Effect of the soils properties on the sorption capacity of phosphorus and ammonium by alkaline soils of the semi-arid areas.

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Abstract: Soils samples were collected at different depths (from 0 to 120 cm) from tree sites of Tunisia (Chott Mariem, Enfidha and Kondar). The minerals and physicochemical properties were analyzed. Then the capacity sorption of phosphorus and ammonium was carried only in the samples collected from the surface depth (0-25cm) using the batch processes. The results showed that most soil samples have a clayey texture. The available of nutriment and heavy metals was different and varied with the sites and depths. The sorption of phosphorus and ammonium was rapid initially and gradually diminished to attain equilibrium. The equilibrium was reached after 72 h for phosphorus sorption and 300mn for ammonium sorption. Also the levels of P adsorbed were; 6.27, 6.84 and 6.92 mg P g⁻¹ and ammonium adsorbed were 5.83, 6.5 and 6.3 mg NH₄+g⁻¹ respectively from the soil Chott Mariem, Enfidha and kondar. Applications of the following kinetics models: pseudo-first-order, pseudo- second-order and Elovich model to the data show that the rates of phosphorus and ammonium sorption were best predicted by the pseudo-second-order kinetic model as seen from the correlation coefficient R² (\geq 0.98).

Keywords: Soil proprieties, sorption, Phosphorus, Ammonium, Semi-arid areas.

I. Introduction

Soil is dynamic natural bodies composed of organic and inorganic solid particles with properties which result of pedogenic process. It is one of the key elements for all terrestrial ecosystems. It supports and provides nutrients and water for the plants that provide us food and forest products. It combines several properties specially physiochemical all of which affect directly or indirectly nutrient dynamics and availability who can evaluate the degree of fertility. Soil fertility is a manageable soil property and its management is of utmost importance for optimizing crop nutrition on both a short-term and a long-term basis to achieve sustainable crop production. However a sound understanding of variation soil properties and their relationships with crop species distribution is believed to be highly essential for integrated and sustainable crop management programmes [1]. In this context many studies have emphasized the influence of varying soil properties on the distribution and abundance of crop species in different locations [2]. On the others hand soils proprieties provide a suitable natural environment for biodegradation of wastes and therefore serve as a sink for the sorption and absorption of ions and as a medium for the restoration of vegetation and normal land use [3] and they represent a powerful natural biogeochemical barrier, which limits migration of chemical elements and pollution of ground water. Although two groups of soil properties are important among them: the ability of soils to adsorb chemical elements and to distribute them among the soil components. In the present work, physicochemical characterization of soils namely texture, pH, cations exchangeable capacity (CEC), nutriment available and heavy metals from three soil profiles located in the three different semi-arid areas, which have been carried out at different soil depths. The specific objectives included (1) to identify soils profiles physicochemical and mineralogy properties that can be influence the distributional pattern of crop species in the areas and (2) to study the capacity sorption of some pollutant such a phosphorus and ammonium by theses soils in order to improve a better understanding of the relationship between soil characteristics variability and mobility of some pollutant in soil profiles that control groundwater contamination.

Site description

II. Material and Methods

The study areas are located in the Sousse region, Tunisia. Sousse is a local government area in Sahel of Tunisia. The topography is irregular dominated by a string of folds generally oriented NE-SW (N045) [4]. The climate is semi-arid with an annual precipitation varied between 170 and 540 mm. Annual temperatures varied between 12 to 18 °C in winter and 19 to 38°C in summer. The soils in Sousse are generally deep, well drained with low to moderate status, and where crop cover is removed due to human activities. The area serves as a corridor of development to complement the tourism development initiatives of the country. The area is currently undergoing rapid development and changes in vegetation cover as a result of the influx of people into the country and the increasing need for housing.

Soil sampling and analysis

Soil samples were obtained at four depth, 0-25, 25-60, 60-90, and 90-120 cm from three areas situated in the region of Sousse: Chott Mariem (40° 3' N 9°10' E) in a plot occupied by citrus trees, Enfidha (40° 23' N 8° 86' E) in a plot occupied by olive trees and Kondar (39° 98'N, 8°87'E)) in a plot occupied by olive trees. The soil (0-25 cm) is fine sandy loam (Isohumic soils) at Chott Marien, clay soil (Calcic-magnesic) at Enfidha and clay soil (Solonetz) at Kondar [5]. Soil analysis was carried out on the air-dried, sieved (<2 mm). The soil pH was measured in distilled water using a 1:2 (mass) soil: solution ratio [6]; the particle size distribution was determined with the pipette method [7]; the cation exchange capacity (CEC) by Ammonium Acetate. The organic carbon (Corg) was determined by Walkley-Black procedure [8], in which the sample is digested with potassium dichromate $[K_2Cr_2O_7]$ and concentrated sulfuric acid. The solution was titrated against ammonium ferrous sulfate [Fe(NH₄)₂(SO4)₂.6H₂O], using diphenylamine indicator. Concentrations of the following elements (P, Ca, Mg, K, Fe, Na, Al, Cd, Cu, Mn) in the extracts were determined by Mehlich-III methods [9] were determined by equilibrating 2.5 g of air-dried soil with 25 mL of Mehlich-III extracting solution for 5 min and filtering through Whatman No. 40 filter paper. Concentrations of the various elements in the extracts were determined by inductively coupled plasma optical emission spectrophotometer (CP-OES, Perkins Elmer, Model 4300DV). Total nitrogen (N total) was determinate by Kjeldahl methods. Finally, the nitrogen nitrate (N-NO₃⁻) and the nitrogen ammonium (N-NH₄) concentrations were analysed by HPLC Dionex DX500 with UV detector. The mineralogical analysis was extracted from the powder XRD data using an internal standard for each mineral [10]. The clay fraction was quantified, after purification, and based on a pure, standard clay mineral [11].

Experimental sorption study

Both sorption capacity of ammonium $(NH_4^{+)}$ and phosphorus (P) were separately carried by the using of batch process. The batch sorption experiments were carried out in 250-mL Erlenmeyer flasks where 1 g of each soil sample combined separately with 100 mL of the NH_4^+ and 100mL of the P solutions prepared by dissolving NH_4Cl and K_2HPO_4 in distilled water. The Erlenmeyer flasks were subsequently capped and agitated in an isothermal shaker at 120 rpm and $20\pm2^\circ$ C to achieve equilibration. At different time intervals, 10 ml of solution was sampled from each flask, centrifuged at 2800(g) for 15 min and the supernatant was immediately analysed for NH_4^+ using the double beam UV-vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at 668 nm and for P at 882 nm using the ascorbic acid method. The amount of sorption at equilibrium, Qe (mg.g⁻¹), was $(Ce - C_0)xV$

calculated by: $Qe = \frac{(Ce - C_0)xV}{M}$; Where C₀ and Ce (mg.L⁻¹) are the liquid-phase concentrations at initial and

equilibrium, respectively; V is the volume of the solution (L) and M is the mass of dried soil (g).

Sorption kinetic study

The following kinetic models: the pseudo-first order, the pseudo-second-order and Elovich, were using in this studies.

The pseudo-first-order model

The pseudo-first-order model expressed as follows equation: $\log(Qe - Qt) = \log(Qe) - \frac{k \times t}{2,303}$, where k is

a constant and Qe is the amount of phosphorus (P) adsorbed at equilibrium in mg g^{-1} . The constants k and Qe can be calculated using the slope and intercept from the plot of log (Qe–Qt) versus time (t).

The pseudo-second-order model

The pseudo second-order kinetic model is expressed as follows equation: $\frac{dQ}{dt} = k_2 \times (Qe - Q)^2$ where k_2 is the second-order rate constant (gmg⁻¹min⁻¹). By plotting t/Qt versus t in a linear relationship, values of k_2 and Qe were calculated from the intercept and slope of the plots.

The Elovich equation

The Elovich equation is generally described by the following equation: $\frac{dQt}{dt} = \propto e^{-\beta qt}$, where α is the initial adsorption rate (mg g⁻¹ min⁻¹) and β is the desorption constant (g mg⁻¹).

Statistical analysis

All soils samples measurements are means of three laboratory replicates from the compounds samples soils collected from each of the three areas profiles. Statistical analyses were conducted using SPSS.13. All results were analysed by ANOVA, and significance (P<0.05) between means tested by the student test. To assess relationship between elemental data, a Principal Components Analysis (PCA) was performed by using the R statistical software.

Soil texture

III. Results and Discussion

Soil texture is probably the important physical property determining such fundamental soil properties as fertility, aeration and plant available water. Differences in many of these properties among soils can be attributed to the strong dependence of texture on soil mineralogy. The results of the textural properties of the various sampling locations at different depths are illustrated in Table 1.

Table 1: Soils	physico-chemical	proprieties
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		Chott-M	lariem si	ite	Enfidha site				Kondar site			
Depth (cm)	0-25	25-60	60-90	90-120	0-25	25-60	60-90	90-120	0-25	25-60	60-90	90-120
pH (H ₂ O)	8.12	8.41	8.56	8.54	8.26	8.14	7.97	7.87	8.66	8.86	8.35	8.12
CEC(meq/100g soil) 19,72	22,04	23,45	23,45	37,53	39,28	41,13	44,45	22,28	26,58	31,48	31,15
C org(mgKg ⁻¹)	10980	8250	20980	27050	20200	18480	18560	17900	42730	41400	32960	31000
Ptot(mgKg ⁻¹)	93,68	20,90	4,12	4,99	4,48	2,19	3,70	3,79	1,98	1,53	1,27	1,91
N tot(mgKg ⁻¹)	900	540	510	260	860	630	610	660	610	470	300	300
N-NO ₃ (mgKg ⁻¹)	86,4	36,1	169,2	38,2	22,7	59,77	131,4	151,2	283,4	268,3	193,4	164,8
N-NH ₄ (mgKg ⁻¹)	6,68	3,29	3,5	3,39	6,60	14,76	6,4	7,01	3,52	3.6	3,9	4,04
Ca (mgKg ⁻¹)	5450	5508	5874	5450	10026	9495	7885	11360	17784	10108	12786	20337
Al (mgKg ⁻¹)	76	87	72	51	230	159	108	198	34	19	14	34
K(mgKg ⁻¹)	491	299	135	106	294	310	298	376	143	129	160	234
Na (mgKg ⁻¹)	57,5	232,3	533,6	124,2	798,1	1978	2389	2224	264,5	775,1	1932	2210
Mn(mgKg ⁻¹)	59,15	52,5	22,95	4,2	76,8	84	68,9	58,12	11,27	15	20,9	21,25
Fe (mgKg ⁻¹)	33,57	24,62	9,01	3,38	41,1	41,9	45,57	44,17	12,2	19,5	30,48	31,94
Zn (mgKg ⁻¹)	3,64	0,81	0,463	0,42	1,205	1,14	0,97	1,2	0,54	0,55	0,7	0,92
Cu (mgKg ⁻¹)	2,74	1,77	1,13	1,05	2,05	2,16	1,66	1,94	0,87	0,94	1,02	1,2
Cd (mgKg ⁻¹)	0,05	0,03	0,02	0,018	0,042	0,048	0,047	0,05	0,036	0,03	0,037	0,057
Texture	Fine sandy loam	Loam sandy clav	Clay	Loam sandy clav	Clay	Heavy clay	Heavy clay	Heavy clay	Clay	Clay	Sandy clay	Heavy clay

The textural class of the soils was observed to be a mixture of sand, clay and loam in all the areas investigated. However, it can been seen that the particle size composition of Enfidha soils and Kondar in the different deeps is dominate by the fraction of clay; as soils in the areas are texturally similar and having been derived from the same parent material under the same climate and topography. Although from the Chott Mariem site it can be show that texture in the (0-25cm) was fine sandy loam and become dominated by the clay with increasing depth. From the different areas profiles, the clay fraction was dominating. This is so as the study area is a part of the coastal plain of Sousse region which is characterized by very clay soils over wide expanses of land [12].

Soil chemical element composition

Some chemical characteristic as the pH, CEC, nutriment availability and heavy metal were show in the Table 1. The samples soils of the different profiles areas are basic with a pH range of 7.87 to 8.86. Moreover the

ANOVA results show that not significantly effect (P < 0.05) of variation of pH values in different depths in areas profiles. The basic nature of the studied soils is attributed to the high concentration of some basic cations especially calcium and magnesium from the different horizons of the soils [13, 14]. The values of the CEC of all profiles soils increase with increasing depths. The content of CEC happened to be higher in the profile Enfidha site with values ranged from 37.53 at 44.45 (meq/100 of soil) respectively in the first and last layer. In the soils profiles of the Chott Mariem and Kondar areas the CEC values ranged from 19.72 to 23.45 (meq/100 of soil) and 22.28 to 31.48 (meq/100 of soil) respectively in the first layer and the last layer. The high values of CEC in Enfidha profile soil may be attributed of high content of clay. Reid and Dirou, [15] revealed that both clay and organic matter serve as potential sources of nutrients by attracting cations; as such, soils with large amounts of clay or organic matter have higher exchange capacities than sandy and silt soils, which are usually low in organic matter. The organic (C org) content of the soil in the study area which is an indicator of the organic matter content of the soil was found to be low within the Chott Mariem and Enfidha when the amount respectively ranged from 0.82 gkg⁻¹in the (25-60 cm) depth at 2.7 gkg⁻¹ in the last layer profiles and from 1.7 gkg^{-1} in the last layer to 2.0 gkg^{-1} in the first layer. While in the Kondar site the amount of C_{org} was moderate. It can be ranged from 3.1 gkg^{-1} recorded in the last layer to 4.2 gkg^{-1} recorded in the horizontal layer. This variation of C_{org} level can attribute essentially at the roots mass of citrus and olive crops. The total (N tot) content varies substantially with soils profiles areas. The most N_{tot} storages are recorded in the surface layer with value of 900, 860 and 610 mgkg⁻¹ respectively in Chott Mariem, Enfidha, and Kondar. This variation of N_{tot} amounts between the different areas depending on the applied fertilizers. Similar dependencies were also described by Sainju et al. [16]. However, it can be seen that N_{tot} content in each soil profile for different areas decreased significantly (P < 0.05) with soils depths. The low amounts can recorded in the deeper layer were 260, 610 and 300 mgkg⁻¹ respectively in Chott Mariem, Enfidha and Kondar soils profiles areas. The decreasing can be attributed to higher mineralization of organic matter content in the top soil [17]. The nitrogen nitrate (N-NO₃⁻) can also be utilized by plants and microorganisms as a nitrogen source; under certain conditions it can serve as an electron acceptor for microorganisms and be reduced and released as molecular nitrogen. The analysis result revealed a variation of the (N-NO₃⁻) concentration with areas and profiles depth variation. The highest concentration was seen in the case of Kondar profile at 283.44 and 268.37(mgkg⁻¹) respectively in the (0-25 and 25-60cm). This can be attributed to the presence of extremely high clay mineral and organic matter content. All soil series had slightly higher value of total phosphorus (Ptotal) except for the surface depth from the Chott Mariem areas when it recorded 93.68 (mgKg⁻¹). This high concentration can be explained by phosphate fertilizer applied recently. The ANOVA analysis revealed significantly (P <0.05) decreasing of the Ptot concentration with the increasing depths especially in the Chott Mariem and Enfidha areas (Table1). This decreasing of the P_{tot} amounts with the depths due that the phosphorus is not readily leached through the soil profile as it reacts with soil minerals and tends to stay tightly associated with the soil mineral surfaces. The major loss of phosphorus is by plant removal and erosion of topsoil. The amounts of cations (Ca, Mg, K, Na and Al) in the soil in this work varied differently as a result of profiles soil areas and within the profiles depths (Table 1). The calcium (Ca) was the highest cation detected in the different soils profiles areas. The ANOVA results show that the amount of Ca significantly (P < 0.05) varied with the variations of profiles soils areas. It can be seen that the Ca content of Chott Mariem profile soil significantly (P<0.05) increase with the depths. It evolved from a value of 5450.38 (mgkg⁻¹) recorded in the surface horizon to a value of 17306.04 (mgkg⁻¹) recorded in the last deep. The increase may as a result of leaching of Ca to the deep layers. This finding coincides with that of Iwuafor et al. [18]. From Enfidha soil profile site the amount of Ca range from 7885.16 (mgKg⁻¹) recorded in the deep (60-90) cm to 11360.93 (mgkg⁻¹) recorded in the last deep (90-120cm). Finally from the profile soil Kondar site the amount of Ca range from at 10108.91 ($mgkg^{-1}$) in the (25-60) cm to 20337.43 ($mgkg^{-1}$) in the last deep (90-120cm). In general the amount of Ca recorded in different areas was very high. Some studies indicate that in soil from arid or semiarid zones, high calcium concentrations have always been found [19]. Additionally lower levels of acidity and less rainfall increase the stability of minerals such the calcium in the soil's clay. As a result, the high calcium content will tend to flocculate in the upper profile of the soil's clay [20]. Phillips and Chiy [21], after applying sodium fertilizers, observed an enhancement leaching of calcium. Also from the Table 1 it can be seen that the rate of potassium (K) in the different profile soils was lowest than Ca. From the Chott Mariem site, the amount of (K) can significantly (P<0.05) decrease with the deep. It decline from 491.23 (mgkg⁻¹) recorded in the first layer at 106.6 (mgkg⁻¹) recorded to deep layer. From the others areas, the high amount recorded from the last deep at 376.57 (mgkg⁻¹) and 234.11 (mgkg⁻¹) respectively in Enfidha and Kondar areas. But the low amount recorded from the surface horizon at 294.1 (mgkg⁻¹) and from the depth of (25-60 cm) at 129.08 (mgkg⁻¹) ¹) respectively in Enfidha and Kondar areas. There was also a similar reduction in the amount of soil magnesium (Mg) content relative to the amount of Ca, where the amount from the Chott Mariem, Enfidha and Kondar ranged respectively between 356.83 (mgkg⁻¹) in the (60-90cm) of depth to 461.68 (mgkg⁻¹) in the last deep, 668.70 (mgkg⁻¹) in the first deep to 841.43 (mgkg⁻¹) in the last deep and 680.21 (mgkg⁻¹) in the last deep and 1000.05 (mgkg⁻¹) in the (60-90cm) of depth. The availability of Mg in the different samples soils was in related

with the pH. When the soil's acidity increases, a diminishment of available magnesium is observed due to the fact that hydrogen ions occupy a high number of the exchange areas [22]. The amount of aluminum (Al) is very low than the others cations. It can be recorded respectively from Chott Mariem, Enfidha and Kondar areas a range of value at 51.55 (mgkg⁻¹) in the last deep to 87.23 (25-60cm) deep at 108.25 (mgkg⁻¹) in the (60-90cm) of depth to 230.41 (mgkg⁻¹) in the first deep and at 19.06 (25-60cm) of depth to 34.44 (mgkg⁻¹) in the first deep. The low of Al due essentially of the high pH recorded in the different areas that can be reducing the availability of acid cations.

Mineralogical composition of the soils

The mineralogical results obtained for the whole samples of the soil profiles (surface and subsurface layers) are given in Table 2. The same minerals are observed in all horizons of the different profiles. These are quartz calcite, smectite, Kaolinite, illite and chlorite. The abundance of these minerals is the following classification: quartz \geq calcite \geq smectite \geq kaolinite \geq illite \geq chlorite. According to this estimate, the distribution of minerals in each profile can be described in the following way: for the soil profile of Chott-Mariem, it can be revealed a relative homogeneity of the proportions in quartz in the all layer, increasing of calcite in the deep layer and different abundance of the kaolinite illite and chlorite. For the Enfidha soil profile, it can show a relative homogeneity of the distribution of the proportions in kaolinite, quartz, calcite, smectite in the all horizons and different abundance of the illite and chlorite. Finally for the Kondar soil profile, it can suggest a preponderance of quartz, calcite in all the horizons and then become less abundant in the deep horizons. The smectite is detected with stable values in all layers but the kaolinite, illite and chlorite are there in irregular abundance. According to Duchaufour, [23] the process of evolution of clays is mainly inheritance, while the fact that same phyllites were observed in the geological substrate of the same area [24]. The abundance of clay in the different profiles soils is good index to fixe enough water, which contributes to the good nutrition of crops and ensures their growth under optimal conditions [25].

Sites	Depths		Identification of mineralogy							
	(cm)	Kaolinite	Quartz	Calcite	Smectite	Illite	chlorite			
	0-25	+	+++	+	-	-	-			
Chott-Mariem	25-60	-	+++	+	+	-	-			
	60-90	+	+++	+	+	+	-			
	90-120	+	+++	++	+	+	+			
	0-25	+	+++	++	+	-	+			
Enfidha	25-60	+	+++	++	+	+	-			
	60-90	+	+++	++	+	+	-			
	90-120	+	+++	++	+	+	+			
	0-25	-	+++	+++	+	-	-			
Kondar	25-60	+	+++	+++	+	-	+			
	60-90	+	+++	+++	+	+	+			
	90-120	+	++	++	+	+	+			

 Table 2: Mineralogical composition of the different soils profiles

Relationships between physic-chemical elements contents

The principal component analysis (PCA) was used for all soil samples to identify the relationships between some elements concentration and the results are show in Fig 1.



The analysis of this Fig1, it can be reveled two axes D_1 and D_2 who can be explain respectively 46.35% and 29.02 % of the variance. Moreover at this Fig 1 it can be reveled four groups of elements that are positively correlated. The first chemical group (CG₁) on positive D_1 and negative D_2 contained two principal clusters of variables with large positive correlation. The first cluster includes K, N, Corg, Zn, and Cu. The second cluster includes C/N, and P total. The second chemical group (CG₂) on the D₁ and D₂ positive side includes two principal clusters of elements with large positive correlation. The first cluster contains N-NH₄, Fe, Mn and Al and the second cluster contain Na and S. The third chemical group (CG_3) on positive D_2 and negative D_1 side associate the N-NO₃⁻, and Ca. Finally the fourth chemical group (CG₄) on negative D_1 and negative D_2 regrouped the values of pH. The separation of element concentrations in the projections is caused most probably by the origin of these elements. The results suggest that there is relationship between some elements recorded in the same chemical group. It can be revealed a positive correlation between CEC content and pH proportion for the soil samples. This relationship can be due that the soil clay fraction size influences the chemical reaction such adsorption and co-precipitation, thereby affecting the solubility and mobility of elements. Thus, it can be noticed that the high concentrations of Na related with increased clay size fraction in all soil profiles but not enough to explain the distribution of others elements as the content of N-NO₃ and P into the different soils profiles. Moreover the correlation analysis shows that N org, K, Cu and Zn, were associated with C org of soil samples. The content of C org estimate the content of organic matter in soil with has a direct effect on the elements retention in the soil. In our study, organic carbon was differently distributed in the surface, subsurface and deepest layers of all soil profiles. The absence of correlation between the different elements adsorption and soil organic matter is probably caused by the weakness reactive fraction of the organic matter. Another hand the relationship between elements concentration and soil pH values in the different soil samples is studied. However, the stability of elements concentrations in the soil is strongly pH dependent. The pH of the soil system is a very important parameter, directly influencing the sorption/desorption, precipitation/dissolution, complex formation, and oxidation-reduction reactions. The results indicate that there are negative relationship between pH and acid cations concentrations as N-NH4, Cu, Fe, Mn and Al. Therefore, increasing pH soil causing acid anions were strongly adsorbed at the colloidal surfaces by decreasing the form. It has also been suggested that in the pH highest than 7, Fe, Al and Cu tend to precipitate in the form carbonate and hydroxide.

Phosphorus sorption capacity by different soils studies

The sorption capacity of P by the all soils series was illustrated in Fig.2. I can be seen that the sorption capacity for each soil studies was rapid initially and gradually diminished to attain equilibrium after which there was no significant increase in the adsorption rate.



Fig 2. Capacity of phosphorus sorption by different soils Fig 3. Capacity of ammonium sorption by different soils studies

The results of this experiment were in agreement with the results of the research of Ranjbar et al. [26]. The equilibrium was reached after approximately 72 h and the levels of P adsorbed were; 6.27, 6.84 and 6.92 mg P g⁻¹ by the Chott Mariem, Enfidha and Kondar soils, respectively. In the fact, the fast initial sorption rate may be explained by high availability of active binding sites on the adsorbent surface. Sorption occurs rapidly and is normally controlled by the diffusion of P from the substrate to the surface [27]. In the latter phases, sorption is likely an attachment-controlled process such as the penetration of the P ion into the pores of

soil micro aggregates and the P ion saturation of the adsorbent surface prevents P ion sorption for each increase of soil P application [1]. Also the results also indicate that the soil of the Chott Mariem site adsorbed the smallest amount of P, probably because this soil had lower content of clay, organic matter and Ca (Table 1). In the same way, it is possible that several other processes may have played an important role in P sorption in the different soils as well; for example, a decrease in surface area during adsorption and the precipitation due to the high values of pH and Ca associated with low contents of Fe and Al oxides [28]. Another hand, the kinetics sorption constant values (k, k_2 , α and β), and the predicted Qe values for all tested combinations and the correlation coefficients R^2 of each model pseudo-first order, pseudo-second order and Elovich models are given in Table 3.

		P	seudo-first orde	r	Pseudo-second order				Elovitch		
Sites	Qa	\mathbb{R}^2	$Qe(mg.g^{-1})$	\mathbf{k}_1	\mathbb{R}^2	Qe(mg.g ⁻¹)	k	\mathbb{R}^2	$\alpha(\text{mg.g-}^1.\text{min}^{-1})$	β (g.mg ⁻¹)	
Chott Mariem	6,27	0,90	2,04	0,067	0,98	6,85	0,015	0,91	2,60	0,82	
Enfidha	6,74	0,92	2,14	0,091	0,97	7,93	0,014	0,89	3,26	0,68	
Kondar	6,94	0,88	2,11	0,079	0,98	7,94	0,016	0,90	3,54	0,67	

Table 3: Modeling parameters	of phosphorus kinetics sorption.
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The results indicate that the pseudo-second-order model had the highest R^2 values. For this it has been adequately employed to describe reactions. This model is based on the sorption capacity of the solid phase and indicates that the sorption P by soils studies was quickly.

Ammonium sorption capacity by different soils studies

The sorption capacity of NH_4^+ by the all soils series is shown in Fig.3. I can be seen that the sorption capacity was rapid initially and gradually diminished to attain equilibrium after which there was no significant increase in the adsorption rate. It can be due to the presence of unsaturated and active sites in the initiation of sorption process and fast diffusion in the pores [26]. By over of time, pores are occupied due causes to increase the NH_4^+ ion sorption. But, with increasing of contact time, the driving force decreases during mass transfer process that leads to increasing of NH_4^+ sorption slowly and reaches to the constant value considered as the equilibrium time [29]. Also the results indicate that the amounts of NH_4^+ sorption by different soils were respectively 5.83, 6.5 and 6, 3 mg NH_4^+ g⁻¹ from the soil Chott Mariem, Enfidha and kondar. The maximum amount of strongly sorption NH4⁺ was observed in soil profile of Kondar area, which had the highest CEC and clay content. Elmaci et al. [30], by evaluation of NH_4^+ sorption in some agricultural soils, reported that sorption had positive and negative correlation with silt and sand contents, respectively. Clay content and its composition are two important effective factors on NH₄⁺ sorption. The study results of Zhang et al. [31] revealed that the NH_4^+ sorption had positive correlation with clay content and CEC. Balci [32] indicated that NH_4^+ often related to organic matter rather than clay minerals and calcium carbonate. Boatman and Murray [33] by studying NH_4^+ sorption on marine sediments reported that in sediments rich in organic matter, clay-organic matter complex was controlling the NH_4^+ sorption, while in sediments poor in organic matter, type of clay minerals affected behavior of NH4⁺ sorption. Same others researches have reported that NH4⁺ sorption capacity remarkably depends on the degree of k saturation of the interlayers of 2:1 clay minerals [29,32]. Moreover, the kinetics sorption constant values (k , k_2 , α and β) and the predicted Qe values for all tested combinations and the correlation coefficients R² of pseudo-first order, pseudo-second order and Elovich models are listed in Table 4.

Table 4: Modeling para	meters of ammonium	kinetics	sorption.

]	Pseudo-first ord	er	Pseudo-second order			Elovitch		
Sites	Qa	\mathbf{R}^2	$Qe(mg.g^{-1})$	k	\mathbb{R}^2	Qe(mg.g ⁻¹)	k	\mathbf{R}^2	α (mg.g- ¹ .min ⁻¹)	β (g.mg ⁻¹)
Chott Mariem	5,8	0.99	5,877	0.037	0.99	7,166	0.0002	0.98	0.059	2.243
Enfidha	6,3	0.98	6,342	0.040	0.98	7,564		0.98	0.060	3.168
Kondar	6,5	0.97	6,384	0.044	0.99	7,517	0.0003	0.99	0.063	3.988

The results indicate that the model pseudo-second order had the highest R^2 values. For this it can be success to describe the kinetics of NH_4^+ sorption. This result is in accordance with reported results by Liu et al. [34].

IV. Conclusion

The study investigated the distribution of elements content in sampled soils collected from four layers of fixed depth, which should describe the topsoil or subsoil layers of three soils sites from the region of Sousse, Tunisia. The results show a graduation of the variation with the deeps in the different areas soils especially soil Chott Mariem site and it can be conclude that the variation between the sites is very higher than the variation in within a same soil profile. The principal component analysis (PCA) was used to identify the relationships

between some elements concentration for all soil samples. Correlation diagram exhibited four groups of elements when it can be revealed some relationship correlations as the positive correlation between clay proportion and CEC values and the negative correlation between pH values and acid cations concentration. Another hand it appears that sorption of phosphorus and ammonium by the each soil was rapid initially and gradually diminished to attain equilibrium. The variation of level phosphorus and ammonium sorption was related with the soil proprieties variation. Applications of three different kinetic equations to the data show that the rate of phosphate adsorption was best predicted by the pseudo-second-order kinetic model.

References

- Y.Wang, A.Shen, J. Niu J and R. Liu, Adsorption of phosphorus on sediments from the Three- Gorges Reservoir (China) and the relation with sediment compositions. Hazard Mater J, 162, 2009, 92–98.
- [2]. S.Zare, M. Jafari, A.Tavili, H. Abbasi and M. Rostampour, Relationship between environmental factors and plant distribution in arid and semi-arid area (Case Study: Shahriyar Rangelands, Iran). American-Eurasian J Agric and Environ Sci, 10(1), 2011, 97-105.
- [3]. E. Ekundayo, Suitability of waste disposal sites for refuse disposal in Benin City, Nigeria. Nig. J. Soil Sci, 13, 2003, 21-27.
- [4]. E.Haller, Effect of the germinating seed environment on crop yields. I. Effect of soil acidity at germination on yields of sweet clover and alfalfa. Experimental Agric, 19, 1983, 55-56.
- [5]. FAO, Forest policy in Tunisia. By Chakroun, M.L. Rome, 1989, 27.
- [6]. W.Hendershot, H.Lalande, M. Duquette, Ion exchange and exchangeable cations. In: Carter, R. (Ed.), Soil Sampling and Methods of Analysis Edited by Canadian Society of Soil Science. Lewis Publisher, Boca Raton, 1993, 167–176.
- [7]. G.Gee, J. Bauder, Particle-size Analysis. InA.L.Page (ed.) Methods of soil analysis, Part1, Physical and mineralogical methods. Second Edition, Agronomy Monograph 9, American Society of Agronomy, Madison, 1986, 383 - 411
- [8]. M. Jackson, Soil Chemical Analysis 1st Edn. Prentice Hall. Eaglewood Cliffs, New Jersey, USA M.C, 1962.
- [9]. A. Mehlich A, Mehlich 3 soil test extractant: A modification of the Mehlich 2 extractant. Commun. Soil Sci. Plant Anal, 1984, 1409-1416.
- [10]. R. Cody, G.Thompson, Quantitative X-ray powder diffraction analysis of clays using an orienting internal standard and pressed disks of bulk shale samples. Clays and Clay Minerals, 24,1976, 224–231.
- [11]. N. Hamdi, E Srasra, 2008. Interaction of aqueous acidic-fluoride waste with natural Tunisian soil. Clays and Clay Minerals, 56, 2008, 259–271.
- [12]. A. Aweto, G. Enaruvbe, Catenary Variation of Soil Properties under Oil Palm Plantation in South Western Nigeria. Ethiopian Journal of Environmental Studies and Management, 2010, 3:1.
- [13]. M, Abua, R. Offiong, A. Iwara, U.Ibor, Impact of Newly Constructed Roads on Adjoining Soil Properties in Tinapa Resort, South-Eastern Nigeria. Annals of Humanities and Development Studies, 1, 2010, 176-184.
- [14]. Iwara AI, Ewa EE, Ogundele FO, Adeyemi, JA, Otu, CA, Ameliorating Effects of Palm Oil Mill Effluent on the Physical and Chemical Properties of Soil in Ugep, Cross River State, South-Southern Nigeria. International Journal of Applied Science and Technology, 1, 2011, 106 – 112.
- [15]. G.Reid and J. Dirou, How to Interpret Your Soil Test. [Online] Available: http://www.dpi.nsw.gov.au/agriculture/resources/soils/testing/interpret, 2004.
- [16]. U.Sainju, B. Singh and W.F. Whitehead, Long-term effects of tillage, cover crops, and nitrogen fertilization on organic carbon and nitrogen concentrations in sandy loam soils in Georgia, USA. Soil Tillage Res, 63, 2002, 167-179.
- [17]. I- Busaidi and P. Cookson, Leaching potential of seawater. Journal of Agricultural and Marine Sciences, 9, 2005, 27-30.
- [18]. E.Iwuafor, B.Tarfa, E.Pam and D.Yaro, Effect of soil heating on soil properties and maize growth in an Alfisol in Northern Guinea Savanna. Nig. J. Soil Res, 1, 2000, 35-41.
- [19]. C.Young, T.Juang and C.Chao, Effect of Rhizobium and VA mycorrhiza inoculation on nodulation, symbiotic nitrogen fixation and soybean yield in subtropical tropical fields. Biol. Fertil. Soils, 6, 1988,165-169.
- [20]. R. Ruhe, Soil climate system across the prairies of midwestern USA. Geoderma, 34, 1984, 201–219.
- [21]. C.Phillips and P. Chiy, Effects of applying sodium and sulphur fertilizers on the concentrations of elements in water leached from permanent pasture. J. Sci. Food Agr, 82, 2002, 806–815.
- [22]. J.Sutcliffe, D. Baker, In: Suministros de Sales, Cuadernos de Biolog´ıa, Las Plantas y las Sales Minerales (Sutcliffe, J.F. and Baker, D.A., Eds.), Barcelona, Omega SA, 1983.
- [23]. Duchaufour, Pedogenesis and classification, 1^{ed}, Masson, Paris, 1997, 7–25.
- [24]. A. Mori, Vertic soils. Vertisols and soils tirsifiés Tunisia North, in: Proceedings of the Conference on Mediterranean soils, Madrid, Spain, 1966, 451-462.
- [25]. H. Ben Hassine, Mineralogical nature and nutritional role of cereal soil clays in subhumid and semi-arid zones (Tunisia), Geoscience, 338, 2006, 329–340.
- [26]. Ranjbar and Jelali, Ionic liquid based dispersive liquid-liquid microextraction combined with ICP-OES for the determination of trace quantities of cobalt, copper, manganese, nickel and zinc in environmental water samples. Microchimica Acta. 17, 2012, 119-127.
- [27]. -N. Devau, P. Hinsinger, Le Cadre, F. Gerard, Root-induced processes controlling phosphate availability in soils with contrasted Pfertilized treatments. Plant Soil, 348, 2011,203–218.
- [28]. L.Gustafsson, S. Baker, J.Bauhus and W. Beese, Retention forestry to maintain multifunctional forests: a world perspective. Bioscience, 62, 2012, 633–645.
- [29]. H. Huang, X.Xiao, B.Yan and L.Yang, Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent. J. Hazard Mater, 175, 2010, 247–252.
- [30]. O.Elmaci, S. Delibacak, M. Secer and A. Bodur, 2002, Fertility status, trace elements and heavy metal pollution of agricultural land irrigated from the Gediz River. Int. J. Water, 2(2/3):184-195.

- [31]. Y.Zhang, S.Huang, D.Wan, J. Huang, W. Zhou, Y. Zou, Fixed ammonium content and maximum capacity of ammonium fixation in major types of tillage soils in Hunan province, China. Agric Sci China, 4, 2007, 466–474.
- [32]. Y. Balci, Phytophthora species in oak ecosystems in Austria and Turkey and their role in the oak decline syndrome. Ph.D Thesis. BOKU, Vienna, Austria, Y, 2002, 117.
- [33]. C.Boatman and D. Murray, Modeling exchangeable NH₄⁺ adsorption in marine sediments: process and controls of adsorption. Limnology and Oceanography, 27, 1982, 99–110.
- [34]. H.Liu, Y. Dong, H.Wang and Y. Liu Y, Ammonium adsorption from aqueous solutions by strawberry leaf powder: equilibrium, kinetics and effects of coexisting ions. Desalination, 263, 2010, 70–75.