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Adsorption Characteristics of Phosphorus on Calcite, Mg Calcite and Calcareous Soils: Effect of Dissolved Organi Carbon

Maher E. Saleh[1*], Eman H. El-Gamal[2], Mahmoud A. Kamh[1], Ahmed F. Saad[1]
[1]Department of Soil & Water Science, Faculty of Agriculture, Alexandria University pos
code 21545 El-Shatby, Alexandria, Egypt;
[2]City of Scientific Research and Technological Applications, New Burg El-Arab, Egypt;
* Corresponded Author, E mail: maher.saleh@alexu.edu.eg

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ABSTRACT

Influence of incorporated magnesium (Mg) into synthetic calcite and dissolved organic carbon (DOC) on P
by synthetic calcite (SC), synthetic Mg-calcite (SMC), and some selected calcareous soil samples were exar
different laboratory experiments. The sorption of P onto SC or SMC was time dependent particularly by SMC.
of reaction, 81% of P was removed from solution by SC which represented 9 folds of that removed by SMC. The
progress is characterized by C shape for SC and S shape for SMC, indicating retardation effect of Mg. Sorpt
throughout 24 h reaction period was significantly positive correlated with the equilibrium solution pH (r = 0.90
incorporated into SC reduced the adsorption of P onto calcite and/or hindered nucleation and crystal growt
precipitated P. Soils were selected based on Mg/Ca ratio of their carbonate fraction. After 24 h of the sorption, re
P by soil samples ranged between 22 to 50% of the added P that accompanied with slight increase of pH ranged fr
to 0.31 units. The multivariable regression analysis showed that not only calcium carbonate is the sole factor cont
sorption in calcareous soils, but also soil texture, ionic strength and organic matter are important factors.
dissolved organic carbon (DOC) of poultry manure (PM), wheat straw (WS), and faba bean straw (FBS) inh
sorption by SMC and soils containing 49.8 and 40% total carbonate while, had no effect on P sorption by SC a
containing 30 and 19% carbonate . It seems that incorporation of Mg into calcite and addition of DOC can en
availability through decreasing P adsorption and/or precipitation and can also add a value to the effect of DOC.

Key words: Carbonate reactivity, Mg/Ca ratio, synthetic calcites, crop residue extracts.

INTRODUCTION

Calcareous soils cover more than 30% of the earth surface, mainly in arid and semi-arid regions, and characterized by the presence of calcium carbonate in the parent material and by a calcic horizon, a layer of secondary accumulation of carbonate (usually Ca or Mg) in excess of 15% calcium carbonate equivalent and at least 5% more carbonate in the underlying layer (United States Department of Agriculture, 2014). Calcareous soils containing amounts of calcium carbonate to affect distinctly the soil properties related to plant growth, whether they are physical, such as the soil-water relations, and crusting, or chemical such as the availability of plant nutrients (FAO, 2000).

Addition of P fertilizers to calcareous soils resulted in a series of chemical reactions with soil solids that decrease its solubility, a process named as P retention. Therefore, low availability of phosphorus is considered one of the major problems facing the fertilization management in calcareous soils. The mechanisms of P retention involved adsorption of P on carbonate surfaces and precipitation of Ca phosphates (Samadi, 2006; Wandruszka, 2006; Sanches, 2007). These reactions lead to immobilization of phosphorus and d
its phytoavailability (Samadi and Gilkes,
Amer *et al*., 1980). The immobilization c
calcite depends mainly on calcite-surface pr
such as specific surface area and the gra
roughness (Berg *et al*., 2002 and 2004)
factors, rather than carbonate content, such
(Sanches, 2007; Karageorgiou et al.,
associated anions in soil solution (Amer *et al*
and dominance of Ca^{2+} and Mg^{2+} in soil
(Wandruszka, 2006), can also aff
immobilization in calcareous soils.

The properties of solid carbonates form
soil may affect the P immobilization in cal
soils where $CaCO_3$ which containing
impurities) in structure lattice of calcium ca
decreased P adsorption (Amer *et al*., 198
studies interested with the effect of
replacement of Ca by divalent metal ions
Mn and Zn (Temmam *et al*., 2000), Co, Cd,
Mg (Elzinga and Reeder, 2002), Mn (Nas
Aboukais *et al*., 1998), Mg (Mavromatis
2013; Jimenez-Lopez *et al*., 2004; Stanley
2002) and Sr and Mg (Nielsen *et al*., 2013

calcite lattice and its influence on reactive affinity toward the nutrient and/or contaminant ions .

Factors such as soil organic matter and applied organic amendments can play an inverse role and facilitate the availability of P to crops grown in calcareous soils (Wright *et al*., 2008; Wandruszka, 2006). Animal manures and crop residues have been utilized as beneficial soil amendments for centuries and as a source of essential nutrients as well as physicochemical benefits to soils (Sims and Pierzynski, 2000). Dissolved organic carbons (DOC) have an important roles in delaying the adsorption process on soil colloid surfaces by forming stable complexes with adsorption surfaces or in competing with adsorbed ions on adsorption sites as organic ligands (Guppy *et al*., 2005 and Genza *et al*., 2004). The DOC speciation using exchange and chelating resins showed that DOC may occur in cationic, anionic or neutral forms depending on pH and Eh status of soil solution (Saleh, 1994). Consequently, DOC amendments can alter the chemistry of P in pure carbonates or calcareous soils environments. The Objectives of the current study are focused on (1) sorption reactions of phosphorus onto synthetic calcite (SC), synthetic Mg-calcite (SMC) and calcareous soils to investigate the role of Mg substitution in the lattice of calcite and calcareous soil on P retention and, (2) the effect of DOC application on the behavior of phosphorus in both systems.

MATERIALS AND METHODS

Synthetic carbonates preparation

Analytical reagent-grades: calcium carbonate, magnesium carbonate, hydrochloric acid and sodium hydrogen carbonate ($NaHCO_3$) were used to synthesize the calcite and magnesian calcite. Carbonate salts were reacted with the acid to form chloride forms of calcium and magnesium. Stoichiometric volumes of Ca^{2+}, Mg^{2+} and HCO_3^- solution were used to precipitate calcite (SC) or Mg-calcites (SMC). The SC was precipitated by stirring (500 rpm) of one equivalent per liter (1 mol L^{-1}) $NaHCO_3$ with 0.5mol L^{-1} $CaCl_2$ at ambient temperature (23 - 25^oC) for 24 h. Same procedure was used to precipitate SMC (6.72 mole % Mg) by stirring 1 mol L^{-1} $NaHCO_3$ with 0.5 mol L^{-1} $CaCl_2$ + $MgCl_2$ (Devery and Ehlmann, 1981). Precipitated SC and SMC were separated from solution by sedimentation, washed three times with distilled water, and then dried at 100 ^oC for 24 hr

Half g of SC or SMC samples were shaken with 100 ml distilled water in 250 ml-conical flasks, covered with parafilm having small holes for equilibration with atmospheric CO_2, for 1 h (Amer *et al*., 1985). Then, Zeta potential (ZP) was determined using a micro electrophoresis apparatus (Zeta meter Inc., New York) employing a Pt-Ir cathode and a Mo anode. Results of ZP measurements showed no charges of both ca samples (ZP = 0.0 mV). Specific surface are for both SC and SMC were measured with Pe apparatus (Research Laboratory, Tapiola, F Measurements were based on the determina flow resistance through the powdered sampl specific surface area of the prepared SC an were 17,680 and 33,460 m^2g^{-1}, respectively.

Soil samples characterization

Eighteen calcareous soil (*typichaplocalcids*) were collected from th Western Egypt. The collected samples w dried, ground and sieved through a 2-mm Electrical conductivity EC and water solub were measured in the saturated soil paste according to Rhoades (1982a). The p measured in soil:water suspension (1:2.5). T content of calcium carbonate equivaler determined by calcimeter method (Nelson, Soil organic matter was determined b oxidation according to Walkley-Blake (Nelson and Sommers, 1982) and a phosphorus was determined by Olsen metho $NaHCO_3$, pH 8.5) and followed by measuri in solution by the ascorbic acid method (Ol Sommers, 1982). Cation exchange capacity was determined in soils using sodium displacement method (Rhoades, 1982b). size distribution analysis was determined hydrometer method (Gee and Bauder, 1986).

Three fractions of Ca^{2+} and Mg^{2+}: water (F1), exchangeable (F2), and carbonate bour were also investigated in all soil sample grams of soil were shaken with 30 ml distille in G 24 Environmental incubator shake Brunswick Scientific Co., New Jersey, USA rpm for 30 min (Bhattacharyya et al., Suspension was then centrifuged at 2000 rpm min followed by filtration through filter Whatman no 42 to obtain the clear soluti water soluble fraction. To determin exchangeable fraction, the residue soil was with 30 ml of 1.0 M of sodium acetate (adjusted to pH 8.1 for 2 h follow centrifugation and filtration as above. The was then treated with 30 ml of 1.0 M adjusted to pH 5 and shaken for 5 h, cent and filtered as above (Tessier et al., 1979; Al and Parker, 1999; Bhattacharyya et al., 200 concentrations of Ca^{2+} and Mg^{2+} in th solutions which obtained from each fractio measured using ICP-OES Spectrometer (ICAP 6000 Series, UK). All fractions were c at ambient room temperature.

Source and Preparation of Dissolved Carbon (DOC)

Poultry manure (PM), wheat straw (W faba bean straw (FBS) were used as a so dissolved organic compounds (DOC). Th organic residues were collected from the local markets then air-dried and cut into small pieces and stored in plastic containers at 4.0 ^oC. 10.0 Ten g of residues were shaken in 500-mL conical flasks containing 200.0 mL distilled water (5% w/v) for 24 h at 150 rpm using horizontal shaker and then centrifuged at 5000 rpm for 20 min, the supernatant was filtered through filter paper 0.45 µm (Gelman Sciences, USA). Concentration of total dissolved carbon was determined by Walkley–Black Wet Combustion Method (Nelson and Sommers, 1982). pH was measured in the clear solutions using pH meter (WTW inLab pH/Ion 735).Water soluble P in the clear solutions was analyzed colorimetrically by the ascorbic acid-molybdate blue method (Murphy and Riley, 1962).

Adsorption of phosphate

By SC and SMC

Phosphate retention by SC and SMC samples was determined. Duplicate (0.250 g) of samples were placed in 250-ml conical flask and 50 ml 0.001 mol L^{-1} KH_2PO_4-P (in 0.02 mol L^{-1} KCl as background electrolyte) were added. The flasks were covered with parafilm having two small holes for equilibration with atmospheric CO_2 and shaken in an incubator shaker at 200 rpm for 5 min, and 2, 4, 6, 12, and 24 h. The shaking was carried out at constant temperature (30 ± 1ºC). After the equilibrium, pH of the suspension was measured then samples were centrifuged at 4000 rpm for 20 min, and filtered using filter paper whatman 42. Phosphorus was determined in the clear solution as mentioned above.

By Calcareous Soils:

The above experiment was repeated with calcareous soil. Duplicate (1.000 g soil) samples were shaken with 50 ml 0.001 mol L^{-1} KH_2PO_4-P in presence of 0.02 mol L^{-1} KCl as a background electrolyte. After the shaking periods, pH was measured in suspensions. EC and P were measured in the clear solution after the centrifugation and filtration as mentioned above.

The phosphorus concentration retained in the adsorbent phase was calculated by subtracting equilibrium soluble P from the initial concentration of added P (6200 µg gm^{-1} $CaCO_3$ or 1550 µg gm^{-1} soil) as follow:

$$q_e = \frac{(C_i - C_e)V}{W * v} \qquad (1)$$

Where :Ci and Ce are the initial and equilibrium solution-P concentrations (mgL^{-1}), respectively; V is the volume of the suspension, W is the weight (g) of the adsorbent, and V is volume of aliquot.

Effect of Dissolved Organic Carbon

To investigate the effect of DOC on P adsorption by SC, SMC and four selected calcareous soils (represent the wide spectrum of total carbonate content and Mg/Ca ratio), adsorption expe were conducted using the above me concentration of P and solid to solution presence of 1000.0 µg DOC g^{-1} adsorbent. experiments, a stirred batch technique was Constant Temperature Circulating Pump w to drive H_2O through jacketed Pyrex 1 reaction vessel. The temperature was maint 30^{o}C and monitored by thermometers subm the reaction medium. The reaction vessel sealed by covers that have holes for pH el thermometer, sample withdrawing and equil with atmospheric CO_2. After each period, suspensions and P concentration in clear s were obtained by same method mentioned ab

The results from the different experime statistically analyzed using SAS (version 8 Microsoft Office Excel 2007 programs.

RESULTS AND DISCUSSION

Soils Characterization

The results of physicochemical prope studied soils are presented in Table (1). It that sandy loam (SL) and sandy clay loam (S the dominant soil textures. One soil collected from EL-Banger village 26 (0-20 a loamy sand (LS) texture. The highest v available P were found in two soils in EL- village 2 and EL-Banger village 1 (48.8 - 35 kg^{-1} soil), respectively. Carbonate contents varied from 19.11% (Fukah 1) to 55.18 Banger village 25, at 55-90 cm). Soil organi (OM) was very low in all soils except EL- village 1 was 2.24%. The high value of C associated with soil that has the highest co OM (EL-Banger village 1). On the othe similar CEC content was found in the soils have low values of $CaCO_3$ content.

Chemical fractionation of calciu magnesium in studied soils are listed in Ta The results showed that soil solutio characterized by narrow Mg/Ca ratio (1:0.9 - in about 50% of tested soils. Ma concentration was found by about 10 folds in one sample (at the depth of 0-20 cm, villa Bangar Essokkar) which could refle occurrence of dissolved Mg-containing associated with calcite in soils. The extre value of Mg/Ca ratio (0.05) obtained at (45- horizon of village 26 could reflects accumulations. Arnaud (1979) stated that p of magnesium-bearing calcites in se carbonate accumulation layers of soils is s be associated with soluble Mg^{2+}/Ca^{2+} ratios or greater in that layers. The molar ratio of in the soil carbonate fraction reveale occurrence of Mg ions in soil carbonate ranged from 5 to 50 mole percent (Table 2 explains the probability of presence of ma calcites and dolomite minerals.

Table 2: Mg/Ca mol ratio in soluble (F1), exchangeable (F2) and carbonate bound (F3) forms selected soil samples.

Location	Depth, cm	F1	F2	F3
EL-Banger val. 1	0-30	0.50	0.50	0.37
EL-Banger val. 2	0-25	0.33	0.91	0.19
EL-Banger val. 23	0-30	0.36	0.71	0.15
EL-Banger val. 24	0-30	1.00	1.00	0.34
	30-70	0.63	1.25	0.34
EL-Banger val. 25	0-20	0.63	0.83	0.09
	20-55	0.77	0.67	0.42
	55-90	1.11	1.43	0.23
	90-130	0.59	1.43	0.23
	130-150	0.59	1.43	1.00
EL-Banger val. 26	0-20	10.00	1.00	0.42
	20-45	0.91	0.91	0.29
	45-70	0.05	0.91	0.19
	70-105	2.50	0.91	0.19
	105-130	0.38	2.00	0.05
Fukah 1	0-40	3.33	3.33	0.23
Fukah 2	0-50	0.28	1.67	0.63
EL-Hammam	0-30	0.56	0.67	0.10

These results investigate the probability of Mg substitution of Ca ions in calcite lattice during the carbonate formation or dissolution – precipitation reactions in calcareous soils. The results of Mg/Ca ratio in the listed different fractions (Table 2) indicate that the chemistry and mineralogy of calcareous soils under investigation suggest that the carbonate materials were deposited as a continuous unit and subsequently modified (Hutton and Dixon, 1981). On the other hand, occurrence of Mg ions in all tested soil samples is an indicator on marine deposit origin of these soils where Muller *et al.*, (1972) stated that the only difference between non-marine and marine carbonates is the absence of calcite in the marine environment. The dissolution of both calcite and dolomite within the solum and the precipitation of only calcite in the developing carbonate horizons lead to a buildup of Mg^{2+} in the soil solution. If leaching depth is considerably below the carbonate horizon, the secondary calcite is Mg free. The inconsistent trends in Mg/Ca molar ratio in all fractions of soil profiles can be interpreted by geologic (digenesis) the non-pedogenic formations of carbonate minerals in the soils and most of occurred minerals are secondary origin types (Arnaud and Herbillon, 1973). Behavior of applied P will varied from site to site depending on the carbonate reactivity as a result of formation and diagenesis of Ca-Mg carbonates in each site.

Characterization of Dissolved Organic (DOC)

The chemical characteristics of DOC are presented in Table (3). FBS had the value of DOC (6.5 %) followed by WS (2.5 PM (1.9 %). It was observed that PM ha values of pH, EC, dissolved and total phos while the lowest values were found in WS pH (7.56).

Adsorption of P by calcite and Mg-calcite

The changes of pH and P sorption percent w hours of P reactions with synthetic calcite (S Mg-calcite (SMC) are shown in Table 4. was significantly more effective in P sorpti SMC. The P removal from the equilibrium was time dependant particularly with SMC the first two hours, nearly 60% of the addec removed by SC which represented 10 folds removed by SMC. A rapid reaction between solution and $CaCO_3$ is usually ascril adsorption on its surface (Griffin and Jurinal Amer and Mostafa, 1981), Amorphous phosphate formation (ACP) has also its role the first 5 minutes especially at high pH (Ka Mostafa., 1993). The distinction between ads and precipitation process is not clear (Sposito since the chemical bonds formed in both can similar.

Table 3: Some selected characteristics of the DOC of studied organic residues.

DOC Source	DOC g kg^{-1}	pH	EC, dS m^{-1}	P, $mgkg^{-1}$	
				WSP	TP
PM	0.190	8.16	6.00	903.55	7000
WS	0.250	7.56	5.46	77.50	2400
FBS	0.650	6.84	5.50	812.70	5200

Table 4: pH, EC, and P Sorption with time onto SC and SMC.

Treatment	SC		SMC	
Reaction time h.	pH	Sorbed P (%)	pH	Sorbed P (%)
0.08	7.58	3.50	7.62	3.50
2	7.87	59.40	7.64	5.80
6	7.84	81.60	7.63	9.00
12	7.84	92.80	7.89	69.20
24	8.04	96.90	8.07	81.10

Results also showed that the removal of P was associated with increase of pH values through the 24-h reaction period (Fig. 1). Regardless the type of sorbent (SC or SMC), the increments in sorbed P were statistically correlated with the increase in pH values (r = 0.90). The sorption of phosphorus onto SC behaved the same trend comparing with SMC. The sorption progress of P with time (Table 4 and Fig. 3) indicates that P sorption on SC is characterized by high affinity (C-shape type) whereas by Mg-calcite ($Mg_{0.067}Ca_{0.933}CO_3$), it characterized by low affinity (S-shape type
orthophosphate species ($H_2PO_4^-$, HPO_4^{2-} an
are initially chemically adsorbed onto calcit
values greater than 8.2, for the current p
(between 7.58 and 8.07), adsorption seems t
both to electrostatic and chemical inte
including a series of surface reactions such a
hydrolysis of SC and SMC, dissociat
orthophosphate, and association of Ca^{2+}
Mg^{2+}) with orthophosphate anions.

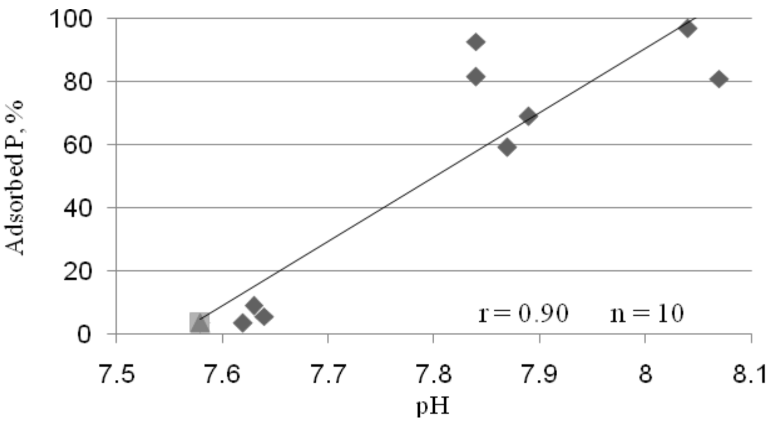

Fig. 1: Correlation between sorbed P on SC and SMC and pH throughout 24 h adsorption

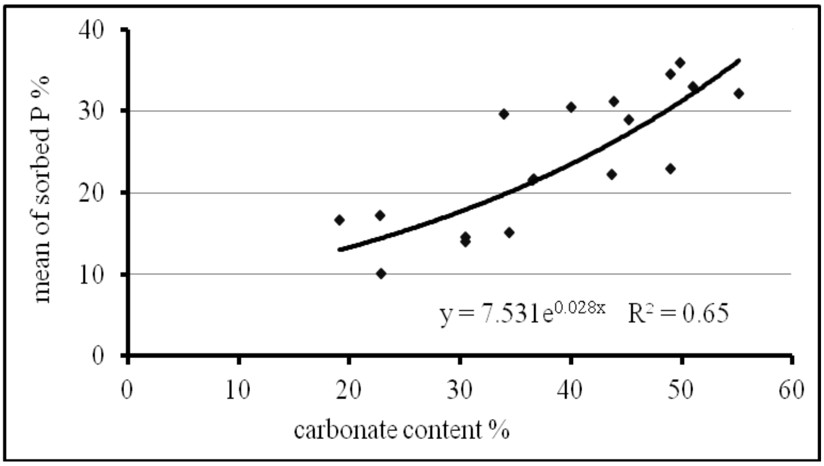

Fig. 2: The relationship between soil carbonate content and means of phosphorus sorption by soi

The protons (H^+) released from dissociation reactions will facilitate proton requirements by hydrolysis reactions according to the following equations (Karageorgiou *et al*., 2007; Lindsay, 1979):

$$2H_2PO_4^- = 2HPO_4^{2-} + 2H^+ \qquad \log K^o = -7.20 \quad (2)$$

$$CaCO_3(\text{calcite}) + 2H^+ = Ca^{2+} + CO_2 + H_2O \qquad \log K^o = 9.74 \quad (3)$$

$$CaCO_3(\text{calcite}) + 2H_2PO_4^- = Ca^{2+} + 2HPO_4^{2-} + CO_2 + H_2O \qquad \log K^o = 2.54 \quad (4)$$

With the progress of pH increase, the divalent orthophosphate anion will be the dominant fraction in solution and reacts with calcite surfaces to form more basic orthophosphate anion in solution as follow:

$$2HPO_4^{2-} = 2PO_4^{3-} + 2H^+ \qquad \log K^o = -12.35 \quad (5)$$

$$CaCO_3(\text{calcite}) + 2H^+ = Ca^{2+} + CO_2 + H_2O \qquad \log K^o = 9.74 \quad (3)$$

$$CaCO_3(\text{calcite}) + 2HPO_4^{2-} = Ca^{2+} + 2PO_4^{3-} + CO_2 + H_2O \qquad \log K^o = -2.61 \quad (6)$$

The reaction proceeded slowly after 12-hr which may be attributed to a formation of calcium phosphate coating on the surface of carbonate though which diffusion had to take place.

Mg content in the crystal lattice of $CaCO_3$ limited P removal from solution (Amer et al., 1985). The S-shape isotherm characterizing P sorption on SMC suggested an induction/nucleation period precedes the retention or precipitation of P with surface Ca^{2+} and/or Mg^{2+} ions. The effect of Ca^{2+} is greater than Mg^{2+} due to the stronger interactions of Ca^{2+} with PO_4^{3}. The $Mg^{2+}$and Ca^{2+} on the surface sites can increase the adsorption of PO_4 by forming $>CO_3$—Mg—PO_4 and $>CO_3$—Ca—PO_4 bonds as shown by Millero *et al*. (2001). The ion-dipole interaction between $Ca^{2+}$and P is stronger than that between Mg^{2+} and P due to the higher ionic radius of Ca^{2+} (Ca = 0.99 A°, Mg = 0.72 A°), therefore the hydration of Mg^{2+} ion is greater than Ca^{2+}. This might be the reason limited adsorption of phosphorus on to SMC. In other words, the higher hydration of Mg causes disruption of the crystal lattice structure retarded the crystallization/precipitation of calcium phosphate when Mg is incorporated (Kuo and Mikkelsen, 1979 and Millero *et al*., 2001).

By calcareous soils

Interaction of phosphate with the selected calcareous soils showed increase in P sorption with time (Table 5). There was a great variation in P sorption rate among the selected calcareous soils. After 48-h of adsorption reaction, about 28% of tested soils showed low affinity toward P retention by soil colloids where maximum adsorption did not exceed 22% of total added P. on the other hand, 56% of the tested soils adsorbed more than 50% of added P, with an average 69.68% overall th soil samples. The changes in soil pH acco the adsorption reaction showed some incr their values ranged from 0.07 to 0.31 units.

Carbonate content in calcareous s considered as one of the major player and c in P sorption process (Lindsay, 1979). variation in P sorption among soil samples observed for those having nearly same co total carbonate. These results may ref important efficacy of some other soil facto retention by soil particles. Figure (2) sh highly significant regression coefficient 0.65**) between sorbed P and soil total ca In this context also, the Pearson correlation between soil physical and chemical propert total P sorption (Table 6) indicated that, bes total carbonate content (r = 0.81**), soil text organic matter and ionic strength of the soil (represented as electrical conductivity solution) are considered important factors a P sorption by soil collides. Increasing th content (r = -0.8**) renders the sorption whereas increasing both silt (r = 0.82**) and = 0.49*) content enhanced the process. Soil matter as well as the ionic strength of soil play a significant role in retardation of P so calcareous soils (correlation coefficient r = This is in agreement with several studies (De Datta, 1985; Fageria and Filho, 1987; *al*., 2010). They found that numerous influence P sorption in the soil such concentration in the soil solution, conta temperature, clay content, free Fe and Al pH, OM, redox potential, ionic strength solution, soil mineralogy, parent materi surface area of colloidal particles.

Effect of Dissolved Organic Compound Sorption

Calcite and Mg-calcite Systems:

Addition of DOC extracted from PM, FBS to SC-P or SMC-P systems and their ef sorbed P and pH with time are illustrated i (3). The inhibition effect of the different DOC on P sorption onto SC was pronounce the first 6-h of the adsorption reaction. Th was afterword not effective to the end of reaction. After the 24-h reaction, pH of the PM, WS and FBS extracts–treated calcite in by 0.68, 1.03, 0.9 and 0.93 units, respectiv the other hand, DOC extracts applied to system obviously inhibited P adsorption by 85.73, and 76.25% in PM, WS and FBS tre respectively (Fig. 3). Similar changes in p observed in SMC-P system during the ad reaction. It seems that the interaction betw surface of SMC and DOC is more likely tha SC.

Table 5:Changes in pH and P sorption after various intervals of reaction with different calcareou

			Reaction time, hours					
Location	**Depth, cm**		**2**	**4**	**6**	**12**	**24**	**48**
EL-Banger val. 1	0-30	pH	7.54	7.53	7.60	7.67	7.62	7.54
		P[a)]	10.90	10.90	11.59	11.70	20.04	38.39
EL-Banger val. 2	0-25	pH	7.83	7.82	7.84	7.88	7.85	8.03
		P	8.01	10.93	11.47	11.82	38.03	49.35
EL-Banger val. 23	0-30	pH	7.87	7.91	7.94	8.01	7.92	8.05
		P	9.17	11.05	11.93	14.12	22.53	21.94
EL-Banger val. 24	0-30	pH	7.83	7.89	7.90	7.96	7.90	8.05
		P	6.40	9.63	11.93	13.43	24.81	21.61
	30-70	pH	7.89	7.99	7.96	8.00	7.97	8.07
		P	13.66	14.93	16.78	22.89	59.63	69.68
EL-Banger val. 25	0-20	pH	7.90	7.94	7.94	7.99	7.97	8.00
		P	12.51	16.20	15.51	19.43	28.96	37.42
	20-55	pH	7.88	7.90	7.93	8.00	8.03	8.08
		P	15.05	15.97	18.74	19.43	46.57	61.94
	55-90	pH	7.94	7.94	8.02	8.01	8.12	8.15
		P	15.28	17.89	18.16	26.58	51.48	63.55
	90-130	pH	7.94	7.96	8.03	8.02	8.13	8.17
		P	16.55	16.32	29.11	37.99	50.33	65.16
	130-150	pH	7.95	7.97	7.95	8.12	8.10	8.15
		P	12.97	17.12	22.08	37.30	54.71	63.23
EL-Banger val. 26	0-20	pH	7.81	7.86	7.88	7.94	7.89	8.03
		P	8.36	13.20	13.43	13.20	18.97	16.77
	20-45	pH	7.91	7.90	7.94	8.02	7.98	8.11
		P	12.28	13.82	15.16	16.89	22.08	52.90
	45-70	pH	7.90	7.91	7.92	7.98	7.56	8.08
		P	11.70	13.28	14.12	38.80	47.41	61.94
	70-105	pH	7.89	7.94	7.96	8.00	8.06	8.15
		P	9.51	10.90	13.66	31.19	53.17	64.84
	105-130	pH	7.83	7.94	7.95	8.05	8.08	8.14
		P	10.09	10.51	17.58	31.65	43.18	60.65
Fukah 1	0-40	pH	7.90	7.89	7.96	7.98	7.95	8.00
		P	11.20	12.36	13.89	20.24	20.97	21.29
Fukah 2	0-50	pH	7.91	7.82	7.96	8.03	8.01	7.98
		P	2.48	3.75	8.59	8.24	19.74	17.74
EL-Hammam	0-30	pH	7.91	7.85	7.95	8.00	7.97	7.98
		P	12.32	11.97	11.36	15.39	29.58	56.77

[a)] P measurement units are mg L^{-1}

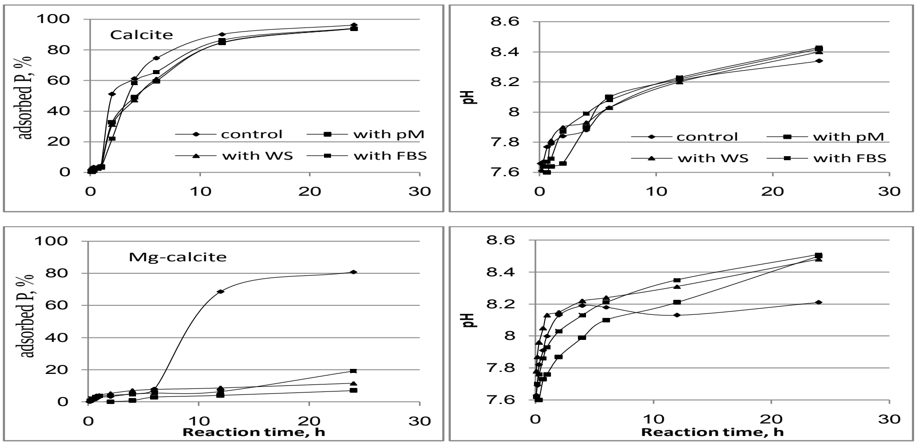

Fig. 3: Changes in adsorbed P and pH with time as influenced by DOC application to P so containing calcite and Mg-calcite

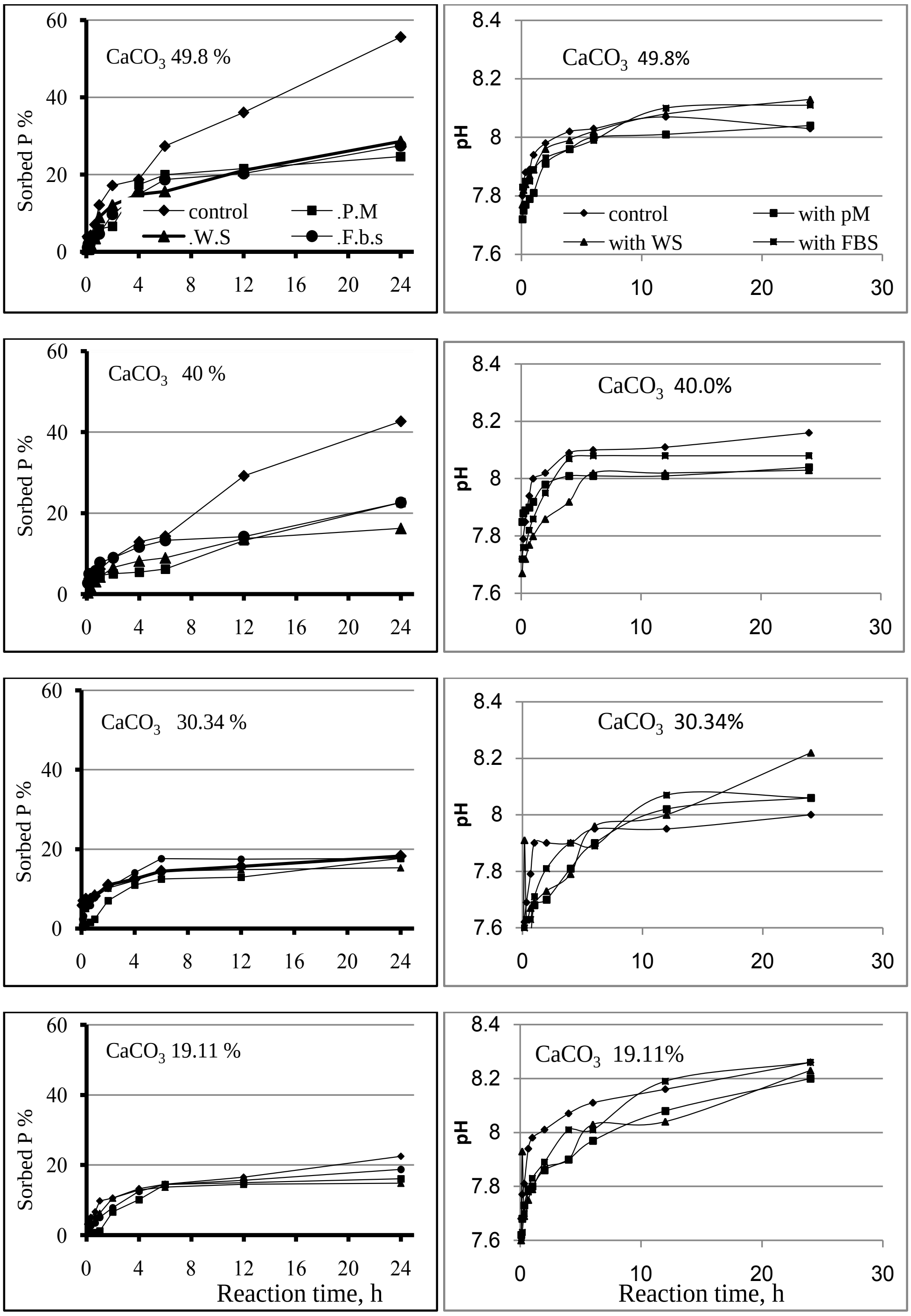

Fig. 4: Changes in adsorbed P and pH with time as influenced by DOC application to calcareo varied in their carbonate contents

Therefore, the organic ligands were more effective in blocking SMC surfaces and accordingly diminished the P retention. Also, an additive effect of Mg and DOC as inhibitors for P sorption cannot be excluded. Yadav *et al*. (1984), Bachra *et al*. (1965) and Kamh and Mostafa (1993) showed that Mg^{+2} ions and DOC extracts (clover extract) reduced adsorption of P on carbonate surface and/or stabilized the amorphous precipitates of calcium carbonate phosphate and disturbed the crystallization of the apatite.

Calcareous Soil System:

The changes in adsorbed P and associated pH of studied calcareous soils as affected by DOC addition are illustrated in Fig 4. Results indicated that applied DOC significantly reduced P sorption onto soil samples containing high $CaCO_3$ content. In the soil sample containing 49.8% $CaCO_3$, PM was the superior in adsorption prohibition by 90% after the first 5 minutes of the reaction, and by 55.6% after 24 hrs.

Also, other DOC sources such as WS and FBS showed a meaningful effect in retardation of P sorption after 24 h by 48.6 and 50.6%, respectively.

Surprisingly, The DOC was less effective in prevention of P sorption by soil samples containing 30.34% and 19.11% $CaCO_3$. Decreasing the content of soil carbonate (as a dominant reactive solid phase in calcareous soils) may enhance the role of other factors to become more effective in soil-P behavior, and therefore, diminish the inhibition effect of applied DOC. Recent previous study (Fekri *et al*., 2011) found that application of poultry manure together with P fertilizer to calcareous soils increased P recovery.

CONCLUSION

The results of the current work show that incorporation of Mg ions into calcite lattice retard and reduce its affinity to retain P. But in calcareous soils, the role of Mg ion incorporation was interfered with soil properties which have some influence on P sorption such as texture, soil OM and ionic strength of soil solution besides carbonate content. Presence of DOC in solutions by amounts near 1.0 mg g^{-1} adsorbent diminished P immobilization by Mg-calcite and high carbonate contained soils. Recognition of soil carbonates not only its content but also the divalent ion incorporation in calcite lattice might help in management of P fertilization of crops grown in calcareous soils. The obtained results reflect the importance of organic amendments application to calcareous soils to maintain P availability.

~~1- Yield/ vine:~~

~~Data in Table (1) clearly show that s~~
~~clusters of Early sweet grapevines with GA$_3$~~
~~40 ppm or Sitofex at 2.5 to 10 ppm was signi~~
~~effective in improving the yield relative to th~~
~~treatment. The promotion on the yiel~~
~~accompanied with increasing concentrations~~
~~plant growth regulator. Using GA$_3$ at 10 to~~
~~significantly preferable than using Sitofex a~~
~~10 ppm in improving the yield. A slig~~
~~unsignificant promotion on the yield was at~~
~~to increasing concentrations of GA$_3$ from 2~~
~~ppm and Sitofex from 5 to 10 ppm. The m~~
~~yield was produced on the vines that recei~~
~~spray of GA$_3$ at 40 ppm but the best treatme~~
~~economical point of view was the applic~~
~~GA$_3$ at 20 ppm (since no measurable prom~~
~~the yield was recorded between 20 and 40~~
~~GA$_3$). Under such promised treatment, yiel~~
~~reached 13.6 and 14.0 kg during both~~
~~respectively. The control vines produced 9.1~~
~~kg during 2013 and 2014 seasons, respectiv~~
~~percentage of increase on the yield~~
~~application of GA$_3$ at 20 ppm over the~~
~~treatment reached 49.5 and 45.8 % duri~~
~~seasons, respectively. The beneficial effects~~
~~on the yield might be attributed to their~~
~~action on increasing cluster weight. The pr~~
~~effects of GA$_3$ on the yield was supported~~
~~results of Dimovska *et al*., (2011) and Abu~~
~~and Salameh (2012) on different grapevine c~~

~~The results regarding the beneficial ef~~
~~Sitofex on enhancing the yield are in harmo~~
~~those obtained by Juan *et al*. (2009); Abdel~~
~~*et al*., (2010) and Al- Obeed (2011).~~

~~2- Harvesting date:~~

~~It is clear from the data in Table (1) that~~
~~and Sitofex treatments had significantly del~~
~~the harvesting date of Early Sweet grapevine~~
~~than the control treatment. The degree of d~~
~~on harvesting date was correlated to the inc~~
~~the concentrations of both GA$_3$ and Sitofex~~
~~GA$_3$ significantly delayed harvesting~~
~~comparing with using Sitofex. In~~
~~concentrations of GA$_3$ from 20 to 40 p~~
~~Sitofex form 5 to 10 ppm failed to show sig~~
~~delay on harvesting date. A cons~~
~~advancement on harvesting date was obse~~
~~untreated vines the great delay on harvesti~~
~~was observed on the vines that received GA~~
~~ppm during both seasons. GA$_3$ and Sitof~~
~~shown by many authors to retard the rel~~
~~ethylene and the disappearance of pigments~~
~~chlorophylls and carotenoids and onest of~~
~~start. Also they were responsible for prolong~~
~~maturity stages Nickell (1985). These~~
~~regarding the delaying effect of GA$_3$ and Sit~~
~~harvesting date were in harmony with~~
~~obtained by Wassel *et al*., (2007), Kasse~~

~~(2011), Abu- Zahra and Salameh (2012) and Refaat *et al*. (2012).~~

~~3- Cluster weight and dimensions:~~

~~It is evident from the data in Table (1) that treating clusters with GA_3 at 10 to 40 ppm or Sitofex at 2.5 to 10 ppm was significantly accompanied with enhancing weight, length and width of cluster relative to the control treatment.~~

~~The promotion was significantly associated with increasing concentrations of GA$_3$ and Sitofex. Using GA$_3$ was significantly favourable than using Sitofex in this respect. The maximum values were recorded on the vines that received one spray of GA$_3$ at 40 ppm. Meaningless promotion was detected with increasing concentrations of GA$_3$ from 20 to 40 ppm and Sitofex from 5 to 10 ppm. The untreated vines produced the minimum values during both seasons. The positive action of GA$_3$ on cluster weight and dimensions might be attributed to its essential role on stimulating cell division and enlargement of cells, the water absorption and the biosynthesis of proteins which will lead to increase berry weight. Dimovska *et al*., (2011); Abu Zahra and Salameh, (2012) and Dimovska *et al*., (2014).~~

~~The previous essential role of CPPU on cluster weight was attributed to its higher content of cytokinin when applied to plants (Nickell, 1985).~~

~~4- Shot berries %:~~

~~Data in Table (2) obviously reveal that percentage of shot berries in the clusters of Early Sweet grapevines was significantly controlled with spraying GA$_3$ at 10 to 40 ppm or Sitofex at 2.5 to 10 ppm relative to the check treatment. Using GA$_3$ was preferable than using Sitofex in reducing the percentages of shot berries. There was a gradual reduction on the percentage of shot berries with increasing concentrations of GA$_3$ and Sitofex. There was a slight reduction on such unfavourable phenomenon with increasing concentrations of GA$_3$ form 20 to 40 ppm and Sitofex from 5 to 10 ppm. The minimum values of shot berries (7.3 and 6.9 % during both seasons, respectively) were recorded on the clusters harvested from vines treated with GA$_3$ at 40 ppm. The maximum values of shot berries (12.0 & 12.5 %) during both seasons were recorded on the untreated vines during both seasons. The reducing effect of GA$_3$ on shot berries might be attributed to its important role on enhancing cell division and the biosynthesis of proteins Nickell, (1985). These results were supported by the results of wassel *et al*. (2007) and Abu Zahra and Salameh (2012).~~

~~5- Fruit quality:~~

~~Data in Tables (2, 3 & 4) clearly show that spraying clusters with GA3 at 10 to 40 ppm or Sitofex at 2.5 to 10 ppm significantly was accompanied with enhancing weight, longitudinal and equatorial of berry, total acidity%, proteins % and percentages of P, K and Mg and T.~~
~~reducing sugars %, T.S.S. / acid an~~
~~carotenoids relative to the check treatme~~
~~effect either increase or decrease was as~~
~~with increasing concentrations of each auxi~~
~~GA$_3$ significantly changed these paramete~~
~~using Sitofex. A slight effect was recorded~~
~~quality parameters with increasing concentra~~
~~GA$_3$ from 20 to 40 ppm and Sitofex from~~
~~ppm. From economical point of view, t~~
~~results with regard to fruit quality were o~~
~~due to treating clusters with GA$_3$ at 2~~
~~Untreated vines produced unfavourable eff~~
~~fruit quality. These results were true duri~~
~~seasons. The effect of GA$_3$ on increasin~~
~~weight and dimensions might be attribute~~
~~effect in promoting cell division and enlarge~~
~~cells, water uptake and the biosynthesis of~~
~~Nickell (1985). These results were in conc~~
~~with those obtained by Williams and Ayars~~
~~and Dimovska *et al*., (2014).~~

~~The higher content of Sitofex from cy~~
~~surly reflected on enhancing cell division~~
~~elongation of berries Nickell (1985). These~~
~~were in agreement with those obtained b~~
~~Zahra (2013) and Retamales *et al*. (2015).~~

~~CONCLUSION~~

~~Treating Early Sweet grapevines once w~~
~~average berries reached 6mm with GA$_3$ at~~
~~was responsible for promoting yield an~~
~~quality.~~

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الملخص العربى

ائص ادمصاص الفوسفور على الكالسيت والكالسيت المغنسيومى والأراضى الجيرية: تأثير المركبات العضوية الذائبة

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~~رش حامض الجبريليك والسيتوفكس فى تحسين المحصول وجودة حبات العنب الايرلى سويت فى منطقة المنيا –مصر~~

ماهر السيد صالح[1]، إيمان حسن الجمل[2]، محمود عبد السلام قمح[1]، أحمد فريد سعد[1]

[1] قسم علوم الأراضى والمياه – كلية الزراعة – الشاطبى– جامعة الاسكندرية، الاسكندرية – مصر

[2] مدينة الأبحاث العلمية والتطبيقات التكنولوجية، برج العرب الجديدة – الاسكندرية – مصر

~~محمد على مجاور عبادة، ماهر خيرى يواقيم، بسام السيد عبد المقصود بلال~~

~~قسم بحوث العنب – معهد بحوث البساتين– مركز البحوث الزراعية– الجيزة– مصر~~

~~محمد على مجاور عبادة، ماهر خيرى يواقيم، بسام السيد عبد المقصود بلال~~

~~قسم بحوث العنب – معهد بحوث البساتين– مركز البحوث الزراعية– الجيزة– مصر~~

جراء مجموعة من التجارب المعملية لدراسة تأثير الاحلال الجزئى لأيون المغنسيوم محل أيون الكالسيوم فى
المخلق معمليا ودراسة تأثير إضافة المواد العضوية الذائبة على ادمصاص الفوسفور بواسطة الكالسيت
ت المغنسيومى وبعض العينات المختارة من الأراضى الجيرية. أوضحت النتائج أن ادمصاص الفوسفور على
أو الكالسيت المغنسيومى يعتمد على الوقت خاصة الأخير. بعد مرور 6 ساعات من تفاعل الادمصاص
الة للفوسفور بنسبة 81% من المحلول بواسطة الكالسيت وهذه النسبة تمثل 9 أضعاف المزال بواسطة الكالسيت
مى مما يشير الى التأثير التثبيطى لأيون المغنسيوم على الادمصاص. بعد 24 ساعة من الادمصاص كان
باط قوى($r = 0.9^{**}$) مع درجة حموضة المحلول (pH). دخول أيون الماغنسيوم الى داخل بللورات الكالسيت
خفض ادمصاص الفوسفور من خلال دوره فى تأخير تكوين نويات الترسيب ونمو بللورات الفوسفور المترسب.
الأراضى بناء على نسبة المغنسيوم الى الكالسيوم فى مكون الكربونات بالأرض وبعد مرور 24 ساعة من
دمصاص على الأرض، تراوحت نسبة ازالة الفوسفور 22 و 50% وصاحب ذلك حدوث زيادة فى ال pH
مابين 0.07 و 0.31. من ناحية أخرى بينت قيم معامل الارتداد المتعدد أن كربونات الكالسيوم ليست العامل
متحكم فى ادمصاص الفوسفور على الأرض ولكن قوام الأرض والقوة الأيونية للمحلول الأرضى والمادة
بالأرض تعتبر عوامل مؤثرة. المواد العضوية الذائبة والمستخلصة من مخلفات الدواجن وتبن القمح وتبن الفول
لبيئة التفاعل عملت على تثبيط ادمصاص الفوسفورعلى كل من الكالسيت المغنسيومى والأراضى المحتوية
ونات كلية مابين 49.8 و 40% بينما لم تؤثر على ادمصاص الفوسفور على كل من الكالسيت والأراضى
على كربونات كلية مابين 30 و 19%. وخلصت الدراسة الى أن وجود احلال جزئي للمغنسيوم فى بللورات
و/أو اضافة المواد العضوية الذائبة يمكن أن يعمل على زيادة تيسر الفوسفور من خلال خفض الادمصاص
ير الترسيب.

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