Distribution of different forms of phosphorus in calcareous soils from middle and south of Iraq

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Abstract : **A survey of the chemical way to determine the amount of different phosphorus forms in calcareous soils was carried out on 22 calcareous soils fertilized for many years with phosphate fertilizers from central and southern Iraq. Extraction methods were developed by combining the technique of individual traditional methods of different forms with sequentially extraction technology. Soil samples were collected from surface (0-30 cm) and subsurface (30-60 cm) horizons. Forms of soluble, ready available, organic and total phosphorus were extracted independently and in addition to the successive extraction were carried out according to Jiang and Gu (1989) method. The amount of soluble and available phosphorus extracted were low and ranged from 0.17 to 2.12 mg kg^{-1} and 7.28 and 34.3 mg kg^{-1} respectively. Organic phosphorus was medium and the values ranged 30.9 and 93.1 mg kg^{-1} while the total phosphorus content was high and the values ranged between 206.9 and 570.6 mg kg^{-1}. The quantities of phosphorus extracted sequentially by chemical extracts and the possibility of diagnosing different forms of phosphorus associated with calcium Ca2-P, Ca8-P and Ca10-P (apatite) in addition to P associated with OM and free iron and aluminum oxides. The average values of Ca2-P, Ca8-P, Fe-P and occluded (O-P) extracted were nearly similar and the values were 20.47, 25.28, 25.4, and 26.23 mg kg^{-1} respectively while the Ca10-P was much higher (194.54 mg kg^{-1}) than the other forms.**

KEYWORDS: words: di-, octa- and deca-calcium phosphates, Fe phosphate, soluble, available and total phosphates.

I. INTRODUCTION

Phosphates, the most abundant form of phosphorus in the environment, are available for assimilation; thus, they have been traditionally used as fertilizers. Phosphorus (P) is an essential element for plant growth and maintenance of an adequate amount of soil P through an application of inorganic and/or organic P is critical for the sustainability of cropping systems. The availability and fractions of soil P may change due to long-term continuous P fertilization besides its yield increasing effect [1,2].

Total and available phosphorus have been extensively carried out but little work is done on the distribution of the various discrete chemical forms of inorganic phosphate. The distribution of various forms of inorganic phosphorus in soils is affected by the activities of different ions in the soil, pH, age, drainage, fertilizer practices, mineralogical nature, climate, and management practices [3]. Generally, 10-20% of P applied is available for crop uptake in the year of application, whereas the remaining 80-90% soil P (residual P) is adsorbed on the soil constituents and builds up as the soil P capital. The residual P is partitioned into different fractions and pools [4]. In calcareous soils, soil inorganic P (Pi) represents the dominant component of the soil P pool in calcareous soils. Soil Pi was divided into various fractions such as Ca-P (HCl extractable P), Fe- and Al-P (non occluded Fe- and Al-bound P), and occluded P However, in calcareous soils, the majority of Pi exists in the various Ca bound forms and there was a great difference in P availability among the Ca-P fractions. These P fractions have remarkable differences in mobility, bioavailability, and chemical behaviors in soil and can be transformed under certain conditions [5].

To better characterize Pi transformations, using a sequential extraction procedure, based on their availability and solubility to define them in soils both as qualitatively as well as quantitavely. A wide

variety of extraction procedures for soil and sediment P have been developed, varying with the aim of the study and the P fractions targeted [6]. The P forms commonly separated include soluble and loosely sorbed (labile) L-P, redox-sensitive iron (Fe), aluminum (Al) bound and non-reducible Fe (surface-bound), calcium (Ca)-bound P (apatite-P), and organic P. and non-reducible Fe (surface-bound), calcium (Ca)-bound P (apatite-P), and organic P. Phosphorus adsorbed or precipitated with Ca, Fe, and Al is stable when soils are maintained under conditions leading to P fixation, but may be susceptible to dissolution and regeneration upon change in land use or environmental conditions [7]. The aim of investigation is to identify the organic and inorganic pools of phosphorus, total P, and to characterize soil P reserves by using different extraction method and to assess the validity of a phosphorus fractionation procedure, in chemical characterization of soil P.

II. MATERIAL AND METHODS

The experiment was carried out at Kut, University of Waist, Iraq, during July 2018 to June 2019. The calcareous soils in this investigation were collected from middle and south of Iraq, where the soils had amended to phosphorus fertilization for many years (Table 1). The soils were taken from (0-30) cm and (30-60) cm depths and l samples were air dried, grind and sieved to pass through 2 mm sieve and stored in the plastic container for further analysis. Particle size distributions were determined according to international pipette method with removing carbonate [8]. Soil pH was measured in 1:5 soil-water suspensions with a glass electrode [9], by using a Microprocessor pH meter model-pH 211-HNA Com. Italy. Electrical conductivity of soil extract (ECe) was measured in 1:5 soil-water dilution [10], by using EC meter, and model WTW 82362 Weilheim, Germany, after being adjusted to 25 °C. Soil organic matter was determined by Walkley and Black method as described by [11]. Total calcium carbonate was determined with calcimeter. Active calcium carbonate was determined titremetrically using Droulinean procedure [12]. The extraction procedure used in this study principally follows the classical method of [13], and involved five fractionation steps in addition to soluble phosphate S-P.

III. RESULTS AND DISCUSSION

The particle size distribution of soil (sand, silt, clay) varied between soils and most of soils samples were rich in fine grains (clay + silt). The clay content ranged from 224 to 581g kg^{-1} with average 383.8 g kg^{-1} while the silt content ranged between 219 to 440 g kg $^{-1}$ with average value 327.2 g kg^{-1}. There is no difference in the content between the surface horizons and the subsurface horizons in sand, silt and sand.

Table (2) refers to the values of electrical conductivity (ECe) of the study soils ranged from 3.11 to 6.99 dS m^{-1} with average 4.65 dS m^{-1} and the vales were higher at the surface horizons. The difference in electrical conductivity may be due to a difference in the quality of the water used for irrigation the crops or the presence of salts that are difficult to dissolve in these soils. Also, it may be due to the low amount of rain fall in these arid region. So, the increase in the amount of salts in the surface layers indicates the lack of leaching process or high salinity of irrigation water, which led to the accumulation of salts in the surface layer.

Soil pH of the studied soils are shown in the Table (2), and the pH values were ranged from 7.0 to 7.9 with the average value7.25. The soil reactions were slightly alkaline and this may be due to parent material rich in carbonate materials [14], or due to using irrigation water high in Ca^{2+}. In addition, the studied area is arid region, the leaching process was very low which may lead to increase the pH in the surface horizons than sub- surface horizons. On the other hands, the surface soils have higher salinity than subsurface soils, and an increase in the values of the pH of surface soils can be observed. It had been found that the soil reaction values were decreased by increasing the salinity of the soil. The reclamation of saline soils in Iraq leads to a decrease in the proportion of salts in the soil and increase the degree of reaction due to hydrolysis that leads to the formation of sodium hydroxide [15,16]. The decrease in soil reactivity values may be attributed to the accumulation of neutral reaction salts in the soil, which caused a decrease in pH values towards neutralization [17]. The reason for the existence of a near inverse relationship between the salinity of calcareous soils and the degree of their reaction was attributed to the presence of calcium ions that have an inverse relationship with the degree of soil interaction and a direct relationship with the salinity of the soil [18].

Table 1: The location and GPS reading of the studied soils.

Soil No.	Soil samples location	Latitude N	Longitude E
1	Baghdad	33° 16'4.5444"	44° 22'44.382"
2	Alsowaera	32° 57' 14.076"	44° 45' 58.626"
3	Tagalden	32° 58' 59.448"	44° 51' 35.352"
4	Alshehemeya	32° 41' 41.8992"	44° 58' 23.4516"
5	Alzobaidea	32° 42'9.821"	45° 7'14.423"
6	Alnumania	32° 32' 40.1784"	45° 24' 26.8272"
7	Alahrar	32° 31' 1.6536"	45° 36' 35.3628"
8	Shik Saad	32° 33' 53.9604"	46° 16' 51.4596"
9	Technical Institute in Kut	32° 26' 53.538"	45° 54' 0.7416"
10	Almoafakia	32° 16 15.9024"	45° 55'32.5668"
11	Alhay	32° 12' 4.0644"	45° 59' 0.1356"
12	Albashaer	32° 7' 27.5664"	46° 7' 1.7688"
13	Aldewania	31° 56'45.2652"	44° 47'8.1528"
14	Abo Almash	31° 40' 54.5376"	46° 13' 12.72"
15	Refaee1	31° 43' 9.4404"	46° 6' 18.954"
16	Alrefaee2	31° 43' 5.7144"	46° 6' 25.0848"
17	Alfager	31° 54'55.89"	45° 57'56.8944"
18	Almothana	30° 35'32.5464"	45° 17'29.7744"
19	Alsemawa distrecet	31° 19'7.8204"	45° 16'50.2248"
20	Alsalman disstrect	30° 30'20.6676"	44° 32'18.3156"
21	Alkufa	32° 2'50.0748"	44° 22'15.3876"
22	Kerbala	32° 36'24.6456"	44° 0'37.4112"

The results of some chemical analysis were shown in Table (2) and indicated that the total calcium carbonate equivalent (TCCE) values of the study soils ranged between 155 and 482 g kg $^{-1}$ with average of 309.1 g kg^{-1}. Washing processes of carbonate minerals from surface to sub-surface horizons were very low due to lack of rain and irrigation water in addition to the lack of solubility of carbonates minerals in water lead to abundance of calcium minerals and accumulation at surface horizons. Studies indicated that most calcium carbonate had been transported with the waters of the Tigris and Euphrates rivers and their tributaries in the form of fine minutes from the upper north and deposition accumulated with other soil minutes in the sedimentary plain [19]. He explained that the carbonate minerals move from the surface horizons of the soil to the sub-surface horizons and its quantity increases with increasing depth with increasing the amount of the carrier (water).

The results in Table (2) indicated that the values of the active calcium carbonate equivalent (ACCE) of the study soils ranged from 101 to 390 g kg^{-1} with average of 225.2 g kg^{-1} and the content of surface horizons were higher than subsurface horizons. The distribution pattern of ACCE in the study soils were depending on the origin of the materials transported with the Tigris River water as well as the lack of weathering and washing processes because of the lack of rain with the abundance of calcium ions and bicarbonate which led to their accumulation in the surface horizons more than subsurface horizons. Organic matter (OM) content were shown in Table (2) and the results showed that the content was relatively low and the values ranged between 3.35 to 19.8 g kg^{-1} with an average a rate of 10.42 g. kg $^{-1}$ .The content of aluminum oxides (Al_2O_3) of study soils ranged between 29.3 to 64.9 g kg^{-1} and an average

of 42.67 g kg^{-1}, while the free iron oxides (Fe$_2$O$_3$) value ranged values from 21.5 to 64.9 g kg^{-1} with the average 46.42 g kg^{-1}.

Table (2) : Some physicochemical properties of soil samples

| Soil NO	Depth	Texture	Sand	Silt	Clay	OM	Al$_2$O$_3$	Fe$_2$O$_3$	TCCE	ACCE	pH	ECe
	Cm						g kg^{-1}					dSm^{-1}
1	0- 30	Clay	159	260	581	15.4	49.1	50.2	482	290	7.8	6.71
	30-60	Clay	152	268	580	11.9	45.8	49.2	351	271	7.4	4.60
2	0- 30	Clay	172	348	480	14.6	36.5	42.9	397	390	7.2	5.60
	30-60	Clay	170	349	481	11.2	31.9	40.9	240	201	7.0	3.20
3	0- 30	Clay	356	244	400	4.49	49.9	61.9	254	180	7.5	7.80
	30-60	Clay	340	260	400	3.42	45.9	52.9	155	151	7.1	3.20
4	0- 30	Clay	276	224	500	19.8	41.9	56.9	381	288	7.3	9.14
	30-60	Clay	260	240	500	17.9	33.9	46.9	297	199	7.0	5.11
5	0- 30	Clay	310	250	440	16.5	39.3	40.9	337	309	7.1	13.2
	30-60	Clay	308	252	440	14.1	29.3	31.9	295	234	7.0	9.90
6	0- 30	Sand clay loam	516	220	264	9.90	64.9	38.9	376	243	7.3	8.50
	30-60	Sand clay loam	517	219	264	7.70	54.9	40.9	267	201	7.0	2.50
7	0- 30	Loam	376	380	244	4.60	63.9	51.7	367	285	7.1	3.40
	30-60	Clay loam	348	371	281	3.50	53.6	41.1	260	241	7.0	1.40
8	0- 30	Loam	416	320	264	5.20	49.3	50.9	326	317	7.2	3.50
	30-60	Loam	413	322	265	4.29	33.8	41.9	283	281	7.0	3.10
9	0- 30	Clay	336	264	400	17.1	37.9	58.9	327	228	7.2	5.10
	30-60	Clay	335	264	401	10.6	31.9	46.9	227	203	7.0	4.90
10	0- 30	Loam	336	440	224	7.41	52.9	61.9	165	132	7.3	4.40
	30-60	Loam	335	440	225	6.91	45.8	45.9	162	128	7.2	2.20
11	0- 30	Clay loam	276	420	304	4.60	44.9	49.2	280	150	7.4	3.20
	30-60	Clay loam	279	419	302	3.35	40.6	38.6	193	101	7.2	2.30
12	0- 30	Clay loam	296	342	362	15.7	43.9	56.6	402	230	7.2	20.5
	30-60	Clay loam	298	341	361	11.4	39.9	55.5	321	205	7.0	15.3
13	0- 30	Silty clay loam	199	421	380	15.4	46.1	49.9	384	204	7.8	3.30
	30-60	Silty clay loam	196	423	381	11.9	39.1	41.9	248	178	7.2	4.30
14	0- 30	Sand clay loam	436	280	284	14.1	39.2	37.5	291	241	7.7	4.20
	30-60	Sand clay loam	430	281	289	9.15	38.9	21.5	203	192	7.0	3.30
15	0- 30	Clay	188	366	446	14.6	37.9	60.9	466	223	7.2	3.90
	30-60	Clay	187	364	449	8.64	31.9	53.9	342	176	7.0	2.40
16	0- 30	Clay	202	320	478	11.8	48.6	50.2	381	200	7.9	8.10
	30-60	Clay	200	339	461	10.3	38.1	40.9	262	190	7.4	5.40
17	0- 30	Clay	176	340	484	13.3	52.2	49.2	315	280	7.2	8.50
	30-60	Clay	165	345	490	10.4	42.4	38.1	251	201	7.0	4.10
18	0- 30	Clay	196	320	484	12.2	49.1	41.7	323	301	7.5	6.10
	30-60	Clay	189	321	490	6.50	31.8	32.9	239	221	7.1	5.40
19	0- 30	Loam	376	380	244	9.10	49.9	61.9	295	212	7.4	8.20
	30-60	Clay loam	346	371	283	8.20	40.9	50.9	210	186	7.0	6.20
20	0- 30	Clay loam	336	380	284	11.5	39.9	64.9	477	273	7.9	13.1
	30-60	Clay loam	330	379	291	9.50	35.7	40.9	389	200	7.3	10.9
21	0- 30	Clay	266	314	420	13.2	41.7	38.9	453	311	7.7	4.70
	30-60	Clay	264	315	421	11.6	32.9	39.8	327	228	7.1	2.80
22	0- 30	Clay	224	340	436	8.34	42.9	47.5	304	238	7.3	4.30
	30-60	Clay	226	343	431	7.51	36.9	25.7	295	199	7.0	2.90
mean			228.9	327.2	383.8	10.42	42.67	46.42	309.1	225.2	7.25	4.65

Generally, the amount of Fe- and or Al- oxides were low because of the low content of Fe parent materials and high soil pH These results were in agreement with the results found by [20], conducted on Syrian basaltic soil content of aluminum oxides and iron oxides from 18.83 to 23.22%. The content of aluminum oxides in calcareous soils were usually low due to high soil reaction values [21]. These Fe^{3+}oxides were insoluble in neutral and high pH, making iron unavailable to plant in alkaline and in calcareous soils. Furthermore, in these types of soil, iron readily combines with phosphates, carbonates, calcium, magnesium and iron hydroxides. The results of extraction of different forms of phosphorus from studied soils and the results were shown in Table (3) and indicated that the soluble phosphorus (S-P) values ranged from 0.17 to 2.12 mg kg^{-1} and the average value was 0.81 mg kg^{-1}.

Table (3): Phosphorus fractionations of soil samples

Soil NO	Depth	S-P	Ca2-P	Ca8-P	Fe-P	Occluded -P	Ca10-P	Recovery-P	A-P	T-P
	cm				mg kg^{-1}			%	mg kg^{-1}	
1	0- 30	0.77	30.11	33.9	25.75	39.1	321.9	100.2	15.2	450.5
	30-60	0.31	18.10	27.05	20.29	33.35	155.9	84.4	10.3	302.1
2	0- 30	1.54	32.35	38.35	26.15	31.35	307.5	92.8	31.2	471.2
	30-60	0.91	22.85	23.55	24.55	24.55	132.65	65.4	12.9	350.2
3	0- 30	1.02	18.90	24.3	35.70	31.65	171.9	98.4	17.1	288.1
	30-60	0.71	15.65	13.85	30.05	23.28	83.10	70.8	14.4	235.5
4	0- 30	1.92	26.35	43.3	23.05	25.50	454.45	99.8	34.3	570.6
	30-60	0.76	19.60	21.85	21.10	16.80	119.80	73.9	16.2	270.7
5	0- 30	0.93	20.50	39.90	25.45	20.35	379.3	99.1	25.1	490.7
	30-60	0.3	17.40	15.55	24.20	17.22	122.40	74.4	20.1	265.0
6	0- 30	0.61	11.95	19.55	29.70	30.95	325.05	97.6	20.8	428.2
	30-60	0.29	11.75	11.80	22.30	12.30	109.50	69.9	12.1	240.3
7	0- 30	0.81	16.10	27.70	32.50	20.90	287.45	97.3	17.2	396.3
	30-60	0.39	13.65	12.05	29.60	16.40	92.20	77.9	12.6	210.9
8	0- 30	0.75	19.70	23.10	39.55	35.80	226.75	100.2	15.3	343.9
	30-60	0.32	12.90	18.20	28.20	23.15	167.70	89.5	13.1	280.0
9	0- 30	0.75	20.25	22.50	30.14	30.30	218.7	93.7	16.1	344.4
	30-60	0.36	15.10	18.55	24.35	21.20	77.75	67.8	10.7	232.0
10	0- 30	1.12	19.95	27.75	40.95	33.30	186.25	91.6	13.9	337.8
	30-60	0.81	16.30	21.75	26.75	23.10	98.45	83.7	10.3	223.5
11	0- 30	0.98	10.90	17.05	32.44	32.40	152.65	90.6	9.19	271.9
	30-60	0.45	6.95	10.60	29.25	20.30	73.95	68.4	7.28	206.9
12	0- 30	0.63	22.15	43.75	27.40	37.11	181.8	94.5	18.6	330.9
	30-60	0.35	18.15	36.30	23.30	29.23	92.25	73.1	13.9	273.2
13	0- 30	0.91	26.35	35.30	29.55	24.25	254.7	93.8	27.2	395.5
	30-60	0.49	14.15	20.50	17.80	18.45	127.0	82.6	20.8	240.1
14	0- 30	0.89	20.60	33.80	19.95	25.56	255.7	93.0	25.4	383.4
	30-60	0.36	13.70	18.20	17.23	20.23	108.3	81.3	19.9	218.9
15	0- 30	0.77	32.50	32.15	19.70	30.9	170.65	95.1	18.4	301.5
	30-60	0.29	10.65	18.15	17.10	19.30	117.45	88.1	11.8	207.6
16	0- 30	0.86	28.80	31.40	20.06	36.85	223.7	88.5	15.2	386.2
	30-60	0.41	19.83	14.20	15.95	17.40	111.3	71.4	11.9	251.0
17	0- 30	2.12	36.10	23.85	20.80	29.85	320.85	85.0	34.3	510.0
	30-60	1.19	13.40	22.55	19.20	19.65	148.80	74.9	19.8	300.1
18	0- 30	0.32	28.50	21.70	21.00	38.95	338.45	91.2	29.6	492.1
	30-60	0.17	26.80	19.10	18.60	29.20	247.30	85.1	24.5	400.9
19	0- 30	1.99	19.70	22.10	24.40	31.40	233.35	85.7	12.1	388.4
	30-60	0.51	11.45	14.60	17.20	23.45	138.95	54.8	9.50	376.2
20	0- 30	1.55	30.6	33.25	29.80	36.23	224.55	97.1	19.1	366.5
	30-60	0.71	24.1	24.75	28.70	30.30	198.65	92.0	12.5	334.1
21	0- 30	1.36	26.6	45.45	33.12	23.20	308.15	98.0	14.9	446.7
	30-60	0.79	19.4	36.20	21.10	18.15	107.40	76.0	10.2	267.0
22	0- 30	1.42	30.44	30.35	32.95	31.80	269.45	99.7	25.3	397.5
	30-60	0.91	29.45	22.65	21.30	25.15	116.0	71.1	20.8	302.9
Mean		0.81	20.47	25.28	25.41	26.36	194.54	85.44	17.5	335.9

The content found in the surface soils horizons was higher than the content of subsurface soils and this due to the addition of mineral fertilizers to the surface soils for many continuous years. The concentration of S-P was entirely dependent on the soil properties in terms of its total and active calcium carbonate content, the amount of clay and minerals type, the dominance of clay minerals, the amount of iron oxides and free aluminum as well as the quantity and quality of organic matter in the soil [22]. This is in addition to the amount of phosphorus added annually in the form of mineral fertilizers, which increases the readiness of dissolved phosphorus by reducing the degree of soil minerals interaction and increase the availability of the phosphorus in the soil solution by replacing the phosphorus ion on the soil surfaces particles [23].

The percentage of mean dissolved phosphorus represents a very small fraction 0.24% of the mean total phosphorus extracted by $HClO_3$ digestion as in Fig.1 .In the studied soils, the availabilities P (A-P) were found to be higher in the surface horizons as compared to subsurface soils and the value ranged from 7.28 to 34.3 mg kg^{-1} with average 17. 5 mg kg^{-1}. This may be due to the addition of mineral fertilizers to the surface soils. This may be due to higher fresh OM input and/ or higher root plant activity in the soil surface. This may be because organic matter reduces phosphorus adsorption and reduces the energy of phosphorus binding with mineral soils [7]. It had been found a significant and positive correlation between OM and available P in soils (Fig.1) [24], and they summarized how organic compound may increase P availability by formation of organophosphate complexes that were more easily assimilated by plant, anion replacement of $H_2PO_4^-$ on adsorption sites. In addition, decreasing the pH value of the soil caused an increase in P availability especially in alkaline soil. On the other hands, the coating of Fe and Al particles by humus to form a positive cover and this may reduce P adsorption.
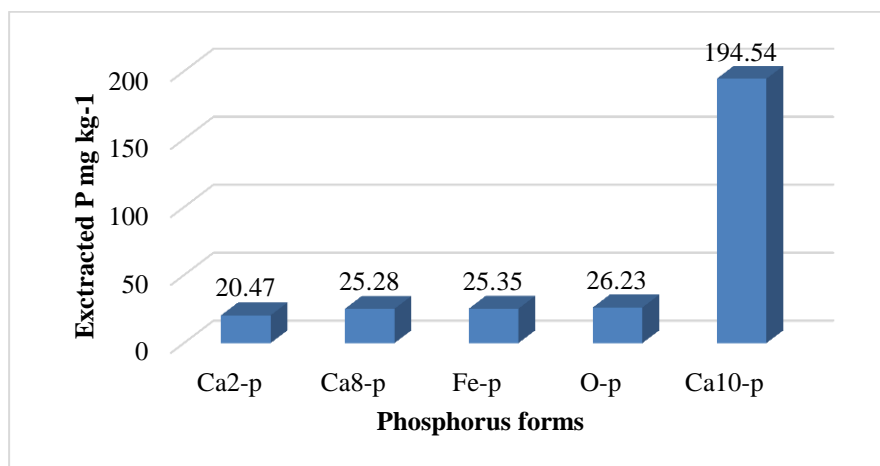
Fig 1 : Sequential phosphorous image recovery rate

Organic matter may reduce phosphorus adsorption and reduce the energy of phosphorus binding with mineral soils [7]. Experimentally, El-Baruni and Olsen [25], indicated that the application of four levels (0, 11, 22, and 44) tons ha^{-1}of OM to calcareous soil used in laboratory experiment lead to a significant increase in P availability. Also, similar results had been found by [3]. On the other hand, the effect of fertilizer application on the surface horizons may lead to lower the soil pH in situ and increase the availability of phosphorus in the soil locally. Also, increases of fresh organic matter may inhibits the process of adsorption of phosphorus in the soil and increases of organic matter due to plant residue which leads to increase available phosphorusl [26,27], and that organic matter is an important source of phosphorus during microorganisms decomposition of OM to soil solution [28].

Since the A-P values for most of the studied soils within the critical limit 25 - 15 mg kg $^{-1}$ for the all the surface horizon, which was determined by [26], in calcareous local soils in Iraq, so these soils do not suffer from the lack of A-P. The mean percentage of A-P represents a very small fractions (5.21%) of the mean total phosphorus (T-P) which extracted by acids extraction (Fig.2). Total P of the studied soils are shown in the Table (3). The amount of total P values ranged from 206.9 to 570.6 mg kg^{-1} soil, and the

average was 335.9 mg kg^{-1}. Generally, the total P were high in these soil and this was expected because of addition of mineral fertilizers to these soils for many years which lead to high total P content.
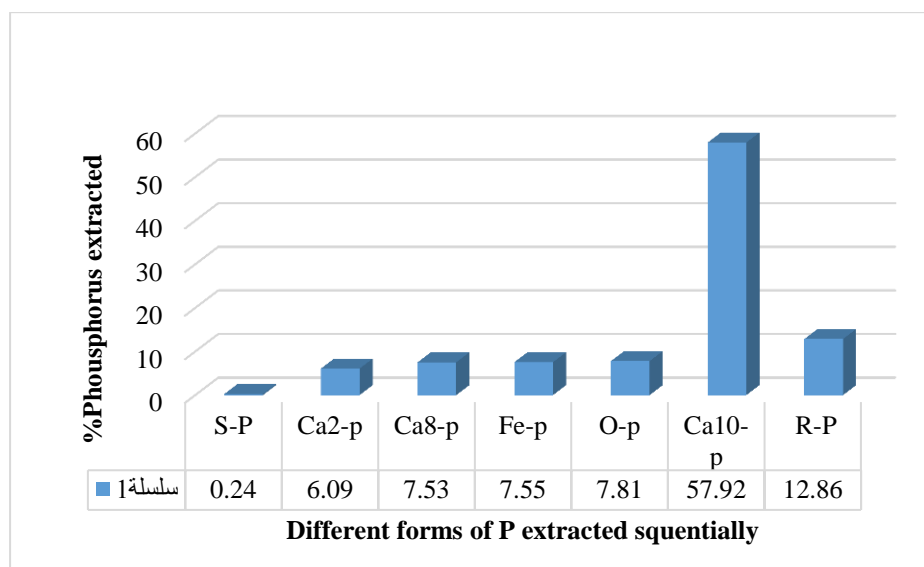

	S-P	Ca2-p	Ca8-p	Fe-p	O-p	Ca10-p	R-P
سلسلة1	0.24	6.09	7.53	7.55	7.81	57.92	12.86

Different forms of P extracted squentially

Fig 2 : Percent of different forms of phosphorus extracted sequentially.
IV. P fractionation

In the second, third and sixth steps, extraction and phosphorus fractionation associated with calcium carbonate were used, especially in calcareous soils where it can differentiate between the dominant forms of carbonate present in calcareous soils such as Ca2-P and Ca8-P, mainly from the apatite minerals (Ca-P). It was assumed that hydrochloric acid was the extraction of phosphorus from dicalcium phosphate minerals in Table 3 , Fig.2 . The values of phosphorus associated with calcium Ca2-P of the studied soils ranged from 6.95 to 36.1 mg kg^{-1} with an average 20.47mg kg^{-1}. Since the calcium content were higher in the surface soils than subsoil soils, and as a result of increased calcium release in the soil solution and then correlated with phosphorus added or released from one phase to another soil. The mean calcium phosphate associated with calcium represents (6.09 %) a very small fraction of mean total phosphorus extracted with perchloric acid as shown in Fig.2 .

Also, it may be due to addition of mineral fertilizer every year. Generally, these values were higher than the value found in soils from Iran [30], that the average content of hydrochloric acid-P in 16 calcareous soils in Iran was 125 mg kg^{-1}. The content of HCl-P is also more than the content observed by Ruiz et al (1997) in 12 non-calcareous soils in Europe. Saavedra and Delgado [31], found that the average HCl-P content in 17 agricultural soils in southwestern Spain was 14 mg kg^{-1}. Phosphate extracted with a dilute acidic solution was thought to be primary P minerals such as hydroxyl fluorapatite [13,32].

This is attributed to the fact that increasing the calcium concentrations in the equilibrium solution leads to the formation of more stable and less soluble Ca2-P compounds, which makes it difficult to move them with irrigation water [33]. Al-Hiti [34], found that the concentration of calcium phosphate in some soils of the North Iraq ranged between 470-210 mg kg^{-1} and constituted (86.7 - 84.2) % of the metal phosphorus. The results showed in Table (3) and Fig.1,indicated that the phosphorus associated with calcium Ca8-p soils of the study, which ranged values between (45.45 - 10.6) mg kg^{-1} with average of 25.28 mg kg^{-1}. Both adsorption and fixation occur for phosphorus in calcareous soils and it was difficult to distinguish between them which depended on the amount and surface area of calcium carbonate and its size [28]. Through the study of the physical and chemical properties of carbonate minerals in Iraqi soils it was found that the active carbonate is the most effective part in the absorption of phosphate. Extraction with sodium acetate was associated with calcium phosphate (Ca8-P) and primary mineral apatite in soil that cannot be extracted by aluminum acetate.

Thus, in neutral soils the basal degree of reaction P ions will be deposited as: mono – di calcium phosphate or octa calcium phosphate, hydroxyl apatite, and ultimately the less soluble apatite [35]. Also, aluminum acetate extracts Pi associated with apatite [36]. The extraction of phosphorus associated with iron (Fe-p) was shown in Table (3) and Figure (1) and the results indicated that the values ranging from 15.95 to 40.95 mg. kg $^{-1}$ with average of 25.41 mg kg^{-1}. The amount of free iron oxides in calcareous soils usually was low compared to acidic soils [21]. Therefore, some researchers did not obtain values for phosphorus associated with Fe and Al [34]. But AI-Meani [37], obtained values of aluminum phosphate ranging from 6.7 to 28.8 mg kg $^{-1}$ for different areas of Iraq. On the other hand, the decrease in the amount of phosphorus adsorbed on the surfaces of iron compounds in calcareous soils may be attributed to the effect of sodium ions on the volatility of the carbonate minerals and their increased solubility, accompanied by the release and dissolution of the adsorbed iron or sedimentation on the surfaces of the cutin .

They pointed out that there is a movement of iron oxides as a result of the leaching conditions of the soils developed in northern Iraq, located within the high rain areas. Many studies conducted previously in the Mediterranean region and in Syria in particular [38], have shown that iron oxides have a high effect in the initial reactions of soluble phosphate fertilizer in soil despite low quantities [39]. Interactions with long-term reactions have affected the efficiency of phosphorus use.

It had been found that during the extraction of phosphorus associated with organic matter by NaOH and also it can extract a small amount of inorganic phosphorus [9]. Reduction in a small amount, some of which may be associated with Fe in the form of complexes with organic matter [40]. It has been noted that most of the sequence of NaOH calcareous soil fragmentation is due to phosphorus associated with Fe and Al .

Although Chang and Jackson [32], noted that the possibility of a sodium hydroxide solution could dissolve and extract $FePO_4.2H_2O$, it was questioned about its ability to extract phosphorus associated with Fe and Al in the presence of $CaCO_3$ [41]. Generally, the low mean Fe-P in calcareous soils may be the result of low OM, low content of free oxides Fe and Al in these soils and accounted for 7.55% of mean total phosphorus and can be a very small fraction of mineral phosphorus, which is usually less in Soils with neutral and calcareous soils but formed a higher fraction in soils with acidic reactions [20].

Soil residue was extracted from the previous step using sodium - bicarbonate - dithionite (NaBD) to separate a sensitive part of the phosphorus associated within oxides (Fe-P), mainly those found in iron and aluminum compounds. This method mainly and completely dissolve the free iron oxides minerals which are non-silicate minerals in the sample [32]. The results in Table (3) indicated that the O-P values in the study soils ranged between 12.3 to 39.1 mg kg-^{1} with the mean 26.36 mg kg^{-1} and that the content of surface soils was higher than subsurface soils due to the addition of fertilizers to the soils annually. And that the mean percent of O-P represents a very small fraction of 7.81% of the mean total phosphorus extracted with perchloric acid as in Fig.2 .

The phosphorus values associated with these free oxides depend on the type, size and degree of crystallization. The presence of OM, which has a significant role in preventing the formation of iron oxide crystals [42], results in the occurrence and distribution of weakly crystalline minerals such as ferrihydrite which is more active than goethite and / or hematite. The most common iron oxides in arid and semi-arid soils were hematite. Generally, iron oxides are usually found in soil as separate compounds, as coatings on soil molecules, or as amorphous hydroxyl compounds.Fordham and Norrish [34], suggested that iron oxides, especially goethite are very important in the adsorption of phosphates in the soil. Because Goethite has hydroxyl groups in its composition which has a binding capacity and could easily coordinate with P while hematite Fe_2O_3 did not contain any hydroxyl groups. It is well known that hematite is a dominant mineral in arid and semi-arid soils [44]. Therefore, the oxide and hydrous oxide surfaces play a key role in phosphate adsorption in neutral soils .

On the other hand, in a study of phosphorus extraction associated with free oxides of carbonate deposits, it was suggested that NaBD might extract some P from the surfaces of $CaCO_3$ particles [45]. Jensen et al [46], also concluded that the specificity of the NaBD step for Fe-bound P extraction decreased with increasing $CaCO_3$ content. Part of P in the extractable assembly of NaBD may arise in the form of Ca-bound and may cause an overestimation of the phosphorus content associated with these free oxides. This indicates that this extraction step is not selective for this form of P. But the results by other researcher support the assumption that NaBD is selective in distinguishing between reducing and non- reducing Fe – P minerals. These results are in agreement to those of previous studies [32].

The results of phosphorus values associated with Ca10-P shown in Table (3) ranged from 73.95 to 454.45 mg kg^{-1} with an average 194.54 mg kg^{-1} and the percentage of mean CA10-P represents a very small fraction 57.92% of the mean total phosphorus extracted with perchloric acid as shown in Figure (2). In calcareous soils, the total mean of these phosphorus forms represents 71.54% of the total phosphorus rate. They represent more than 90% of the mineral portion.

And that the rate of ready phosphorus represents a very small fraction 57.92% of the total phosphorus rate of the different soil components of organic matter and clay minerals and carbonate and iron oxides effect on the level of phosphorus in different soil, and have found relationships between the different phosphorus forms and soil content of different minerals and organic matter. A significant positive correlation was found between total phosphorus and organic matter at P <0.001 level.

Conclusion

The accumulative P extracted by sequential extraction was an account on average less than 85.44% from the total P. The highest values of phosphorus associated with calcium and account 71.6% of P as di- octa- and deca- calcium phosphate while the decacalcium phosphates account 57.92% of the total P in soils.

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