0.001$), and soil P loss ($F_{1,38} = 28.85$, $P < 0.001$). The highest soil pH, soil P contents (by mehlich-1, water, and resin), and soil P loss were observed in the long-term non-fertilization treatment in Site 2, whereas the lowest values for these variables were found in the pristine area (Site 4). For exchangeable Al, Fe dithionite, and Al dithionite, the pristine area presented the highest values (Table 3).

The results of this study revealed significant effects of short- and long-term farmyard manure use on soil pH, soil P content, soil P loss, exchangeable Al, and oxalate and dithionite extractable Fe and Al. Both short- and long-term use of farmyard manure increased the soil P content and decreased exchangeable Al. Our results suggest that organic fertilization improves soil P content but decreases the soil pH. It was reported that the soil organic matter decomposition reduces the soil pH (e.g., increases soil acidity) through the H^+ release during the decomposition process (Li et al., 2022). The positive effects of farmyard manure use suggest that the accumulation of organic matter, favoured an increase in available P (e.g., $H_2PO_4^-$ and HPO^{-2} by the organic matter decomposition), which led to high vertical P loss (soil P leaching) (Liu et al., 2022). These results agree with the results from Barrow and Debnath (2015), and Barrow (2017) that reported high soil P content and favourable condition for uptake of phosphate by plants in soils with circumneutral values of soil pH. On the other hand, high acidity and low available P are common characteristics of sandy soils from the Brazilian semi-arid. We may expect that P status in sandy Regosol from Brazilian semiarid is modulated by i) soil pH (Rinasoa et al., 2023); ii) long-term use of organic P sources (Selmy et al., 2022); and iii) phosphate sorption status (Chen et al., 2022).

Azevedo et al. (2018), have reported high amounts of readily available P for plants due to the input of farm-yard manure in sandy soils from the Brazilian semi-arid. They also observed an increase in the water-extractable P contents in such soils. Similar results were obtained in the present study. We observed P loss due to leaching or vertical mobilization of P associates to organic colloids and clay (Siebers et al., 2023). P leaching may occur through competition with organic acids for adsorption sites as described by Abdala et al. (2015). These authors highlighted the importance of soil mineralogy, P cycling, and the contents of Fe and Al (hydr)oxides to describe such effects. We found a significant relation between our treatments and Fe and Al (hydr)oxides. In general terms, there was a negative correlation between P loss and amounts of Fe and Al (hydr)oxides. Then, in the current condition, we may expect that the forms of Fe and Al (hydr)oxides act preventing an even larger P loss potential (Abdala et al., 2012). Similar results were found by Kang et al. (2011), who reported high P losses in both inorganic and organic sources under similar conditions of our study.

Principal component analyses

The PCA analyses showed that clay, silt, soil P content (e.g., by mehlich-1, water, and resin), oxalate extractable Fe, dithionite extractable Fe, and Al were the main factors contributing to the variance of the samples. The analysis also showed: (1) a strong negative relationship between Mehlich-1 soil P content and dithionite extractable Fe + Al; and (2) a negative relationship between iron oxalate Fe and soil P loss (Fig. 3).

The positive correlation between P leaching and soil P content in P-rich sandy soils suggests a eutrophication process induced by organic fertilization due to the increase in vertical P mobilization (Peng et al., 2022). Then, the use of farmyard manure by regional smallholder farmers

may contribute to decreasing groundwater quality over time (Moloantoa et al., 2022). Our results also can be related to the study performed by Galvão and Salcedo (2009) which dealt with the long-term *P* dynamics in a tropical flooded ecosystem. These authors found that *P* adsorption by soil was lower under long-term balanced fertilization (farmyard manure + NPK). On the other hand, the desorption potential and *P* availability increased due to fertilization. In semi-arid conditions, this phenomenon could pose a risk to groundwater quality in this region from Paraiba, Brazil which is enclosed in the Mamanguape river basin. It is worthy of note that this is a needy region, where the water is prospected from groundwater sources to supply the Agreste and the Brejo Mesoregions.
Although our experiment was not designed to directly test whether organic fertilization affects annual crop growth through changes in soil *P* availability, the changes in soil pH and soil *P* content that we observed may be related to alterations in soil nutrient resources and physical properties (data not shown) after the continuous use of farmyard manure. Further studies are needed since we do not know of any study reporting the effects of continuous use of organic fertilizers on maximum *P*-adsorption capacity in sandy soils from the Brazilian semi-arid.

4. Conclusion

The short-term use of high rates of farmyard manure increased both soil *P* content and soil *P* loss in a maize-common bean-fennel-follow rotation in a Regosol. The continuous use of farmyard manure enhanced soil pH and the forms of Fe and Al (hydr)oxides, but also it increased soil *P* loss. The results of our study high-light the importance of considering low rates of organic fertilizers in sandy soils on *P* vertical mobilization. Thus, the long-term utilization of high rates of farmyard manure may exploit negative situations jointly with groundwater quality and the eutrophication process.

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Ethical approval
This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval is not applicable.

Author contribution
All the authors have participated sufficiently in the intellectual content, conception and design of this work or the analysis and interpretation of the data (when applicable), as well as the writing of the manuscript.

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Availability of data and materials
Data presented in the manuscript are available via request.

Conflict of interest statement
The authors declare that they have no conflict of interest associated with this study.

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