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RESEARCH PAPER

Using Double Function Solubility Diagram to Study the Effect of Phosphorus Fertilizer on the Availability of Phosphorus in Different Soil Orders.

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ABSTRACT

A pot experiment was carried out during autumn growing season of 2016-2017 at the Gerdarasha field of College of Agriculture Engineering Sciences, to study the effect of three dominant soil orders (Mollisols (M), Vertisols (V) and Aridisols (A)), five levels of applied phosphorus fertilizer (0, 80, 160, 240 and 320 kg TSP ha^{-1}) and combination between them on the availability of phosphorus (P) using solubility diagram at booting stage and wheat yield. The factorial experiment was depended using a completely randomized design (CRD) with three replicates. The results indicated that the soil orders were affected the phosphorus status. It appears that the soil order studied was plotted between di calcium phosphate DCP and octa calcium phosphate OCP. The phosphorus availability of the studied soil orders can followed the following series Mollisols (M) > Vertisols (V) > Aridisols (A). The application of phosphorus caused an increase in phosphorus availability or caused shifting the treatments towards the more soluble forms of phosphorus Di calcium phosphate di hydrate (DCPD). The combination of soil orders and levels of applied phosphorus also influenced on phosphorus status. The application of 320 $kg.ha^{-1}$ of triple superphosphate to the Mollisols soil increased the phosphorus status toward the plotted between DCP and DCPD which were the most soluble forms of phosphorus in the phosphorus solubility diagram, which recorded the highest wheat yield (3.66) *M*g ha^{-1} in combination treatment (Mollisols-TSP_{320}). While the lowest grain yield (2.06) *Mg* ha^{-1} was obtain from (Aridisol-TSP_0) since this combination treatment was plotted between TCP and OCP or non-soluble and low soluble P-compounds.

KEY WORDS: Solubility Diagram; Phosphorus availability, Soil orders.
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INTRODUCTION :

hosphorus is an essential macronutrient for plant growth, and it is limiting crop production in many regions of the world in many agricultural systems in which the application of phosphorus to the soil is necessary to ensure plant productivity.

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The recovery of applied P by plant crops in calcareous soils during the growing season is very small, since more than 80% of the P becomes immobile and unavailable for plant uptake due to adsorption, or precipitation (Esmail, et al 2018; Rekani et al. (2017))

Iraqi soils are containing a large amount of calcium carbonate with slightly alkaline pH which causes chemical and physical fixation of 70-90% of applied phosphorus fertilizers as reported by Esmail (2012)

The previous studies conducted by Roy et al. (2006), (Shand, 2007) phosphorus was absorbed as the orthophosphate ion (either as $H_2PO_4^-$ or HPO_4^{2-})

depending on soil pH. As the soil pH increased, the relative proportion of $H_2PO_4^-$ and HPO_4^{2-} were increased. P is essential for growth, cell division, root lengthening, seed and fruit development, and

early ripening. It is a part of several compounds including oils and amino acids. The P compounds adenosine di phosphate (ADP) and adenosine triphosphate (ATP) act as energy carriers within the plants.

Phosphorus is one of the most important essential macro nutrients for plants, which contributes to numerous vital functions in plants like photosynthesis, energy transfer, respiration and cell division mentioned by Mam Rasul (2016), (Rasheed, 2019).
Iraqi soils illustration different degrees of development according to the dominant local conditions mainly climatic and geological conditions. The results of the morphological, physical and chemical soil properties indicated to the presence of five soil orders included, Aridisols, Entisols, Inceptisols, Mollisols, and Vertisols (Muhaimeed et al., 2014).
For studying the solubility equilibrium of phosphate the double function parameters consisting of phosphate potential $\log H_2PO^-_4$-pH and lime potential ($\log Ca^{2+} + 2pH$) were used to construct a solubility diagram for calcium phosphate minerals. It was assumed that the free ion activity of $H_2PO^-_4$ was controlled by lime potential and pH based on published solubility product (KSP). It was also assumed that the solubility of phosphate in calcareous soils is controlled by a solid phase of calcium phosphate minerals (Lindsay, 1979, Shang and Tiessen, 1998).

Solubility equilibrium experiments generally categorize soils into those with low pH in which iron (Fe) or aluminium (Al) phosphates control P solubility, or those with high pH in which P solubility is controlled by calcium (Ca) phosphates as reported by McDowell et al. (2003).

Phosphorus (P) retention and mobilization take place due to precipitation and adsorption in calcareous soils; however, it is not always easy to distinguish between the two mechanisms. Water-soluble P fertilizers applied to soil react with the soil constituents to form less soluble phosphates. When added to soil containing large amounts of calcium, soluble P is usually precipitated as di calcium phosphate or octa-calcium phosphate as mentioned by (Galaly, 2010, Rasul, 2016, Muhawish and Al-Kafaje, 2017b).

The high response for soil to orthophosphate O.P was recorded with respect to dicalcium phosphate dihydrate (DCPD) at high rate of application and within short and long period of O.P supply within 15and 60 days mentioned by Rahman (2013).

Rasheed, (2019) analysed 120 soils from the wheat grown fields the results indicated that soils that have more available P, the P- compounds were in the form of DCP and TCP but soils that have less available P the P compounds were in the form of TCP and HA (un soluble form).

The objectives of the present work were to investigate the interaction effect of phosphorus levels fertilizer application and soil orders, on grain yield of wheat and phosphorus availability using double function solubility diagram. in calcareous soil.

1.MATERIALS AND METHODS

The studied soils included three dominant soil orders Mollisols (M), Vertisols (V) and Aridisols (A) according to United State Department of Agriculture (USDA) soil Taxonomy (Nachtergaele, 2001), and Global Positioning System (GPS) reading of the selected locations were recorded from **Table (1).**
Soils were included three dominant soil orders which were collected from Hawler, Sulaimani and Duhok governorates from the depth of 0-30 cm, then transported to Gerdarasha field then air-dried and sieved by 4mm sieves for pot experiment. On 24/11/2016 seeds of wheat (*Triticum aestivum* L) was planted.

Table 1. Classification of the studied soils along with their geographic coordinates.

Governorate	Location	Order	Elevation above mean sea level (Altitude (m))	GPS Reading	
				N	E
Hawler	Harrier	Vertisols	619	$36^{o}32.793'$	$44^{o}18.308'$
	Hujran	Mollisols	787	$36^{o}16.387'$	$44^{o}17.796'$
	Makhmur	Aridisol	271	35.7773774^{o}	43.562006^{o}
Duhok	Semeel	Vertisols	569	36.867697^{o}	42.969343^{o}
	Zawita	Mollisols	967	36.900077^{o}	43.146660^{o}
	Fayda	Aridisol	372	36.712639^{o}	42.971565^{o}
Sulaimani	Bakrajo	Vertisols	731	35.529235^{o}	45.335274^{o}
	Halabja	Mollisols	501	35.300880^{o}	45.954688^{o}
	Kfry	Aridisol	177	34.690550^{o}	44.864398^{o}

Wheat (*Triticum aestivum* L) is one of the most important cereal grain crops for human nutrition due to high protein content (9% - 15%) and has been cultivated in calcareous soil in the arid and semi-arid region. directly planted in each pot, using factorial (CRD) with three replicates. Each soil order was taken from three locations and regarded as replications. The weight of soil per pots was 10 kg of air-dried soil.

Five levels of triple super phosphate fertilizer (0, 80, 160, 240 and 320 kg TSP ha^{-1}) which equivalent to (0, 0.2, 0.4, 0.6 and 0.8 g TSP for 10 kg^{-1} soil (pot) in three dominant soils orders (M, V, and A), while fixed amount of urea (0.6 g. urea 10 kg^{-1} soils) which equivalent to (240 kg urea ha^{-1}) was added to all pots. After the seeds were planted the pots were watered to field capacity, while subsequently irrigation depended on weighing method whenever needed. The irrigation was done after depletion 75 % of available water depending on weighing method. The soil samples were taken at booting stage for preparing solubility diagram

2.1.Chemical and physical properties

The soils were air-dried, and sieved by 2 mm sieve and stored for laboratory analysis, **Table (2)** shows some chemical and physical properties for the main soil order at different locations.

The soil analysis included Electrical Conductivity, soil calcium carbonate content ($CaCO_3$) hygroscopic moisture content, moisture at field capacity (FC) and wilting point (W.P), Particle size distribution, Soil pH, and organic matter content which were determined according to the standard methods mentioned by (Bashour and Sayegh, 2007). Used the regression equations to estimate the field capacity and wilting point depending upon the clay fraction % .(Klute, 1986, Karim, 1999).

Table 2. The mean for some chemical and physical properties for dominant soil orders Mollisols, Vertisols, Aridisol in Hawler, Sulaimani and Duhok.

Treatment	Particle Size Destitution			hygroscopic moisture%	FC	WP	SP	$CaCO_3$	pH	EC
					%			g kg^{-1}		dS m^{-1}
Mollisols Hawler	Sand	23.00	Silty loam	5.05	21.25	11.59	39.52	300	7.39	0.36
	Silt	56.93								
	Clay	20.06								
Mollisols Sulaimani	Sand	11.41	Siltyloam	6.00	30.35	19.62	56.45	230	7.31	0.54
	Silt	45.59								
	Clay	43.00								
Mollisols Duhok	Sand	17.62	Siltyclay	4.86	30.25	19.53	56.27	210	7.54	0.485
	Silt	39.63								
	Clay	42.75								
Vertisols Hawler	Sand	45.24	Siltyclay	4.24	32.17	21.22	59.83	300	7.47	0.41
	Silt	7.19								
	Clay	47.57								
Vertisols Sulaimani	Sand	4.32	Siltyclay	4.71	35.37	24.04	65.78	268	7.464	0.31
	Silt	40.05								
	Clay	55.63								
Vertisols Duhok	Sand	3.50	Siltyclay	9.20	33.50	22.39	62.30	240	7.47	0.37
	Silt	45.58								
	Clay	50.92								
Aridisol Hawler	Sand	22.02	Clay loam	2.34	24.01	14.03	44.65	488	7.78	0.51
	Silt	50.96								
	Clay	27.02								
Aridisol Sulaimani	Sand	14.37	Siltyclay loam	3.78	25.76	15.58	47.92	460	7.72	0.45
	Silt	54.18								
	Clay	31.45								
Aridisol Duhok	Sand	22.11	Clay loam	2.89	27.78	17.35	51.67	590	7.92	0.46
	Silt	41.36								
	Clay	36.53								

2-2-Determination of soluble Phosphorus for solubility diagram:

Phosphorus in soil has been extracted by using distilled water with 0.01 *M* KCl and determined spectrometric ally according to Murphy and Riley (1962) as described in Black, (1980) using spectrophotometer model (Shimadzo at wave length 880nm). The chemical analysis and calculations for drawing solubility diagram were recorded in **table (3).**

2-3-Phosphate solubility Diagram :

Double function parameters consisting of phosphate potential log$H_2PO^-_4$-pH and lime potential (log Ca^{2+} + 2pH) were used to construct a solubility diagram for calcium phosphate minerals. It was assumed that the free ion activity of $H_2PO^-_4$ was controlled by lime potential and pH based constant of solubility product (Ksp). It was also assumed that the solubility of phosphate in calcareous soils is controlled by a solid phase of calcium phosphate minerals (Lindsay, 1979).

Table 3. pH, (calcium and phosphorus activity), P-potential and lime potential for studied combination treatments.

Code	pH	Soluble P	Ca	P	Ca	Log		Log	Log
		mg L^{-1}	mg L^{-1}	mole L^{-1}	mole L^{-1}	$H_2PO^-_4$	Log Ca^{+2}	Ca^{+2}+2pH	$H_2PO^-_4$ -pH
Mollisols TSP0	7.53	0.11	64.00	3.66E-06	0.0016	-5.43615	-2.79588	12.26412	-12.9662
Mollisols TSP80	7.55	0.13	64.00	4.11E-06	0.0016	-5.38566	-2.79588	12.30412	-12.9357
Mollisols TSP160	7.88	0.17	108.00	5.34E-06	0.0027	-5.2728	-2.56864	13.18136	-13.1478
Mollisols TSP240	7.84	0.28	50.00	9.14E-06	0.00125	-5.03906	-2.90309	12.77691	-12.8791
Mollisols TSP320	7.87	0.36	111.00	1.15E-05	0.002775	-4.93761	-2.55674	13.18326	-12.8076
Vertisols TSP0	7.58	0.07	68.00	2.3E-06	0.0017	-5.63881	-2.76955	12.39045	-13.2188
Vertisols TSP80	7.61	0.10	108.00	3.17E-06	0.0027	-5.49946	-2.56864	12.65136	-13.1095
Vertisols TSP160	7.66	0.13	72.00	4.21E-06	0.0018	-5.37557	-2.74473	12.56927	-13.0326
Vertisols P240	7.65	0.17	84.00	5.56E-06	0.0021	-5.25527	-2.67778	12.62222	-12.9053
Vertisols TSP320	7.80	0.29	92.00	9.34E-06	0.0023	-5.0298	-2.63827	12.96173	-12.8298
Aridisols TSP0	7.64	0.06	122.00	1.97E-06	0.00305	-5.7056	-2.5157	12.7643	-13.3456
Aridisols TSP80	7.86	0.07	164.00	2.29E-06	0.0041	-5.63946	-2.38722	13.33278	-13.4995
Aridisols TSP160	7.88	0.08	160.00	2.62E-06	0.004	-5.58115	-2.39794	13.36206	-13.4612
Aridisols TSP240	7.88	0.15	132.00	4.7E-06	0.0033	-5.32767	-2.48149	13.27851	-13.2077
Aridisols TSP320	7.89	0.16	140.00	5.06E-06	0.0035	-5.29546	-2.45593	13.32807	-13.1875

3-RESULTS AND DISCUSSION

The results in **Figure. (1)** showed that the soils that have more available phosphate shifted towards DCP the nearest point to DCP was Mollisols, it means an increase in the availability of phosphorus at booting stage for a wheat plant, but for Vertisols located behind Mollisols it means the solubility phosphorus in Vertisols less than Mollisols. On the other hand, Aridisols located near OCP line. It has appeared that the studied soil order plotted between DCP and OCP the first one (DCP) is the more soluble form of P in comparing with OCP. The phosphorus availability of them can follow the following series Mollisols > Vertisols > Aridisols.

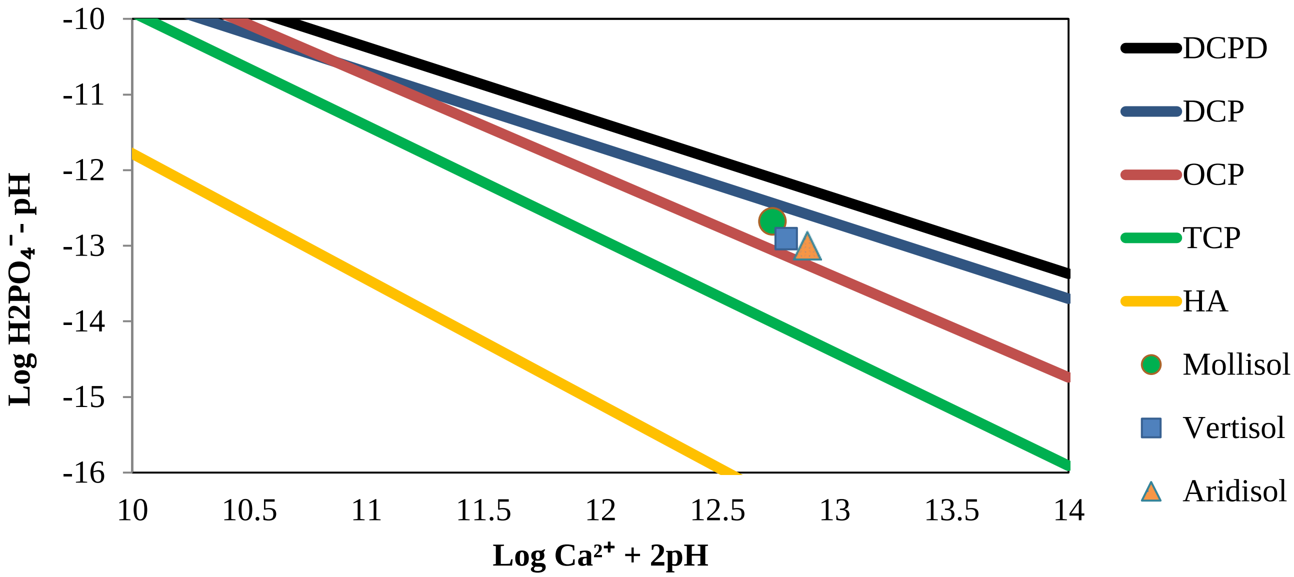

Figure 1. Effect of soil orders on phosphorus status at booting stage for wheat plant

This may be due to higher organic matter content of Mollisols in comparing with other soil orders as recorded in **table (4),** The organic matter is considered as a very important parameter of soil fertility and productivity, however it provides nutrients to the soil, improves water holding capacity and helps the soil to maintain better aeration and soil quality for seed germination and plant root development reported by (Esmail et al., 2018) which could cause hydrolysing P minerals due to releasing organic acids from organic matter reported by Rahman (2013). Or the increase in phosphorus availability at booting stage may be due to the amount of rainfall which may cause dissolving of P due to it is acidic pH (5).

On the other hand, the series of the organic matter content of the soil orders were as follow: M > V >A (31.53, 22,.38, 9,64) mg kg^{-1} **table (4)**. This explains the above series for phosphorus availability depending on solubility diagram. Organic matter may also increase phosphorus solubility through calcium chelating which causes either a permanent or a temporary delay in the formation of basic calcium phosphate.

Table 4.Organic matter content in the soil orders

Orders	Organic matter
	g kg^{-1}
Mollisols	31.53
Vertisols	22.38
Aridisols	9.64

The data analysis in the **table (5)** revealed that the high mean yield value were (3.087, 2.84, 2.71) *Mg* ha^{-1} recorded in soil orders (Mollisols, Vertisols, and Aridisols) respectively explains the above results for phosphorus availability depending on solubility diagram. In Aridisols the amount $CaCO_3$ caused decrease the solubility of phosphorus as mentioned by (Muhawish and Al-Kafaje, 2017a, Rahman, 2013), phosphorus (P) retention and mobilization take place due to precipitation and adsorption in calcareous soils; however, it is not always easy to distinguish between the two mechanisms.

Table 5. Effect of soil orders of wheat yield	
Orders	grain yield *Mg* ha^{-1}
Mollisols	3.087
Vertisols	2.84
Aridisols	2.71

Water-soluble P fertilizers applied to soil react with the soil constituents to form less soluble phosphates. When added to soil containing large amounts of calcium, soluble P is usually precipitated as di calcium phosphate or octacalcium phosphate **Figure (2)** shows the effect of levels applied phosphorus on soluble of phosphorus at the booting stage of wheat. Phosphorus application caused shifting the points towards di-calcium phosphate (DCP) and di-calcium phosphate di-hydrate (DCPD) which are more soluble phosphorus compounds. It has appeared from phosphorus solubility diagram, that TSP_0 located on the low soluble form of phosphorus compounds (TCP). While the soils fertilized with TSP_{80}, TSP_{160} and TSP_{240} were plotted between low soluble (OCP) and soluble phosphorus compound (DCP) or application of mentioned TSP levels caused an increase in the availability of phosphorus. On the other hand application of 320 kg TSP ha^{-1} caused shifting the P-status towards the more soluble phosphorus compound (DCPD) or plotted between (DCP and DCPD).

The wheat grain yields were (2.54, 2.85, 3.29) *Mg* ha^{-1} for treatments (TSP_{80}, TSP_{160} ,and TSP_{240}) respectively. The results in figure (2) also explained that the application of different levels of phosphorus caused shifting the points towards di-calcium phosphate (DCP) and di-calcium phosphate di-hydrate (DCPD) which were more soluble phosphorus compounds, it is appeared from phosphorus solubility diagram that the best level was application of 320 kg TSP ha^{-1}, which located between two more soluble phosphorus compounds (DCPD and DCP) caused increase the grain yield to (3.44) *Mg* ha^{-1}, and the lowest yield from TSP_0, which located on OCP line, or (1.51) times increase in grain yield compeering with control reported by (Galaly, 2010, Rasheed, 2019, Rekani et al., 2017). **Figure (3)** illustrated effect of levels applied TSP fertilizers on P-availability at booting stage of the

wheat plant.

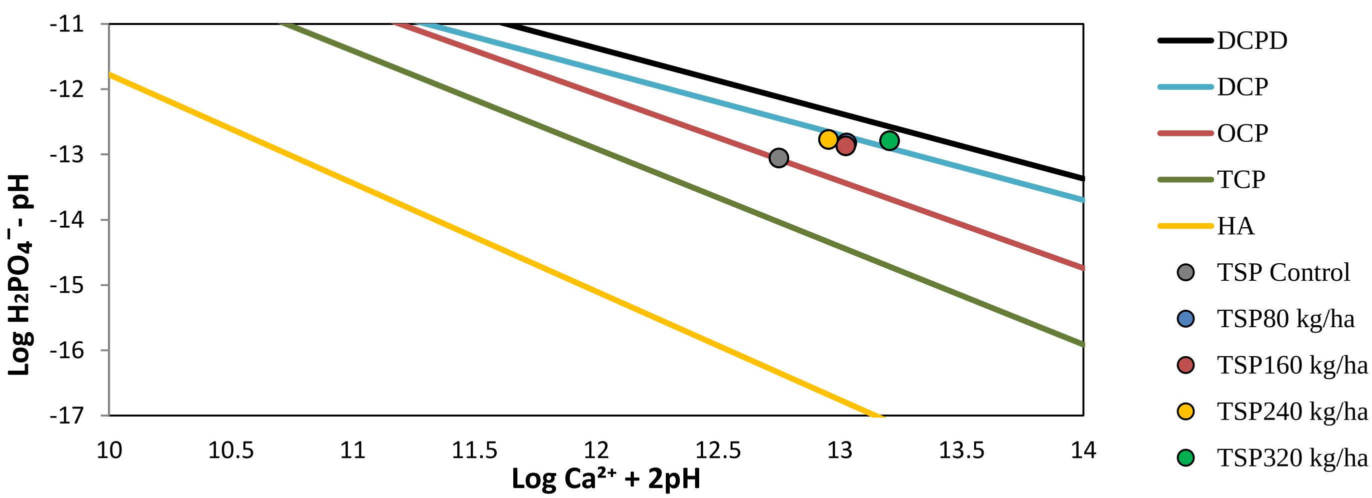

Figure 3. Shows the effect of levels of applaied phosphorus on availability of phosphorus at booting stage of wheat.

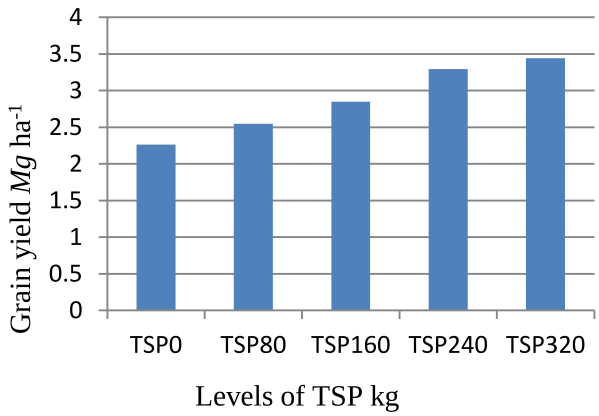

Figure 3. Efect of levels phosphorus on grain wheat

The results in **figure (4)** indicated the effect of combination treatments of phosphorus solubility status. The phosphorus status was divided into four groups as follows:

First group included 6 combination treatments(Mollisols-TSP_0, Vertisols-TSP_0, Aridisols-TSP_0, Mollisols- TSP_{80}, Vertisols-TSP_{80} and Vertisols-TSP_{160}), which were plotted between OCP and TCP or less soluble group since the phosphorus compounds were OCP or very low soluble TCP.

Second group included only one combination treatment which located on OCP line was (Vertisols -TSP_{240})

The third group was represented 7 combination treatment (Aridisols-TSP_{80}, Mollisols-TSP_{160}, Aridisols-TSP_{160}, Mollisols-TSP_{240}, Aridisols-TSP_{240}, Vertisols-TSP_{320} and Aridisols-TSP_{320} which were located between OCP and DCP this group shifted towards DCP.

Fourth group included only one combination treatment (Mollisols-TSP_{320}) which plotted between soluble phosphorus compounds (DCP and DCPD) this regards as the most soluble phosphorus status.

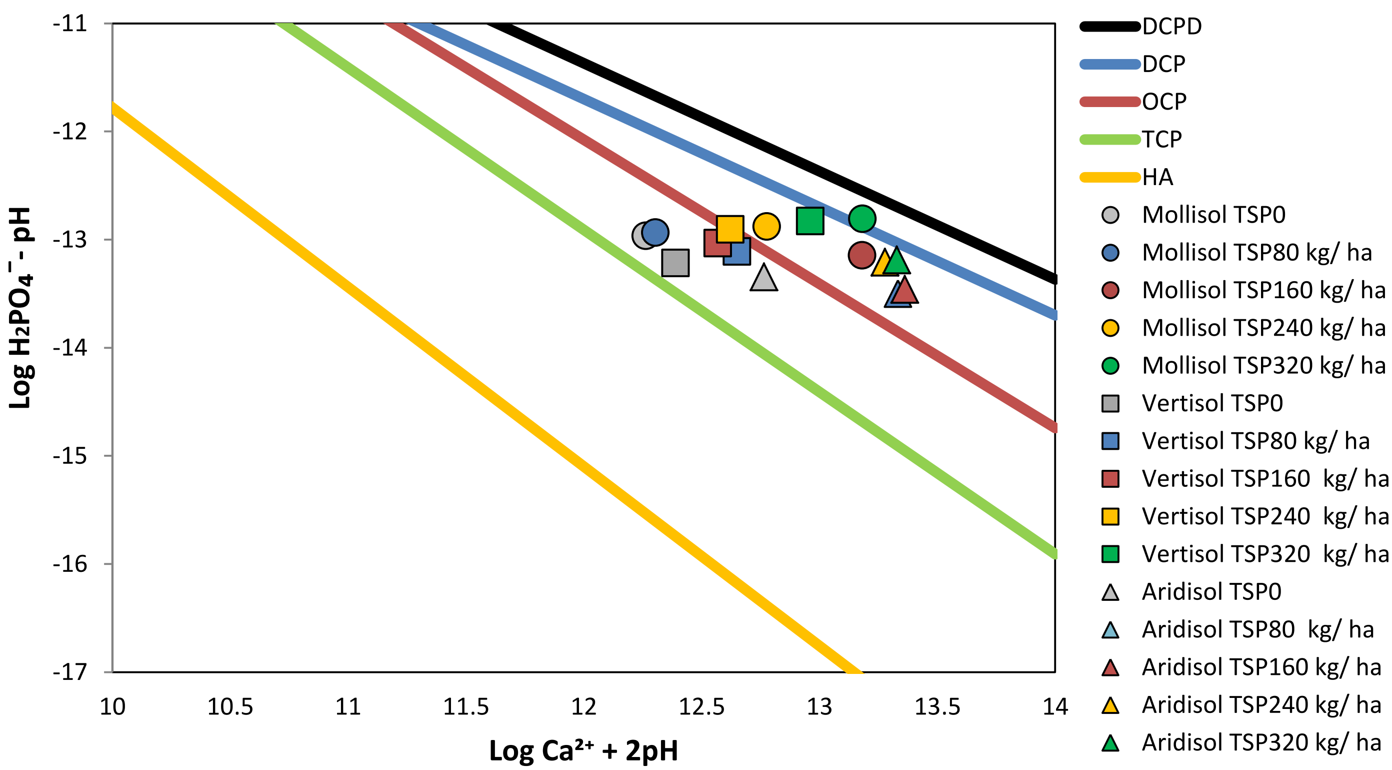

Figure 4. Combination effect soil orders and levels of applied phosphorus on the P- solubility equiliberia at booting stage of wheat plant

The wheat grain yield for the first group were (2.38, 2.38, 2.06, 2.78, 2.55 and 2.88) Mg ha-1 respectively, which the yield for the combination treatment belongs to the second group was (3.06) Mg ha-1, while, the yield for the third group were (2.28, 3.09, 2.58, 3.52, 3.29, 3.34,and 3.31) Mg ha-1 respectively.

On the other hand the highest yield value (3.66) Mg ha-1 was recorded from combination treatment which plotted between DCP and DCPD this may be due to high available phosphorus in the fourth group or the combination treatment of (Mollisols-TSP320) (Figures 4 and 5)

In general moving or shifting the combination treatment toward more soluble phosphorus compound caused an increase in wheat yield due to the role of phosphorus in seed formation and growth mentioned by (Galaly, 2010, Rahman, 2013, Rasheed, 2019, Ahmed and Khoshnaw, 2019). While, the results provide information about the relation between P availability and the dominant soil orders.

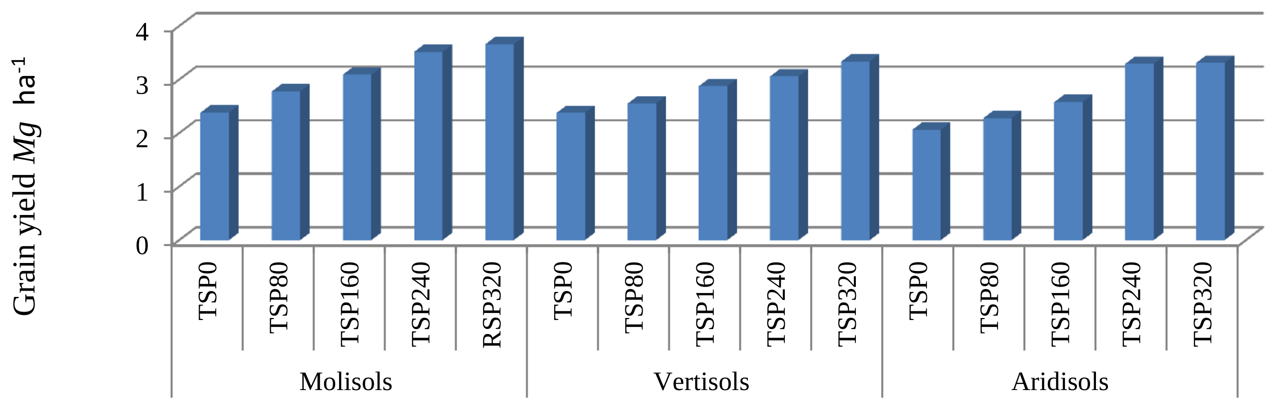

Figure 5. Combination effect of soil orders and levels of applied phosphorus on grain wheat

CONCLUSION

The studied soil orders, levels of applied phosphorus and their combination had a great effect on phosphorus status and wheat yield, due to their effect on forming different phosphorus compounds range between non-soluble to the soluble form of phosphorus compound or from Hydroxyapatite to Di- calcium phosphate di hydrate as explained by solubility diagrams for phosphorus. Application of different levels of phosphorus caused the shifting towards di-calcium phosphate (DCP) and di-calcium phosphate di-hydrate (DCPD). The treatment combination Mollisols TSP_{320} was recorded the highest grain yield.

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