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A Case Study of the Total and Available Phosphorus Concentration in Libyan Agricultural Soils in Different Depths and Seasons in Long-term Chemical and Animal Manure Fertilization

Mansour A. Salem
Faculty of Engineering and Technology,
Sebha University, Libya
awiedat@yahoo.com

Latif A. Al-Ethawi
Faculty of Education,
Sebha University, Libya

Zaho S. M. Eldrazi& Abdullah I. Nouraldien
Faculty of Agriculture,
Sebha University, Libya

Abstract:*The aim of this study was to assess the impact of application of chemical fertilizers (NPK) and manure in long-term on the status of Phosphorus (P) forms in cultivation in sandy soils in five farms of Brack-Ashkada agricultural project in 2010. Accumulations of total and available phosphorus (P) were determined in the samples collected from soil profile at depths (0 to 180 cm) during Jan, Apr, July and Oct. Results showed that total P were decreased with increasing soil depths i.e. 277.64, 160.78, 118.00 and 111.00 µg.g^{-1}; variation between the depths of soils; total P in farms18 and 21; F value at 5% with the soil profile 11.45 and 5.32. Farms 19, 20 and 22 showed no significant results between depths and variations in farms 19, 20 and 22 such as F value at 5% were 4.82, 7.24 and 9.97. Farms showed no significant variation in treatment, however, total P were increased from Jan, Apr and July, but decreased in Oct. The values were 105.88, 152.37, 251.88 and 159.15 µg.g^{-1} soils. LSD test at 5% level marked difference in Jan and Apr in farm 18, and in all times in farm 21; in farms 19, 20 and 22, LSD test showed no significant difference in all times. Available P also decreased with soil depths resulting 51.4, 33.18, 31.7 and 26.7µg.g^{-1}. Analysis of variance showed significant difference in available P in depths in farm 18 and F value was accounted 9.90, at 5%, whereas the rest showed no difference. The treatments showed variation in farms18, 19 and 22 which was significant in available P. The F value accounted 19.14, 13.41 and 4.30 at 5% level. Farms 20 and 22 showed no significant difference. LSD test at 5% level showed significant difference in Apr, July and Oct in farms 18 and 19; farms 21 and 22 showed significant difference in Jul and Oct. whereas farm 20 showed only significant difference in Oct.*

Keywords:*Phosphate, manure, residual, chemical fertilizer, variation, soil depth*

1. INTRODUCTION

Phosphorus (P) is one of the major macronutrients for plant growth and production. It plays an important role in physiological processes that occur within the developing and maturing plants. It is an essential element for cell division as it is a constituent element of nucleoproteins, carbohydrate synthesis and degradation. The main element involved in energy transfer for cellular metabolism. It is structural component of cell membranes and nucleic acids. After nitrogen, P as a constituent of chemical fertilizers has made substantial contributions to increase yields and food nutrition. Food production has been estimated increase about 30-50% since 1950 as a result of P fertilizers application and the globally consumption of P fertilizers had been estimated more than 30 million tons yearly [1,2]. Soil is a complex ecosystem. Its maintenance for productivity is very important in order to maintain and stimulate the growth of plants. In fact, P is present in soils in organic or inorganic forms and supplied as a phosphate such as diammonium phosphate $(NH_4)_2HPO_4$ or as calcium dihydrogen phosphate Ca $(H_2PO4)_2$. The phosphorus content of fertilizer is specified as the amount of P_2O_5 as it is the anhydrous form of phosphoric acid which considered the most concentrated form of phosphate. However phosphorus in organic form is the most stable form in the soil, whereas the inorganic form, it is stable and readily absorbed and used by plants if it is not fixed [3]. P applied to the plants or soils depends mainly on the available reservation of this element in the soil. Therefore negative or positive results may be due to the quantity or sources stored in the soil; and also due to its high capacity of soil in absorbing P whereas sometimes it is low in soil so that all used phosphorus fertilizers in soil cannot be available in plants. Therefore phosphorus exists in soil solution must be continuously decomposed. In most soils, P content is very low in the surface layer. It represents less than 1% of total P. However the total P content of any soil may vary widely and depend on some factors such as organic matter content, climatic conditions, parent materials and degree of fertilization. Over 80% of P becomes immobile and unavailable for plants uptake because of adsorption, fixation, conversion of P to organic form and precipitation, inorganic forms of P are usually exist in virgin soils which are derived from the parent rocks, inorganic P form can be converted to organic form by soil age, microbial populations animals and plants [4].

2. STATEMENT OF THE PROBLEM

There are at least four common problems encountered in the application of P. Firstly, the increasing of P fertilizers over the past decade is not necessarily coincided with improve of nutrient use efficiency, as only small proportion of applied P is used directly by crops thus leaving large amount of the P in soil [5]. Secondly, long-term fertilization with organic or inorganic P fertilizers can accumulate P in the subsoil down to 30-180 cm depth [6]. Long-term application of these fertilizers usually leads to reduction in pH and exchangeable bases thus making them unavailable to crops which cause its productivity declines. Thirdly, the fate of surplus P fertilizer depends on soil type, transport mechanisms, and soil properties such as P sorption capacity and the type and amount of fertilizer added; high P application can cause deeper P translocation in some soils [7]. Fourthly, the addition of lime and farmyard manure over long period of time may influence forms and availability of P due to the release of organic acids and other microbial products which modify soil pH during decomposition [8]. The application of chemical fertilizers and manure to the soils of Brack-Ashkada agricultural project for over the last 35 years without any calculations for the need also accounts for such problems.

3. LITERATURE REVIEW

A number of researches have been conducted related to this. A few selected literatures have been taken for review here. In fact, fertilizers play a substantial role as a key component of the modern farm technology for achieving increased production through improving soil fertility. It is often having low use efficiency because only a portion of the applied nutrients are taken up by plants [9]. Therefore it is very important to determine the amount of applied fertilizer that maximize the yields while minimize the environmental pollution. The long-term dynamics of soil P depends largely on both the physicochemical properties and the plant systems growing on these soils. P fertilizers are among the sources of heavy metals inputs into agricultural activities, in addition to nutrient elements it contains a trace metals such as Cadmium, Lead and Mercury [10]. In agricultural areas, the long-term intensive applications of phosphoric fertilizers to soils and phosphorus recycling in farmyard manure caused the situation when the soil originally a strong sink of phosphorus, became a source of its escape to the environs [11]. P is added to cultivated soils worldwide as a chemical or organic fertilization, triple superphosphate and di-ammonium phosphate are water soluble P fertilizers applied to soils, after its dissolution the phosphate ions in solution react immediately with Ca, Fe or Al ions present in soil solution and precipitated as insoluble compounds or become adsorbed on surface of clay particles [12]. One of the most important factors in agricultural practices in arid and semiarid regions globally is drought stress, however absorbance and availability of P to the crop plants minimizes as calcareous soils over dominant in the cultivated lands along with extended dry by climatic conditions [13]. P deficit is the most important restrictive factor in plant growth and recognition of mechanisms that increase plant P use efficiency, phosphorus deficiency is due to several factors including its high capacity fixation, high intake rate by new cultivars, soil erosion, its sedentary in acidic soils and its low occurrence naturally in some soils. In agricultural calcareous soils application of P fertilizers has introduced some problems mainly due to low recovery, P fixation and accumulation in soil [14]. Due to considerable P chemo-sorption in the soil and low P uptake capacity of crops, P fertilization rates were 3-5 times higher than the actual uptake of P for a good yield, therefore potential contamination of waters by phosphorus with subsequent disturbance of ecological balance in farmed could be happen, runoff waters can also be influenced by the content of labile P forms in soil and by easiness of their conversion to water-soluble fractions [15].

4. AIM OF THE STUDY

The aim of the present study was to evaluate the residual and fate of phosphorus fertilizers added to soils of some farms in Brack-Ashkada agricultural project after long-term cultivation with different crops in the extent of P movement and distribution of soil P among the soil depths. To test the possibility of predicting phosphorus mobilization from top layer of agricultural soils to downwards layers, both total and available P were investigated. The aim was to provide good management and knowledge of proper use of fertilizer in agriculture to maintain soil fertility and overall quality.

5. MATERIALS AND METHODS

Soil samples were collected randomly from five farms cultivated with different crops in long-term of Brack-Ashkada agricultural project in Fezzan province Libya, which is located between North latitudes 23° to 28.5° and East longitudes 10° to 16°, with an altitude of 400m above sea level. This agricultural project was built in 1975, It contains 24 wells each well contains 12 farms. The area of each farm is about 10 hectares. Soil samples were taken from four depths (0-45, 45-90, 90-135 and 135-180 cm) for four times in 2010. In January, April, July and October, since these times represent the middle of winter, spring, summer and autumn seasons. Three replicates of soil samples were collected (1000 grams) in polythene bags and taken to laboratory, air dried and sieved through 2mm sieve. Uncultivated soil samples near to the site were taken as a reference. Physicochemical properties of the soil samples were measured as below. Soil pH and EC were measured as mentioned in [16] & [17]. Soil texture, cation exchange capacity (CEC), percentage of active potassium carbonate and available potassium ions were measured as mentioned in [18]. Percentage of organic matter in soil is measured as described in [19]. Ammonium ion in soil was measured as mentioned in [20]. Total phosphorus in soil was measured as described in [21]. Available phosphorus in soil was measured as mentioned in [22]. Calcium bicarbonate was measured as in [23]. K, Mg, Ca and Na were determined by atomic absorption spectrophotometer (AAS); Ammonium concentration as described in [24] and Total nitrogen was determined by micro Kjeldahlmethod [25].

The data collected were statistically analyzed by using analysis of variance (ANOVA) with the GENSTAT statistical package and significant means were separated using least significant difference (LSD) at 5% probability level.

6. RESULTS AND DISCUSSION

Some of physico-chemical properties of uncultivated (virgin) soil close to the study site (table 1) showed that soil texture was sandy which could facilitate the filtration and leaching of water and other soil minerals.

Table1.

Parameters	Units	Depth (cm)			
		0 - 45	45 - 90	90 - 135	135 - 180
pH		7.57	7.60	7.41	7.29
Electrical Conductivity	$ds.m^{-1}$	0.66	1.78	1.84	1.85
Nitrate	ppm	0.167	0.546	0.466	0.431
Total phosphorus		56.25	49.37	33.62	26.12
Available Phosphorus		3.8	3.8	4.4	4.9
Total Nitrogen	%	0.035	0.035	0.018	0.018
Total Calcium Carbonate		1.75	1.87	2.32	1.5
Active calcium carbonate		0.12	0.07	0.05	0.05
Organic matter		0.06	0.06	0.06	0.05
Humidity		0.031	0.052	0.054	0.099
Saturation		26.25	20.50	26.55	22.85
Field Capacity		14.28	13.55	13.55	10.07

Soil Texture		sandy	sandy	sandy	Sandy
Cation Exchange Capacity	ml equ.g^{-1} soil	2.874	2.330	2.473	2.373
Available Potassium		0.23	0.23	0.11	0.15
Potassium	ml. equ.l^{-1}	5.12	8.80	8.71	8.99
Calcium		40	157	201	188
Ammonium		0.032	0.0013	0.007	0.005
Magnesium		9	34	38	50
Sodium		24.3	42.6	44.1	48.6
Chlorine		0.3	0.8	0.9	1.15
Sulphates		135.4	110.4	102	93.75
Calcium Carbonate $CaCO_3$		0	0	0	0
Calcium Bicarbonate $Ca(HCO_3)_2$		0	0.01	0.01	0.005

The pH of the virgin soil was between 7.29 - 7.60 which was considered a neutral soil, pH of soil samples of the tested farms were between 7.37 - 8.83, and the soil texture was sandy and can ease the leaching of phosphorus. Farmers usually used chemical fertilizer NPK for P fertilization which contains 18% P and 46% N beside the organic fertilizer (animal manure) which contains 0.02% of total P and usually added randomly once in a year in autumn without any calculation or certain quantity. The farms were irrigated by sprinkling way and cultivated with different crops such as alfalfa, wheat and barley or some vegetables.

The results of the soil samples collected from the five farms (18, 19, 20, 21 and 22) showed that total P were decreased in the soil samples (227.64, 160.87, 118.0 and 111.0 µg.g-1 soil) with increasing of soil depth (0-45,45-90,90-135 and 135-180 cm) respectively. This decreasing might be due to immobilize of P in the soil as a result of its fixation and its reaction with Ca++ ions in natural soil pH which cause the formation of stabilize P compounds. The main factor for decreasing of total P is due to soil texture, which was considered as a sandy soil and could ease its leaching with the irrigation water downwards. These results were consistent with the results reported in [26]. Decrease of P concentration was markedly observed in leachate of sandy soil which had irrigated by simulated rainfall.

Total P were increased in soil samples with increasing of time (Jan, Apr and Jul). The results were 105.88, 152.37 and 251.88 µg.g-1 respectively whereas it was decreased in October. This decrease might be due to continues irrigation which cause a leach of P from soil and the changing of the weather. The increasing of total P with time attributed to rising of temperature and prolonged time of the addition of fertilizer beside the existence of calcium, magnesium, carbonate and bicarbonate in the soils, these results were consistent with [27]. It had been reported that P uptake rarely exceeds 20-30% of the annual applied P therefore large amounts of insoluble and residual P can be accumulated in soils with regular application of P [28]. Total P were decreased in well 18, 19, 20 and 21 as a result of the interaction between increasing of soil depth and time.

The analysis of variance has been used based on randomized whole block design. The blocks represents the soil depth, the time was distributed randomly in average of four intervals (Jan, Apr, Jul and Oct) treatments and represent the effect of depth with time. From the analysis of variance table the (ANOVA table) results of total P (as in Table 2) showed that there were significant differences at 5% level (F =4.82, 7.24 and 9.97) among the depths of farms 19, 20 and 22 respectively. These differences might be due to the inconsistent of the addition of fertilizers amounts, time and type of crop cultivated. But there was no difference in the other farms. The treatment including (depth V time) showed significant differences in farms 18 and 2. The value of F calculated matched (11.54 and 5.32) whereas the farms 19, 20 and 22 showed no significant value in F calculated.

Referring to LSD test at 5% the results showed significant different between the mean in Jan and Apr in farm 18, and in Jan Apr and Oct in farm 21 whereas farms 19, 20 and 22 showed no response in LSD test for all times.

It was observed that with the increasing time, total P also decreased in all farms except in farm 18, where total P higher in Oct than Apr and July, but not in Jan. Increasing of total P at Jan was due to the addition of fertilizers either chemical or manure usually in Nov or Dec by farmers; low irrigation; decreasing of temperature in this time; and beginning of cultivation season whereas the decreasing of total P in Apr, Jul and Oct were attributed to the increasing of temperature and activity of microorganisms in farms 19, 20 and 22 in April; farms 19, 20 and 22 in July; in October farms19, 20, 21 and 22 whereas well 18 showed no significant in all times.

From the above results we can say that total P was decreased with increasing of depths in all soil samples of farms, the total P values were considered low. It was noticed that percentage of total P is ranged between 300 - 3000 µg.g-1 soil. However decreasing of total P with increasing depths attributed to slow mobilization of P in the soil downward as a results of fixation and its reaction with Ca++ ions with the soil pH were P compounds becomes more stable. Soil texture which considered a sandy soil can facilitate the leaching of P during the irrigation process [26]. Here, results shows that total P were increased with increasing of time (Jan→Apr →Jul→Oct) respectively.

7. Statistical Data Analysis of Available P

Statistical data analysis showed significant differences between soil depth and increasing of time. In well 22, total P also decreased with time without any significant differences. Increasing of total P in the upper soil layers attributed to the increasing of soil temperature which facilitate its fixing and addition of P fertilizers randomly, whereas it was decreasing in depths attribute to the leaching. However in soil depths total P was decreased as a result of continuous leaching from the sandy soil; these results were also reported by [28]. Soils properties such as the decrease of organic carbon, organic nitrogen, biological activities and deterioration of soil structure can change as a result of long-term cultivation as observed in [29]. Accumulation of P in sub-plow layer horizons varied depending on soil type, extraction method, cultivation period and location in the landscape [30]. The increase of P fertilizer rates and various fertilizer treatments in the lysimeters soil were decrease the cumulative leachate and total P losses in manural in soils at 80cm compared in soil at 50cm depth. Long-term application of low rates of superphosphate fertilizer to the calcareous soil in a semi-arid Mediterranean region results in a significant increase of available P and resin-P in topsoil compared to the control [31]. Total P contents positively correlated with P budget, while P losses increased significantly with the P budget in topsoil (0-20cm). However total P decreased with time in this layer, while its increased in the subsoil layer (30-50cm) this increase accounts for the losses observed in the topsoil as a result of downward movement of P [32]. The rate and nature of transformation of added P in soils were affected by several soil properties such as the behavior in calcareous soils is largely controlled by soil calcium compounds. However Fe and Al oxides are the main factors that control P behavior in acidic to neutral soils [33]. P can be built-up gradually over the years and would reduce the number of exchange sites that tightly fix the soluble P and effectively reduce P sorption capacity and making fertilizer P more effective [31]. Organic P was found correlated positively with total P across a wide range of calcareous soils in the Mediterranean environment [34]. Movement of P downward and upward is concomitant occurrence depending on fertilization regimes in 10 and 13 years old long-term field trials [32). The most marked decrease in P concentration in leachate was noticed in light sandy soils too.

8. Variance Analysis Results of Total P

Variance analysis results of total P (Table 3) showed the effect of depth and time on the available P. However available P was decreased with the increasing of soil depths (51.4, 33.8, 31.7 and 26.7 µg.g^{-1} soil) respectively, available P was also decreased with the increasing of time (Jan - Apr - Jul - Oct). The results were 64.52, 42.88, 17.30 and 13.92 µg.g^{-1} soil respectively. Variance analysis results of treatments showed that there are significant differences at 5% level among different depths for available P in wells 18, 19 and 22 were F calculated equal 19.14, 13.41 and 4.30 respectively. Well 18 showed significant level also between time and depth F = 9.90. The results also showed significant differences among the depths of wells 18 in second, third and fourth. From the table 3, the differences can be observed in depths of soils between farms, were the results showed significant different in farm 18, were the F value has matched 9.90. The others show no significant difference. The treatments which include depth V time have showed significant difference. F calculated was recorded 19.14, 13.41 and 4.30 in farms 18, 19 and 22 respectively. Farms 20 and 21 showed no respond. the LSD test at 5% level showed significant difference in Apr, Jul and Oct in farms 18 and 19 whereas farms 21 and 22 has showed significant difference in Jul and Oct. while in farm 20 showed only significant difference during Oct.

Results showed that concentration of available P decreased with increasing of depth and time. This increase in topsoil due to the accumulation of applied fertilizers in this layer whereas it was decreasing downwards referred to soil type and repeating of soil leaching which facilitate the decreasing of available P in the soil. It is increasing in some depths probably due the accumulation of P fertilizers as a results of differences of soil topography and the rise of calcium carbonates; addition of different amounts of P fertilizers; cultivating different types of crops; and ways and time of irrigation might led to these differences in the results [35] indicated that manure and mineral fertilizers are both influence the available P along soil profiles. Available P significantly increased on the high P input plots in sub-soil layers at sandy soils of Skiemiewice in Poland, indicating significant leaching from the plough layer into the deeper horizon. Conversely soils with high clay content resulted in a large sorption capacity which should easily prevent movement of P [36]. It had been reported that increasing of P concentration in soils lead to the increase of available P too. The relationship between time and available P concentration in soils samples shows decreasing of available P with increasing time Jan→Apr→Jul→Oct in all wells, variance data analysis indicates a significant differences between time and depths of soil except in well 22 were the available P increase in April which might be due to an addition of fertilizer at this time. The increasing of time plays an important role in the decrease of available P in the soil, sandy soils can't preserve the added fertilizers therefore it leachate to the drainage, sandy soils in arid and semiarid regions usually lack of absorption P, increasing of C: P ratio led to an increasing of energy source for microorganisms in the soil therefore these microorganisms can feed on this amount of available P. These results are consistent with results reported in [37]. The amount of P that can be accessed by plants which are equated to isotopically exchangeable P and is generally considered the Plant available P [38].

Table 2.*Analysis of Variance for total P*

S.O.V	**DF**	**S.S**					**M.S**					**F (calculated)**					**F(ta) 5%**
Farm No.		18	19	20	21	22	18	19	20	21	22	18	19	20	21	22	
Block	3	159922	7891	20682	281267	6069	53307	2630	6894	93756	2023	11.54***	1.05	1.01	5.32*	0.73	3.86
Depth x Time	3	16737	36181	148817	131673	83007	5579	12060	49606	43891	27669	1.21	4.82*	7.24**	2.49	9.97**	3.86
Residual	9	41589	22540	61897	158467	24986	4621	2504	6855	17607	2776						
Total	15	218249	66612	231195	571407	114061											
LSD 5%		(108.7)	(80.1)	(132.4)	(212.3)	(84.3)											
A		139*	80	97	91*	123											
B		132*	130	167	167*	166											
C		372	135	195	412	144											
D		274	102	160	87*	172											

Table 3.*Analysis of Variance for Available P*

S.O.V	DF	S.S					M.S					F (calculated)					F(ta) 5%
Farm No.		18	19	20	21	22	18	19	20	21	22	18	19	20	21	22	
Block	3	1962.46	28665.7	6033.8	10112.4	9408.4	654.15	9555.5	2011.3	3370.8	3136.1	9.90**	2.46	2.55	3.72	1.31	3.86
Depth x Time	3	1014.97	5256.9	5312.4	878.3	2855.5	338.32	1752.3	1770.8	292.8	951.8	19.14***	13.41***	2.24	0.32	4.30*	3.86
Residual	9	30.57	6413.0	7110.4	8146.5	6560.1	34.17	712.6	790.0	905.2	728.9						
Total	15	3285.00	40335.7	18456.6	19137.3	18823.9											
LSD 5%		(9.35)	(42.70)	(44.96)	(48.13)	(43.19)											
A		40.8	117.8	71.00	65.8	47.4											
B		21.7***	20.3***	53.3	44.9	65.4											
C		17.5***	25.8***	31.5	5.7**	6.1**											
D		11.0***	15.2***	20.9**	8.9**	13.8*											

- *, **, *** means significant level
- s = significant
- ns = not significant
- A, B, C and D means of treatments (A= Jan, B=Apr, C=Jul and D=Oct.)
- ( )numbers between brackets means LSD values

F (ta) tabulated values of F distribution

9. Conclusion

Total and available P in the examined soils farms of Brack - Ashkada agricultural project after long - term application of chemical fertilizers (NPK), was not accumulated in high concentrations in the depth of up to 180 cm, which means no P had been leached to the surface or ground water. The results of this study showed that addition of P through an application of chemical fertilizer (NPK) to the soils farms of the project for more than 35 years, total and available P were not accumulated in high concentrations either in soil profiles or in different seasons for which the surface or ground waters could not be contaminated by P fertilizers.

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