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Phosphorus Availability and Potential Environmental Risk Assessment in Alkaline Soils

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Abstract: Soil phosphorus (P) is an essential element that is often limiting in ecosystems. Excessive use of P fertilizers has led to P loss from soil and introduction into the environment. However, the behavior and potential risk assessment of P in alkaline soils is not well studied. Therefore, soil sampling was performed in alkaline soils in the northern Nile Delta, Egypt. Three analytical procedures (i.e., Mehlich 3 (P_{M3}), Olsen (P_{Olsen}), and Bray 1 (P_{Bray}) solutions) were used to evaluate P availability and potential environmental risk from P loss. Selected soil properties were determined using standard methods. Mean values of P extracted were in the order $P_{M3} > P_{olsen} > P_{Bray}$, and were significantly correlated with each other. The P_{M3} was the highest in silt clay loam and lowest in sandy and loamy soils. To predict potential P loss from the soils, degree of P saturation (DPS), soil P storage capacity (SPSC), and P stability ratio (P_{sat}) were calculated. Results showed the highest DPS was recorded in sandy textured soils, indicating that they have lower sorption capacity, whereas the SPSC was highest in silt clay textures; hence, it is likely they would act as a P sink. P_{sat} was highest in sandy soils, which indicated a high risk for P leaching. Principal component analysis (PCA) performed on the data identified four principal components that described 83.8% of the variation between P and the studied soil parameters. The results indicated that silt was the critical soil characteristic associated with both P sorption and extractability in different textures of soil. The second component confirmed the positive association between the different soil P extraction methods (P_{M3}, P_{Olsen}, and P_{Bray}).

Keywords: soil phosphorus; alkaline soil; soil texture; potential phosphorus loss; environmental risk assessment; Nile Delta Egypt

1. Introduction

Phosphorus (P) is an essential macronutrient and is commonly limiting to plant growth. Soil available P is primarily supplied by parent material and recycled by organic matter decomposition. It can also be added by fertilization that enriches various forms of P (i.e., available, non-available). If available P is depleted, P replenishment from other sources becomes important. However, continuous long-term applications of P fertilizers and/or other P sources that exceed plant nutrient uptake can result in P accumulation in the soil and release into the environment [1–6], which can create human health concerns through the addition of cadmium to the soil [7]. Indeed, increased application of P fertilizers has led to progressive saturation of P sorption capacity in soil, leading to its

release into surface and/or groundwater through irrigation, drainage, infiltration, and runoff, creating negative impacts on aquatic systems. Excessive P inputs from land to the aquatic system can cause a decline of water quality because P is a main factor in the eutrophication of freshwater and wetlands ecosystems that causes anoxia. Furthermore, P leaching has become a significant limitation to the effective utilization of P fertilizers in agro-ecosystems [3,8–12]. Liu et al. [13] stated that soil can constrain P movement by absorption and fixation; however, the vertical movement of P in soil profiles is evidenced by soil column studies. Furthermore, providing adequate available P to plants can be impaired in alkaline soils through the formation of low-solubility calcium phosphate minerals [14]. Understanding soil P content and how P behaves given different soil properties is essential in the control of non-point pollution [1], but few estimates of soil P storage have been performed to date on alkaline soils.

It has been demonstrated that the hazard of P loss from agricultural soil is strongly linked to P availability [10]. Chemical soil extractions dissolve considered proportions of available soil P; thus, these extractions are often used to predict the potential risk of P loss as a result of their strong correlation with P content in leachate [14]. Phosphorus risk refers to the risk of polluting water bodies if the P levels are excessive and accumulate in the soil [10]. Simplified indicators of the risk of P export from soils have been established for the use of farmers and watershed planners since the 1990s [8]. Of these, the P index (PI) is a commonly used tool for assessing the relative P loss risk from agricultural soils [15]. The degree of P saturation (DPS) has also been proposed as an indicator for assessing the risk of P loss because DPS is often better correlated with P content in surface runoff or subsurface drainage than soil test P (STP) [8]. Crittenden et al. [15] expressed the DPS as a ratio between extractable P (Mehlich 3 (M3)) and extractable (M3) Fe and Al. In addition, they mentioned that inclusion of Fe was proposed in this index for alkaline soils in the eastern United States. In fact, DPS has been widely used in acidic soils (e.g. [16–19]), as well as in alkaline and calcareous soils [15,20–22]. The Olsen extractant was introduced to extract P from neutral, calcareous, and alkaline soils. This extractant decreases Ca in the solution through the precipitation of $CaCO_3$, and thus enhances the dissolution of calcium phosphates. The Olsen extractant also removes dissolved and adsorbed P on $CaCO_3$ and iron oxide surfaces [23]. However, this extractant extracts P only. Allen and Mallarino [24] and Wünscher [25] reported that M3 is used as a standard method for P extraction in many places, and it is considered suitable for a wide range of soils that can be highly variable in their physicochemical properties. Furthermore, M3 is a multi-nutrient extractant determining P, K, Mg, Ca, Na, Zn, Cu, B, Mn, Al, and Fe. Ziadi and Tran [26] also stated that M3 is a universal soil test extractant. The M3 approach to extract P is an acetic acid solution, causing the dissolution of calcium phosphates with the addition of ligand exchange by ammonium fluoride that releases the phosphate by building a new complex with Fe. The element Ca is extracted by ammonium nitrate and nitric acid, whereas Fe is dissolved and complexed by ammonium nitrate and ethylenediaminetetraacetic acid (EDTA), which hereby functions as a chelating agent [25,26]. Hopkins and Ellsworth [14] reported that P availability to plants in alkaline and calcareous soil is impaired because of the formation of poorly soluble calcium phosphate minerals, resulting in a problem in P uptake and plant growth. They emphasized that adding P with ammonium tends to enhance the availability of both, solving the P uptake problem. Ammonium and other acidifying fertilizers can enhance P solubility and uptake by roots. Thus, this is a similar approach to extracting P bound with Ca using M3 in alkaline soils. Kleinman and Sharpley [27] used a variety of soil types, including 25 alkaline soils, to evaluate the use of M3 data in estimating P stability ratio (P_{sat}) in a wide range of soils, spanning the range from acidic to alkaline. They stated that the high correlation between the reference P_{sat} and PM3Ca-1M3 supports the idea that M3 is an appropriate soil test for alkaline soils, in spite of its poorly buffered, acidic nature. Allen and Mallarino [24] stated that research has proven a high correlation between Mehlich-3 extractable P, Al, and Fe ($M3_{sat}$) and ammonium oxalate degree of P saturation (DPSox) in acidic or near neutral soils with a slightly lower but still high correlation in alkaline soils. Jalali and Jalali [22] reported that DPS is commonly obtained using ammonium oxalate extractable P, Fe, and Al. However, they also stated, on the basis of many

other references cited in their study, that DPS has been proposed using other extractants including M1, M3, and P-Olsen. They added that M3 is commonly used for extracting P, Al, Fe, and other elements, and that there is a linear relationship between the PM3 saturation ratio and oxalate P saturation ratio. Additionally, Kleinman and Sharpley [27] indicated that PM3 saturation ratio is often highly correlated to oxalate P saturation ratio in alkaline soils. Thus, PM3 can be used in alkaline soils to assess DPS. Crittenden et al. [15] reported that P stability (P_{sat}) is another indicator and is calculated in the USA using Mehlich 3 (M3) extractable P similar to the P_{sat} approach that originated and is used in the Netherlands on the basis of acid oxalate extractable P. This index indicates the likelihood that P applied to soils will end up entering water bodies. Thus, the high risk of contaminating water with excess soil P has driven research into the effects of soil P sorption on groundwater quality. Consequently, information about available soil P and its relationship with other soil properties is of great interest to enhance the efficiency of P use in agricultural systems [15].

Phosphorus may become unavailable as a result of precipitation and fixation reactions with other cations such as Ca and Mg in alkaline soils or Fe and Al in acidic to neutral soils. As a result, P concentration rarely exceeds 0.1 mg L^{-1} in the soil solution. In the arid and semi-arid Nile Delta, alkaline soils such as Entisols and Vertisols are the most abundant [28,29]. Most of the soils in Egypt are alkaline, with pH values from 7 to 9 [30,31]; thus, they experience deficiencies in phosphorus due to P interactions with Ca and Mg. To cope with this deficiency, P fertilizers (primarily superphosphates and rock phosphate) have been applied for long time in Egypt.

Thus, the study of P extractability and sorption in alkaline soils with different properties is of great importance from agricultural and environmental points of view. Some efforts have been made to improve our understanding of P availability in calcareous [21] and alkaline [32,33] soils. Jalali and Jalali [21] determined the relationship between P content in leachates and soil tests for P and DPS, finding a significant relationship between DPS_{M3} and P in leachate (*r* ranged from 0.50 to 0.55), and also found that 8%–13.7% of their study area was at high risk of P leaching. In a long-term experiment, Pizzeghello et al. [33] determined the distribution of P across various chemical forms in three alkaline soils, as well as the effect of long-term application of mineral and manure fertilizers on P availability and saturation. Among the two soil P tests evaluated, Mehlich 3 P was the best indicator for assessing soil conditions for both agronomic and environmental purposes. On the other hand, Ebeling et al. [32] used three extractant methods to predict crop P needs and P loss risk assessment in alkaline and calcareous soils. Their results indicated that Bray P1 was strongly correlated with Olsen and M3 regardless of carbonate content, where R^2 was 0.83 and 0.98, respectively. However, they did not study the environmental risk assessment of P leaching. Therefore, there is a lack of work using soil samples that includes a range of different textures and calcium carbonate ($CaCO_3$) contents that relate these properties to sorption parameters and potential environmental P loss risk. Thus, this study aimed (1) to assess the availability of P across a range of alkaline soils with contrasting properties using three extractant solutions, and (2) to determine P sorption indices to estimate the potential environmental P loss risk from alkaline soils and its relationship to P availability.

2. Materials and Methods

2.1. Soil Sampling and Analyses

Fifty soil samples were obtained from topsoil horizons (0–20 cm) in the northern Nile Delta of Egypt, and the agricultural history of the region was investigated [34–36] (Figure 1). The goal was to obtain samples that differed in their physio-chemical properties such that they would provide a wide range of textures and P concentrations. The soils were collected from the same area as the studies by [34,35] because long-term inorganic P fertilization with different P inputs has occurred in this area since the 1970s. All sites have a semi-arid climate with annual mean precipitation of approximately 138 mm, mean maximum summer temperatures of about 38.9 °C, and minimum winter temperatures of 11.1 °C [23–25]. Soil pH (1:2 soil/water suspension) was measured by glass electrode [37]. Soil texture

was determined by the hydrometer method [38], and electrical conductivity (EC) was measured in a 1:5 soil/water solution using an EC meter (Jenway, United Kingdom) [39]. The oxidation method was used to determine soil organic matter (SOM), and total organic carbon was calculated on the basis of SOM percentage [40]. The gasometric method was used to measure calcium carbonate equivalent (CCE) where soil samples were treated with 6 M HCl and the change in CO_2 volume was recorded as a CCE indicator [41]. Cation exchange capacity (CEC) was estimated by NH_4OAc pH 7 [42]. Mehlich 3 (M3) extraction was used to extract Fe, Al, Si, and other cations (such as K, Ca, Mg, and Na) [43].
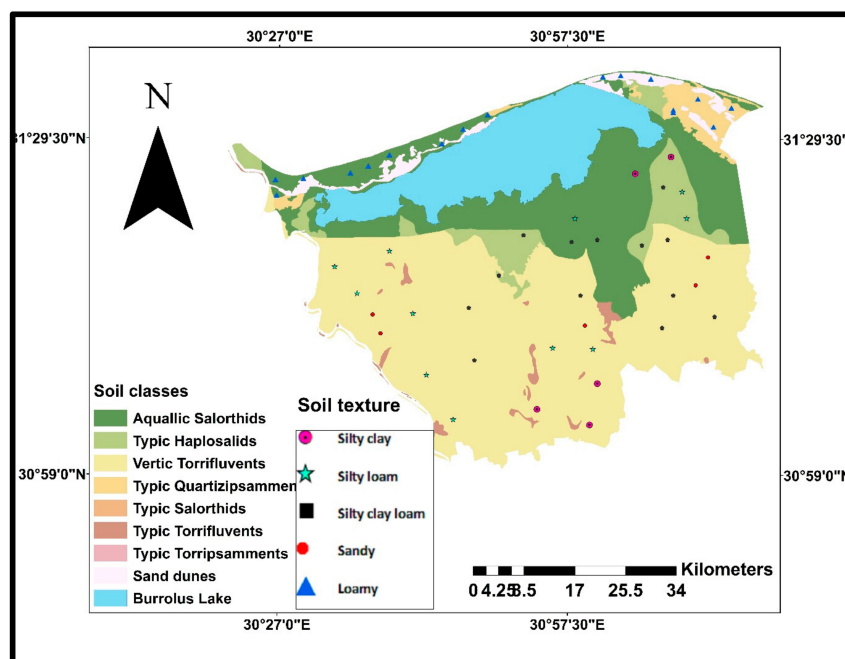

Figure 1. Soil sampling locations in the northern Nile Delta, Egypt, showing the dominant subgroups (U.S. Soil Taxonomy) and the texture of the samples.

2.2. Phosphorus Extraction Methods

The extractability of P from soil samples was examined using three methods—Olsen, Bray 1, and Mehlich 3—because these methods are widely used to determine available P [22,44,45]. Olsen extractable P (P_{Ols}) was performed by shaking soil samples (1.0 g) in 20 mL of 0.5 mol L^{-1} sodium bicarbonate ($NaHCO_3$) solution at 8.5 pH for 10 min, as described in Olsen and Sommers [46]. Bray P (P_{Bray}) was determined using 2 g soil in 50 mL flasks and 20 mL of extraction solution (0.025 M HCl; 0.03 M NH_4F). The samples in the extractant were shaken for 5 min and filtered through Whatman No. 42 filter paper. P concentration was determined by the colorimetric procedure ascorbic acid method [47,48]. Mehlich 3-P (P_{M3}) was determined in a 1:8 soil:solution [49] of Mehlich 3 extracting reagent (0.2 M CH_3COOH + 0.015 MNH_4F + 0.25 M NH_4NO_3 + 0.001 M EDTA + 0.13 M HNO_3) [43]. P in the extract was determined colorimetrically after filtration through Whatman No. 42 filter paper [50]. Al and Fe in the Mehlich 3 solution (Al_{M3} and Fe_{M3}) were estimated using inductively coupled plasma spectrometry (ICP-OES Agilent 5110) [21,51]. Other cations (i.e., Ca, K, Na, Mg) were also extracted by M3 and measured by ICP-OES [52,53]. Each extraction method was performed in duplicate in 50 mL polycarbonate centrifuge tubes. All the extracted samples were centrifuged at 3000 rpm for 10 min before measurement.

2.3. Phosphorus Indices

Degree of P saturation (DPS) is expressed as the ratio of extractable P: P sorption maximum that is obtained using Mehlich 3 extractable P, Fe, and Al [21,54–56]. The Mehlich 3 extractant is widely used

for extracting not only P, but also other elements such as Al and Fe [53]. A linear relationship exists in alkaline soils between the P_{M3} saturation ratio and oxalate P saturation ratio [22,27]. Thus, the DPS, P stability ratio, and SPSC were calculated as follows: (2) [15], (3) [15], (4) [45,57]

$$\mathrm{DPS_{M3}} \% = \frac{P_{M3}}{Al_{M3} + Fe_{M3}} \times 100 \tag{1}$$

where P_{M3}, Al_{M3}, and Fe_{M3} in Equation (1) are in mmol kg^{-1} [22,58].

$$\text{P stability ratio } \% \text{ (based on Al)} = \frac{P_{M3}}{Al_{M3}} \times 100 \tag{2}$$

$$\text{P stability ratio } \% \text{ (based on Ca)} = \frac{P_{M3}}{Ca_{M3}} \times 100 \tag{3}$$

$$\mathrm{SPSC} = (0.1\text{-Soil DSP}_{M3}) \times (Fe_{M3} + Al_{M3}) * 31 \tag{4}$$

2.4. Statistical Analysis

Simple linear correlation analyses among soil properties and the various concentrations of P measured by different extraction solutions were used to investigate their relationships. A simple Duncan test was used for mean comparisons, with $p < 0.05$ assumed to be significantly different. PCA was used to simplify the data and make it easier to identify the factors that explain most of the variance [45]. All statistical analyses were performed using SPSS 18 (IBM Corp, Armonk, NY, USA).

3. Results and Discussion

3.1. Physio-Chemical Properties of Collected Soils

Table 1 shows selected soil physio-chemical properties. On the basis of the USDA soil classification tool (https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/?cid=nrcs142p2_054167), the soil textures were classified into five different classes, including sand ($n = 16$), loam ($n = 5$), silt clay loam ($n = 11$), silt clay ($n = 5$), and silt loam ($n = 13$). The mean sand content ranged from 4.6% to 93.6%, mean silt from 3.6% to 61.1%, and mean clay from 3.5% to 45.8%. The high soil textural variability in the northern Nile Delta is attributed to natural or extrinsic sources [34]. Soil pH ranged from 8.22 to 8.97, and was alkaline with insignificant differences between soil textures. The concentration of the basic cation Na^+ was high. The average SOM content ranged from 0.25% to 1.4%, which is considered a low percentage of SOM [59] and may indicate a deficiency in plant-available nutrients and degraded soil properties [60]. The sand soils had the lowest SOM and mean CCE values, whereas the silt clay and silt clay loams had the highest mean values of SOM and CCE, respectively. The highest CEC content was found in silt clays and silt clay loams, whereas the lowest was in sands. The soil CEC and base saturation reflected the amounts of the exchangeable bases (i.e., Ca, K, Mg, and Na). The CEC values were dependent on clay content, SOM, and pH [34,61,62]. The high variability of CEC was attributed to the variability in soil texture [34,62]. Ca, K, and Mg were also affected by the soil texture, with significantly higher values in silt clay loams and silt clays and the lowest values in sands. The highest Mehlich 3 Na content was observed in sands, whereas insignificant differences were noticed among the other textures. Sands also had the lowest Al and Fe (along with loams), whereas the highest Al and Fe values were recorded in the silt loams and silt clays. Wang et al. [58] stated that soils with higher pH values (their soils had a pH range of 4.2–7.6) would commonly contain greater amounts of extractable Ca and lower amounts of extractable Al and Fe. In this study, there were no differences in pH between the studied textures, but texture controlled soil nutrient contents. This control of texture on soil nutrients agreed with the findings of other studies (e.g., [63–65]).

Table 1. The mean and standard deviation values of selected physiochemical soil properties in the different soil textures investigated.

Soil Parameters	Soil Texture				
	Sand n = 16	Loam n = 5	Silt Clay Loam n = 11	Silt Clay n = 13	Silt Loam N = 5
pH	8.74 [a] ± 0.24	8.61 [a] ± 0.42	8.73 [a] ± 0.45	8.52 [a] ± 0.39	8.97 [a] ± 0.63
EC dS m^{-1}	9.56 [a] ± 3.7	4.0 [b] ± 3.7	2.9 [b] ± 1.8	3.2 [b] ± 1.4	3.8 [b] ± 1.6
SOM %	0.25 [b] ± 0.1	0.95 [a] ± 0.39	1.08 [a] ± 0.39	1.40 [a] ± 0.66	1.20 [a] ± 0.81
Mg mg kg^{-1}	1026 [c] ± 416	2162.1 [b] ± 138.6	3425.5 [a] ± 769.3	3375.3 [a] ± 722.3	2606.3 [b] ± 201.1
K mg kg^{-1}	183.7 [b] ± 97.1	306.6 [b] ± 280.1	745.1 [a] ± 251.4	669.5 [a] ± 236.7	599.1 [a] ± 309.7
Ca mg kg^{-1}	2338.7 [b] ± 1309.8	5951.1 [a] ± 1325	6392.2 [a] ± 1510.1	6378.8 [a] ± 1741.8	6477.4 [a] ± 1978.8
Na mg kg^{-1}	4008.1 [a] ± 2658.5	2064.2 [b] ± 1325.3	2085.3 [b] ± 1165.5	2539.2 [b] ± 1143.1	2460.3 [b] ± 749.8
CEC meq 100 g^{-1}	10.1 [d] ± 3.5	35.1 [c] ± 1.6	42.3 [ab] ± 4.7	44.11 [a] ± 6.6	37.9 [bc] ± 7.3
CCE %	1.5 [b] ± 0.8	2.0 [ab] ± 0.9	4.2 [a] ± 3.8	3.0 [ab] ± 1.2	2.6 [ab] ± 0.9
Fe mg kg^{-1}	84.6 [b] ± 20.6	116.5 [ab] ± 52.5	140.5 [a] ± 41.1	134.7 [a] ± 29.9	143.5 [a] ± 68.5
Al mg kg^{-1}	116.5 [c] ± 44.2	480.1 [b] ± 50.5	524.1 [b] ± 37.9	593.1 [a] ± 51.2	494.8 [b] ± 69.3
Sand %	94 [a] ± 12.5	37 [b] ± 5.1	9 [cd] ± 5.8	4 [d] ± 3.2	15 [c] ± 7.3
Silt %	3 [c] ± 2.9	45 [b] ± 3.6	56 [a] ± 6.3	50 [b] ± 4.4	61 [a] ± 6.9
Clay %	3 [e] ± 3.1	18 [d] ± 7.7	35 [b] ± 4.5	46 [a] ± 3.6	24 [c] ± 1.4

EC; electrical conductivity, SOM; soil organic matter, CEC; cation exchange capacity, CCE; calcium carbonate equivalent. Mean values followed by same letter within a row are not significantly different at probability of α = 0.05 level according to Duncan's test.

3.2. Comparison of P Tests Extraction Efficiency

Extractable concentrations of P measured by the three methods used in this study are shown in Table 2. There were wide variations in the soil extractable P measured by each method; P_{Olsen}, P_{Bray}, and P_{M3} values were in the ranges of 0.4–11.2, 4.1–48.7, and 2.7–81.7 mg kg^{-1}, respectively. The P sources, soil chemical reactions governing P availability, and levels of accumulation in the soil may differ greatly, therefore, analytical methods also differ [66]. Wang et al. [58] and Jalali and Jalali [21] found similar variations in their results. The variation in P extracted by the three different methods can be ascribed to variations in the chemistry of the soils and the way that different methods extract P [22]. Cheng et al. [1] stated that the spatial variation of P in soil is largely heterogenic, and they also reported that the soil P content is mostly affected by factors such as parent material, topography, climate, land use, farming systems, and organisms that drive soil biogeochemical processes.

Table 2. The mean and standard deviation values for available phosphorus concentrations in the different soil textures investigated.

Soil Parameters		Soil Texture				
		Sand $n = 16$	Loam $n = 5$	Silt Clay Loam $n = 11$	Silt Clay $n = 13$	Silt Loam $n = 5$
P_{Olsen} mg/kg	Mean	1.2 [b]	3.5 [ab]	5.0 [ab]	6.3 [a]	4.3 [ab]
	Max	3.13	7.4	11.2	18.0	7.0
	Min	0.12	0.4	0.9	0.7	1.8
	SD	0.81	3.0	2.6	4.1	2.2
P_{Bray} mg/kg	Mean	12.0 [a]	17.3 [a]	21.8 [a]	20.8 [a]	20.1 [a]
	Max	24.8	26.8	34.9	48.7	38.8
	Min	4.1	9.5	9.4	7.5	8.4
	SD	5.2	8.1	9.1	10.5	12.6
P_{M3} mg/kg	Mean	17.2 [b]	26.0 [ab]	42.9 [a]	35.3 [ab]	32.6 [ab]
	Max	40.2	37.4	80.9	81.7	80.2
	Min	2.7	15.5	14.6	4.6	5.6
	SD	9.6	11.1	20.5	20.3	19.5

Mean values followed by same letter within a row are not significantly different at probability of $\alpha = 0.05$ level, according to Duncan's test. P_{Olsen}—available P according to the Olsen method; P_{Bray}—available P according to the Bray 1 method; P_{M3}—available P according to the Mehlich 3 method.

Available P extracted by the P_{Olsen} method was significantly higher in silt clay, silt clay loam, loam, and silt loam textures than in sand-textured soils (Table 2). Jalali [67] and Kabala et al. [66] found that the P extracted by the P_{Olsen} method in their studies was higher than the critical concentration (i.e., 25 mg P kg^{-1}) for most crops, which is the opposite of this study. The maximum P_{Olsen} value in this study was 18.0 mg kg^{-1}, about 4.3 and 9.5 times lower than the maximum P_{Bray} and P_{M3}, respectively. The mean P_{Olsen} values ranged between 4 and 10 times lower than the mean P_{Bray}. Ebeling et al. [32] stated that the P_{Bray} method is appropriate to predict crop P requirements and to estimate risk assessment of P loss in both neutral and alkaline soils in eastern Wisconsin. P_{Bray} values were numerically highest in silt textures followed by loam and sand textures, respectively. However, there was no significant difference in P_{Bray} concentrations between soil textures (Table 2). The P_{Bray} method indicated that available P was greater than the critical concentration (i.e., 4–8 mg P kg^{-1}) in the soils tested for this study [68]. The statistically highest mean concentrations of P_{M3} were found in the silt clay loam, silt clay, silt loam, and loam-textured soils, whereas the lowest value was recorded in the sand. In contrast, Jalali and Jalali [22] found that available P extracted by P_{Olsen} and P_{M3} was higher in sand than loam-textured soils.

The maximum available soil P indicated by P_{Bray} was 48.7 mg P kg^{-1} in the silt clay, compared to 18.0 and 81.7 mg P kg^{-1} for P_{olsen} and P_{M3} (also in silt clay), respectively. These results indicate a greater capacity of the Mehlich 3 method to quantify the residual form of P from previous fertilizations compared to the Bray and Olsen methods. Previous work also indicates that the P_{Bray} extracts less P than P_{M3} in alkaline and calcareous soils [32]. This is because the P_{Bray} extractant is a weaker acid than the P_{M3} extractant, and the P_{Bray} extractant is likely neutralized to a greater extent than the P_{M3} extractant by carbonates in the soil. The P_{Olsen} values are also less than P_{M3}, which agrees with the

results of Jalali and Jalali [22]. This can be ascribed to the acidic pH of the P_{M3} extractant as compared to the basic pH of the Olsen extractant; the acidic P_{M3} extractant induces the release of P from calcium phosphates in calcareous soils [33].

The low levels of available soil P found in this study are common for sandy soils in the Nile Delta region because of the low use of phosphors fertilizers and/or organic manure due to the fact that most of these soils are close to the coast and uncultivated. Generally, the optimum P_{M3} concentration for plant growth in soil is between 45 and 50 mg P kg^{-1}, with maximum values from 70 to 90 mg P kg^{-1} [66,69,70]. The optimum amount of P_{Olsen} for plant growth ranges from 10 to 25 mg P kg^{-1} soil, whereas 25–30 mg P kg^{-1} points to a high P concentration [66,69]. Jalali and Jalali [21] mentioned that the concentration of P_{M3} that generally led to optimum crop growth and yield is 50–60 mg P kg^{-1}, which is greater than the critical levels for P_{Olsen} (10 mg P kg^{-1}). According to Sims [71], the optimum value of P_{Bray} for plant growth is 25–30 mg P kg^{-1}.

The results of this study indicated that 92%, 84%, and 82% of the soil samples were lower than the critical level of $P_{Olsen,}$ P_{M3}, and P_{Bray}, respectively. Available P deficiencies in some alkaline soils may be controlled by solid-phase dicalcium phosphate or by chemisorption of P on calcite minerals, however, there is limited information on the availability and behavior of P in alkaline soils [33]. Pizzeghello et al. [72] reported that in northern Italy, with soils of pH 7.14–8.13, continuous long-term application of fertilizers led to accumulation of available P in top-soils to the point that it exceeded the required limit for optimal plant growth, therefore increasing the potential for P losses to surface and groundwater. Some of the individual P_{M3} values in our study were on the high end of concentrations needed for good plant growth, indicating the potential for P losses to local water systems.

3.3. Environmental Risk Indices for P

3.3.1. Degree of P Saturation (DPS)

The risk of losing P from soil into water bodies can be linked to its degree of saturation in the soil. The saturation of P sorption sites in the soil occurs after the critical concentration (i.e., threshold value or change point) of P in the soil solution is reached, and indicates the point upon which the soil becomes a P source rather than a P sink [73]. Soil P sorption parameters for the different soil textures are presented in Table 3. The DPS of the studied soils increased significantly in sand-textured soils (mean of 10.99%), followed by silt clay loam texture (mean of 6.48%). Non-significant differences were recorded between silt clay, silt loam, and loam textures. This difference was due to variations in the physio-chemical soil properties [33]. In this study, DPS values ranged from 0.61% to 27.9% for all investigated soil textures. For comparison, the DPS values found by Jalali and Jalali [21] ranged between 2.0% to 80.2%. A DPS value of 25% is commonly considered to be a critical value for P leaching; above this point, the risk of P loss into surface and ground waters increases significantly [21,33,74]. Generally, the DPS in all studied soil samples was lower than the environmental threshold according to Hooda et al. [16] and Jalali and Jalali [21] (i.e. $\geq$ 60%), above which the dissolved P becomes an environmental issue. Pöthig et al. [75] and Fischer et al. [76] stated that the critical values of DPS are reached at different quantities of total P accumulation in different soil textures due to different capacities for P sorption. Chen et al. [11] reported that the leaching of P from agricultural soils is a complicated process that depends on soil properties: pH of the soil solution, type and amount of clay minerals, SOM, and Fe/Al oxides. A portion of dissolved organic matter (DOM) may have a positive charge due to protonation. Hence, P can also sorb onto DOM through electrostatic interaction [11]. Liu et al. [13] stated that increased availability of P after excessive application of manure may increase the P loss risk, not only due to increasing the transferable amount of P, but also by accelerating the persistent co-migration among P, dissolved organic carbon (DOC), and metal ions. Thus, P leaching should be of greater concern in organically fertilized soils.

Table 3. P sorption parameters for the different soil textures investigated in this study.

Soil Parameters		Soil Texture				
		Sand $n = 16$	Loam $n = 5$	Silt Clay Loam $n = 11$	Silt Clay $n = 13$	Silt Loam $n = 5$
DPS %	Mean	10.9 [a]	4.3 [b]	6.5 [b]	4.7 [b]	3.3 [b]
	Max	25.9	6.6	13.5	9.9	5.1
	Min	3.07	2.6	2.1	0.6	1.0
	SD	5.3	1.6	2.6	2.8	1.8
SPSC	Mean	5.8 [b]	37.4 [a]	30.6 [a]	43.1 [a]	39..1 [a]
	Max	16.6	48.7	57.4	71.6	54.2
	Min	-2.7	21.3	3.5	7.9	1.6
	SD	3.2	12.4	19.0	18.6	12.1
P_{M3}/Ca_{M3}	Mean	2.4 [a]	0.63 [b]	0.94 [b]	0.85 [b]	0.83 [b]
	Max	5.4	1.03	2.1	2.7	2.2
	Min	0.1	0.3	0.2	0.1	0.08
	SD	1.0	0.14	0.40	0.51	0.50
P_{M3}/Al_{M3}	Mean	14.6 [a]	4.9 [b]	7.3 [b]	5.1 [b]	5.9 [b]
	Max	36.8	7.9	14.4	10.8	16.4
	Min	3.3	2.9	2.3	1.7	1.10
	SD	8.8	2.4	3.8	3.0	2.4

DPS: degree of P saturation; SPSC: soil P storage capacity; P_{M3}/Ca_{M3}: P stability ratio % (based on Ca); P_{M3}/Al_{M3}: P stability ratio % (based on Al). Mean values followed by same letter within a row are not significantly different at probability of $\alpha = 0.05$ level, according to Duncan's test.

3.3.2. Soil P Storage Capacity (SPSC)

The environmental risk of losing P from soil into water can also be assessed by SPSC. This index depends on a threshold of P saturation ratio (PSR) (i.e., molar P ratio to (Al + Fe)). If SPSC is a positive value (+), the soil is a P sink and vice versa [55,77]. In this work, mean SPSC values ranged from 5.8% to 43.1% in sand and silt clay textures, respectively (Table 3). About 35% of the sand-textured samples had negative SPSC values, and there was a linear increase in P release from the soil [77]. All other textures investigated in this study had only positive SPSC values. Nair and Harris [78], Chakraborty et al. [77], and Dari et al. [45] used SPSC to predict the environmental P loss risk for sandy layers in coastal plain soils. The differences between the mean values of SPSC for silt clay loam, silt clay, silt loam, and loam textures were not significant (Table 3), and all would likely act as P sinks. Thus, SPSC reflects the soil's capacity to retain P before becoming an environmental risk by releasing P [45,78]. Pellerin et al. [79] stated that soils with a pH greater than 6 had a reduced SPSC with lower Al_{M3}, resulting in a greater P loss risk through leaching.

3.3.3. P Stability Ratio (P_{sat})

P_{sat} can be calculated on the basis of P_{M3}/Ca_{M3} (P_{sat-Ca}) or P_{M3}/Al_{M3} (P_{sat-Al}). The sand-textured soils had the highest P_{sat-Ca} value at 2.4%, reflecting the high variability of Ca contents in the sandy soils (Table 3). The lowest P_{M3}/Ca_{M3} ratio was in the loam-textured soils (0.6%), but there was no significant difference between the loam, silt clay loam, silt clay, and silt loam-textured soils. These low values were consistent with a lower risk of P leaching. Crittenden et al. [15] found insignificant differences in P_{M3}/Ca_{M3} between textures when the soils had high $CaCO_3$ content. P_{sat-Al} ratios had the same trend as P_{sat-Ca}. The highest P_{sat-Al} value was in sand-textured soils (14.6%), whereas there was no significant difference in the P_{sat-Al} values for loam, silt clay loam, silt clay, and silt loam-textured soils. Changes in P_{sat} depend on pH, Al_{M3}, $CaCO_3$, and SOM contents [15,18]. Further studies are needed to determine which P_{sat} (i.e., based on Ca_{M3}, Al_{M3}, or $Al_{M3} + Fe_{M3}$) is most suitable for use in alkaline soils [15].

3.4. Correlation Analysis

The correlations between P extraction, selected soil physio-chemical properties, and P loss indices are presented in Table 4. All correlations among the different soil P tests were significant. P_{M3} and P_{Bray} were highly correlated with P_{Olsen} ($r = 0.69$ and 0.82, respectively), and P_{M3} was highly correlated

with P_{Bray} ($r = 0.94$). It is usually accepted that the Bray extraction method is more appropriate for extracting P in acidic soils, whereas the Olsen extraction method is more suitable in calcareous soils. The different correlations obtained can be linked to the methods' ability to extract different proportions of available P. In studies by Mallarino [80] and Boem et al. [81], the P amount extracted by M3 was strongly correlated with P extracted by the Bray method in soils that had pH values less than 7.4, as well with P extractable by the Olsen method in soils that had pH 7.4 or greater. Kabala et al. [66] and Pizzeghello et al. [33] found a strong correlation between P_{M3} and P_{Olsen} ($r = 0.77$) in three alkaline soils following long-term application of mineral and manure fertilizers. The findings of these studies agree with our results. However, significant correlations between the Bray 1 and Mehilch 3, Mehilch 3 and Olsen, and Olsen and Bray 1 tests in clay-textured soils (Vertisols with pH of 5.3–6.3) were not found by Hernández et al. [68]; this was a result of their high clay, CEC, and Fe and Al oxide content. A significant correlation was found between the Bray 1 and Mehilch 3, Mehilch 3 and Olsen, and Olsen and Bray 1 tests in loam and silt-textured soils with a pH range of 5.0–6.6 [68].

Fe$_{M3}$ and Al$_{M3}$ had positive correlations with clay, silt, CEC, organic matter (OM), and calcium carbonate, whereas Ca had a positive correlation with calcium carbonate. This is partially in agreement with Daly et al. [82], who found a positive correlation between OM, and Fe and Ca, and with Elbehiry et al. [53], who found a significant positive correlation between Al and clay. Fe$_{M3}$ and Al$_{M3}$ had negative correlations with sand content, whereas Fe$_{M3}$, Al$_{M3}$, CEC, and CCE had strong positive correlations with clay and silt and a negative correlation with sand. In contrast, Jalali and Jalali [22] found negative correlations between Fe and clay, CCE, and silt. There were not any significant correlations between pH, CCE, and OM, and P_{M3}, P_{olsen}, and P_{Bray}. Phosphorus extracted by P_{Olsen}, P_{Bray}, and P_{M3} were negatively affected by EC and sand content. P_{Olsen} was positively correlated with clay, silt, Al, Fe, and CEC, whereas P_{Bray} and P_{M3} were positively correlated with Al, K, silt, and clay. In contrast, Jalali and Jalali [21] found a negative correlation between P_{M3} and CCE, silt, and clay, and a positive correlation with Fe. The results of this study suggest that the buffering capacity of P in alkaline soils is clearly associated with texture. This agrees with Khaledian et al. [60], who found that available P was significantly correlated with texture across four different P tests (Bray, Mehlich, acid oxalate, and New Zealand) in several geographically scattered locations. Hughes et al. [83] reported that dissolved P in the soil related variably with soil taxonomic unit due to variations in the buffering capacity of P between soils because of different levels of Fe and Al hydroxyoxides, clay content, carbonates, and SOM, in addition to land management. Daly et al. [82] showed that the greater the buffering capacity, the slower the decline rate of soil P concentration with time.

DPS was significantly negatively correlated with OM, CEC, CCE, Fe, Al, silt, and clay, whereas it was significantly positively correlated with sand. SPSC had a significant negative correlation with EC, DPS, and sand, and significant positive correlation with OM, CEC, CCE, Fe, Al, silt, and clay. In this study, there were non-significant correlations between all methods of determining available P and both DPS and SPSC. DPS and SPSC correlated (either positively or negatively) with most soil parameters, implying that these indices can be used for evaluating P-buffering capacity in these soils, as indicated by Jalali and Jalali [22]. DPS had negative correlations with Al and Fe and positive correlations with CEC and Ca, which agrees with Jalali and Jalali [22]. However, contrary to this study, Jalali and Jalali [22] found positive correlations between DPS and most methods of determining available P.

Table 4. The correlation between physio-chemical soil properties, soil P tests and potential environmental indices of P loss from soil.

	P_{Olsen}	P_{Bray}	P_{M3}	pH	EC	OM	Mg	K	Ca	Na	CEC	CCE	Fe	Al	Sand	Silt	Clay	DPS	SPSC	P/Ca	P/Al
P_{Olsen}	1																				
P_{Bray}	0.82 **	1																			
P_{M3}	0.69 **	0.94 **	1																		
pH	−0.13	0.11	0.11	1																	
EC	−0.38 **	−0.32 *	−0.30 *	−0.10	1																
OM	0.21	−0.02	−0.01	−0.38 *	−0.49 **	1															
Mg	0.47 **	0.23	0.31 *	−0.10	−0.46 **	0.64 **	1														
K	0.54 **	0.60 **	0.65 **	0.19	−0.34 *	0.28 *	0.69 **	1													
Ca	0.24	0.03	0.09	−0.16	−0.72 **	0.69 **	0.70 **	0.31 *	1												
Na	0.00	0.02	−0.01	−0.05	0.82 **	−0.38 *	−0.20	0.09	−0.53 **	1											
CEC	0.45 **	0.26	0.32 *	−0.22	−0.66 **	0.79 **	0.86 **	0.62 **	0.84 **	−0.33 *	1										
CCE	0.19	0.03	0.09	−0.20	−0.39 *	0.45 *	0.61 **	0.27	0.64 **	−0.36 *	0.55 **	1									
Fe	0.50 **	0.22	0.18	−0.14	−0.29 *	0.49 **	0.67 **	0.47 **	0.40 **	−0.11	0.57 **	0.44 *	1								
Al	0.59 **	0.42 *	0.45 *	−0.16	−0.63 **	0.70 **	0.85 **	0.65 **	0.68 **	−0.26	0.92 **	0.44 *	0.60 **	1							
Sand	−0.55 **	−0.39 *	−0.42 *	0.09	0.65 **	−0.69 **	−0.88 **	−0.71 **	−0.75 **	0.28 *	−0.95 **	−0.52 **	−0.57 **	−0.96 **	1						
Silt	0.53 **	0.43 *	0.45 *	−0.04	−0.65 **	0.64 **	0.83 **	0.68 **	0.74 **	−0.28 *	0.90 **	0.53 **	0.59 **	0.92 **	−0.96 **	1					
Clay	0.51 **	0.29 *	0.32 *	−0.16	−0.59 **	0.67 **	0.84 **	0.63 **	0.68 **	−0.24	0.88 **	0.44 *	0.49 **	0.90 **	−0.93 **	0.82 **	1				
DPS	−0.06	0.25	0.26	0.17	0.22	−0.49 **	−0.55 **	−0.26	−0.48 **	0.07	−0.56 **	−0.31 *	−0.44 *	−0.58 **	0.58 **	−0.55 **	−0.56 **	1			
SPSC	0.14	−0.15	−0.15	−0.13	−0.47 **	0.72 **	0.71 **	0.32 *	0.70 **	0.30 *	0.78 **	0.43 *	0.50 **	0.77 **	−0.77 **	0.74 **	0.74 **	−0.87	1		
P/Ca	−0.12	0.08	0.10	−0.02	0.78 **	−0.54 **	−0.43 *	−0.11	−0.74 **	0.74 **	−0.59 **	−0.40 *	−0.27	−0.49 **	0.53 **	−0.51 **	−0.50 **	0.43 *	−0.59 **	1	
P/Al	−0.11	0.25	0.25	0.25	0.30 *	−0.53 **	0.59 **	−0.25	−0.59 **	0.13	−0.61 **	−0.35 *	−0.42 *	−0.60 **	0.60 **	−0.55 **	−0.60 **	0.94 **	−0.81 **	0.51	1

* Correlation is significant at the 0.05 level (two-tailed). ** Correlation is significant at the 0.01 level (two-tailed).

3.5. Principal Component Analysis

Principal component analysis was applied to evaluate the relationships between the different soil properties, extractable P, and P sorption parameters (DPS, SPSC, P_{M3}/Ca_{M3}, and P_{M3}/Al_{M3} values). PCA has been demonstrated to be an efficient tool to recognize potential sources in combination with correlation analysis [58]. Three criteria were used to define the number of significant components: (1) eigenvalues greater than 1, (2) cumulative variance of at least 70%, and (3) factors that explain at least 5% of the variance. Four factors met these three criteria. The eigenvalues and associated variance for the factors extracted are presented in Table 5, and the plots of loading vectors for the first and second factor components are shown in Figure 2. The first four factors explained 83.8% of the total variance among eight variables, where the first factor explained 51.5%, the second 16.9%, the third 9.7%, and the fourth 5.6% of the total variance. The loadings on the first factor were large and confirmed the negative associations of SPSC, P/Al, P/Ca, and DPS with OM, EC, CEC, CCE, clay, silt, sand, K_{M3}, Mg_{M3}, and Ca_{M3}. This factor indicated the negative association of DPS and P/Al with sand, indicating that sandy soils would probably have lower DPS [22] Additionally, when DPS increases, P will increase in solution as a result of the low retention of P by soils [22,84]. The second factor confirmed the positive association between available soil P (P_{M3}, P_{Olsen}, and P_{Bray}), which might indicate that the extracted P was primarily from the same sources. Thus, the concentration of available P is a valued chemical indicator of human impacts on soil, generally employed as a critical standard in many national and international classifications [66]. These results agree with those of Jalali and Jalali [22], as they indicated that deficiencies in alkaline soils may be controlled by available P through solid-phase dicalcium phosphate or by chemisorption of P on calcite minerals, thus decreasing the risk of P losses.

Table 5. Total variance explained and rotated component matrix (four principal components selected) for P concentrations.

Parameters	Rotated Component Matrix [a]			
	PC1	PC2	PC3	PC4
P_{Olsen}	0.36	0.82	0.04	−0.19
P_{Bray}	0.11	0.98	0.05	0.07
P_{M3}	0.14	0.93	0.053	0.14
pH	−0.14	0.04	0.08	0.94
EC	−0.38	−0.26	−0.85	−0.12
OM	0.73	−0.12	0.34	−0.33
Mg	0.93	0.14	0.12	0.03
K	0.66	0.53	−0.15	0.39
Ca	0.67	−0.07	0.63	−0.10
Na	−0.08	0.06	−0.93	−0.01
CEC	0.89	0.18	0.35	−0.09
CCE	0.55	−0.07	0.36	−0.17
Fe	0.69	0.16	−0.03	−0.15
B	0.63	0.39	−0.30	0.36
Al	0.86	0.34	0.24	−0.06
Si	0.71	0.44	−0.08	0.18
Sand	−0.89	−0.29	−0.28	−0.02
Silt	0.84	0.32	0.30	0.05
Clay	0.85	0.22	0.23	−0.08
DSP	−0.90	0.26	−0.02	0.01
SPSC	0.09	−0.12	0.29	0.03
P/Ca	−0.40	0.11	−0.81	0.05
P/Al	−0.88	0.24	−0.11	−0.08

Table 5. *Cont.*

Parameters	Rotated Component Matrix [a]			
	PC1	PC2	PC3	PC4
Parameters	Component	Initial Eigenvalues		
	Total	Total	% of Variance	Cumulative %
P_{Olsen}	1	10.045	52.866	52.866
P_{Bray}	2	3.076	16.191	69.058
P_{M3}	3	1.605	8.447	77.505
pH	4	1.199	6.309	83.814

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. [a] Rotation converged in 5 iterations.
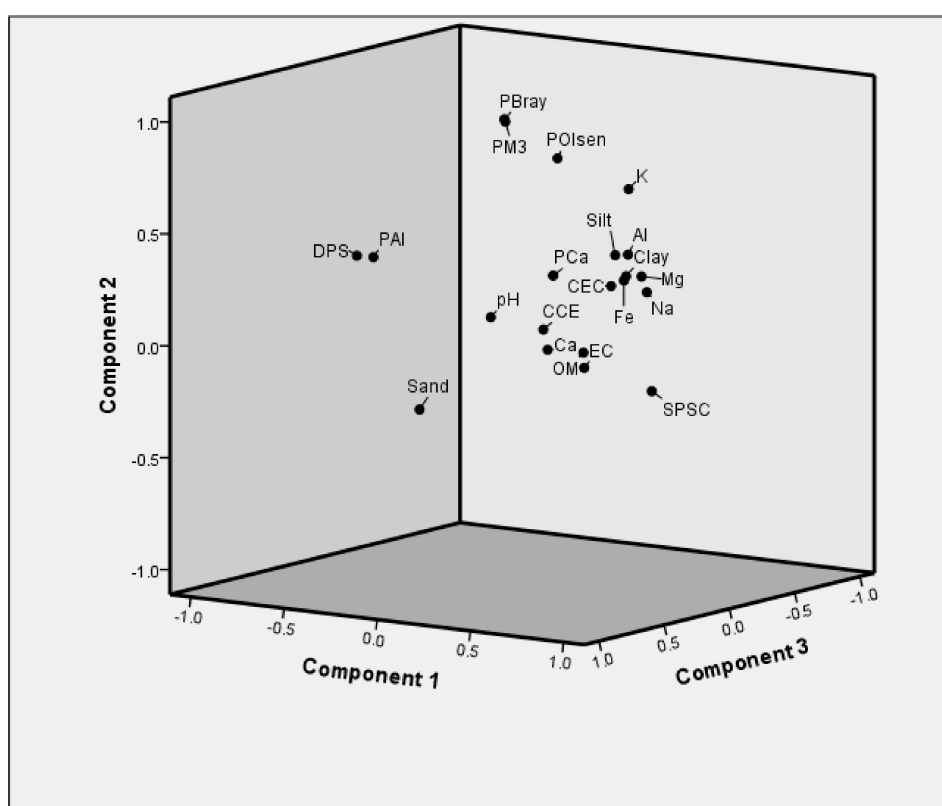
Figure 2. The principal component analysis loading plot of P extraction and soil properties in the studied soil.

4. Conclusions

Three different extractant solutions were employed to study P extractability in 50 surface soils from the northern Nile Delta, Egypt, that differed in their texture. The study's goal was to establish relationships between the P extracted and the parameters of P sorption derived from established equations. Among the extractants, Mehlich 3 extracted the largest amount of P from the studied soils, followed by Bray and Olsen. Differences in P sorption parameters were obtained in the soils, indicating a strong influence of soil texture on P adsorption, with high DPS and low SPSC in sandy soils. The PCA summarized the relations between P extractability, sorption parameters, and soil characteristics. The results implied that DPS can be calculated by Mehlich 3 in different soil textures. The mean DPS values were higher in the sand-textured soils than in other textures, which indicates high environmental concern in the sandy soils. Results indicated that SPSC values decreased with increasing DPS values,

leading to reductions in P retention and increased P leaching. Thus, additional studies that build on these results should be considered to assist in planning for sustainable management for reducing the risk of P leaching from soil to groundwater.

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