

Soil Phosphorus Fractions in Calcareous Vertisols and Aridisols of Northern Jordan

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ABSTRACT

Sequential extraction of the soil by various reagents is designed to remove soil P fractions of varying solubility, with inferences to chemically defined discrete forms of P. This procedure purportedly differentiates between calcium (Ca), iron (Fe), and aluminum (Al) inorganic P fractions, as well as occluded fractions of inorganic P. Vertisols occur in northwestern Jordan, one of the country's major rainfed agricultural areas with intensive agricultural activities. The arid and semiarid lands of Jordan, locally known as the *Badia*, are extremely dry and cover a large part of Jordan. Five sites were selected in areas where Vertisols occur to include different precipitation zones and different lithology, while ten sites were selected to represent the *Badia* in northeastern Jordan, which covers a much larger area. Standard chemical characterization of profile samples was carried out besides determination of P fractions. The Ca-bound P, removed by HCl, was the largest P fraction. The NaHCO₃-P, the non-occluded Al and Fe-P, and the occluded P were insignificant fractions. While the dominance of Ca-P was not unexpected given the calcareous nature of the soils, the relatively high proportion of organic P was surprising given the aridity of the environment.

Keywords: P Fractions, Vertisols, Aridisols, Olsen P, Total P.

INTRODUCTION

Phosphorus being the second major element essential for crop growth and development, much research attention has been focused on the interaction between the soil and the plant with respect to the fraction of plant available P. This is true for soils of the Middle East as elsewhere (Matar et al., 1992), where the focus of agronomic management is on crop responses to P fertilizer with the context of common rotations in the

region (Ryan et al., 2008). Not surprisingly, little attention was given to other aspects of P in soils. While inorganic P fractions reflect the lithology from which the soil was derived, relative changes in P fractions in any environment may provide an indicator of soil weathering intensity or soil age (Ryan and Zghard, 1980).

In most soils in their native state, the dominant minerals involving P are associated with calcium (Ca), aluminum (Al), and iron (Fe) minerals or surface complexes (Lindsay and Moreno, 1960). Even when soils are fertilized, much of the fertilizer P is fixed in the soil through interactions to form compounds/minerals involving Ca, Fe, and Al. In all, but the most heavily fertilized soils, total P is dominated by the original forms in the parent material. While P in soils occurs as organic and inorganic forms, the relative dominance of either

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form is related to soil conditions; for most soils, except soils of colder regions, the mineral form is dominant. Although it is relatively easy to separate and quantify these forms, identification of different fractions within the inorganic matrix is difficult. Nevertheless, several methods have been suggested and applied to partition inorganic soil P into its constituent fractions.

The original sequential extraction procedure, developed by Chang and Jackson (1957) and subsequently modified by others (Peterson and Corey, 1966; Syers et al., 1972; Hedley et al., 1982; Kuo, 1996) or simplified to suit particular purposes, is based on the principle of a stepwise release of P forms of varying solubility that are purported to represent chemically defined P species. Despite the drawbacks in chemical P fractionation, the method is still in vogue (Wright, 2008). This P fractionation procedure in principle differentiates between Ca, Fe, Al, and occluded fractions of inorganic P on the basis of solubility. The extraction steps have a reasonably high selectivity for the main chemical forms of soil inorganic P (Hedley et al., 1982). The difficulty of using only one standard method of soil P extraction in studies of soil-plant relationships and interactions is that plants differ not only in their general P uptake capacity but, more importantly, in their capacity of making various forms of soil P available for uptake. For example, 'Calcicole' plants, adapted to growth on alkaline or neutral soil, may solubilize apatite or apatite-like Ca phosphates, the predominant forms of inorganic P in such soils, by exuding oxalic acid/oxalate and citric acid/citrate (Tyler, 2002).

Vertisols are typically developed on alluvial material in flat inland areas and may form residually from weathered limestone or basalt (Jenny, 1980). These soils are generally developed from parent

materials that are rich in alkali earth cations (Ca^{2+} and Mg^{2+}). The weathering of these rocks produces smectite-type clays (Khresat and Rawajfih, 1999). Vertisols are among the most productive soils given adequate soil moisture conditions for growing crops (Acquaye et al., 1992). These soils are little affected by leaching and may remain calcareous if they were formed from calcareous parent materials and if they have not been weathered during the course of pedogenesis. The high cation exchange capacity and low permeability help in retaining the nutrients when fertilizers are added to these soils. Vertisols occur in northwestern Jordan, which is one of the major rainfed agricultural areas in the country with intensive agricultural activities. They have not been studied in detail and data on the status of major nutrient elements in these soils are very limited.

The arid and semiarid lands of Jordan, locally known as the *Badia*, are one of the driest areas in the world (Allison, 1997). The *Badia* encompasses a wide and significant part of Jordan, covering an area of about 72 600 km², which constitutes 81% of the total area of Jordan. The Jordanian *Badia* is part of the 'Mediterranean Sahara' because it is less arid than the Arabian or African Sahara and has a smaller diurnal temperature range, with all the sparse precipitation concentrated in the winter months; it is classified as a semiarid to arid steppe environment and falls in the arid climate zone (Dutton et al., 1998). Jordan is faced with increasing population pressure in its already settled areas; hence, it will have to utilize the under-populated *Badia* so that it can contribute to the economy in a sustainable way without damaging the fragile desert environments (Rawajfih et al., 2005).

Given the significance of P for plant growth, there is limited information on plant available P, and

little or no information on P characterization with respect to chemical fractions in such non-fertilized soils as the Badia or the Vertisols in the rainfed area in Jordan. Such information may lead towards a better understanding of the soil resources in those two regions, with possible implications for future development.

Materials and Methods

Five sites were selected in areas where Vertisols occur to include different precipitation zones and different lithology. Ten sites were selected to represent the Badia in northeastern Jordan. Detailed description of sampled profiles has been reported in earlier studies (Khresat and Rawajfih, 1999; Khresat et al., 2004; Rawajfih et al., 2005). The location of all sampled profiles is shown on the map in Fig 1. Soil samples were collected from the A horizon of each profile and taken to the laboratory for chemical and physical analysis. The bulk soil samples were air dried, crushed with a mortar and pestle, and sieved to remove coarse ($> 2\text{mm}$) fragments. Duplicate samples were used in all analyses. Particle size distribution was determined by the hydrometer method (Gee and Bauder, 1986). Soil pH was measured on 1:1 soil: water suspensions (Thomas, 1996). Soluble salts were determined by measuring the electrical conductivity of 1:1 soil: water extracts (Rhoades, 1996); organic matter was determined using the Walkley-Black method (Nelson and Sommers, 1996); calcium carbonate (CaCO_3) equivalent values were obtained using the acid neutralization method (Richards, 1954). Cation exchange capacity was determined by the sodium saturation method (Chapman, 1965). Free iron oxides were extracted with sodium Dithionite-

Citrate-Bicarbonate (DCB) and measured using the orthophenanthroline colorimetric method (Jackson, 1973). Exchangeable bases were determined following displacement with 1 M NH_4OAc (Thomas, 1982).

Total P was determined by digestion with perchloric acid (Kuo, 1996). Organic P was estimated from the difference between the HCl-extractable P in a soil sample ignited at 550°C and in an unignited sample (Legg and Black, 1955). The fractionation of P (Kuo, 1996) involved sequential extractions with: (i) a solution 0.1 M in NaOH and 1 M in NaCl to remove nonoccluded Al- and Fe-bound P, (ii) 1 M NaCl and Citrate-Bicarbonate (CB) to remove P resorbed during the preceding extraction, (iii) Citrate-Dithionite-Bicarbonate (CDB) to remove P occluded within iron oxides, and (iv) 1 M HCl to remove Ca-bound P. The P unaccounted for by the sum of these forms and organic P consists probably of occluded forms of apatite (Syers et al., 1969).

In all extracts, P was analyzed by the method of Murphy and Riley (1962); in the CB and CDB extracts citrate interference was eliminated by modifying the method in the following manner (as described by Kuo, 1996): we took 5 mL of the extract, to which we added 1 mL of H_2SO_4 and 15 mL of the mixed reagent enriched with ammonium molybdate (3.2 g in 100 mL of mixed reagent); the volume was brought to 50 mL and the absorbance was read after 15 min. In the CBD extracts, dithionite was oxidized by bubbling air at a rate of 1 mL min^{-1} in 10 mL of extract for 6 h. Citrate-bicarbonate extractable P was also determined without any pretreatment, by shaking 1 g soil in 50 mL of the CB solution at pH 8.5 for 16 h at 298 K. This is called "direct" CB-P.

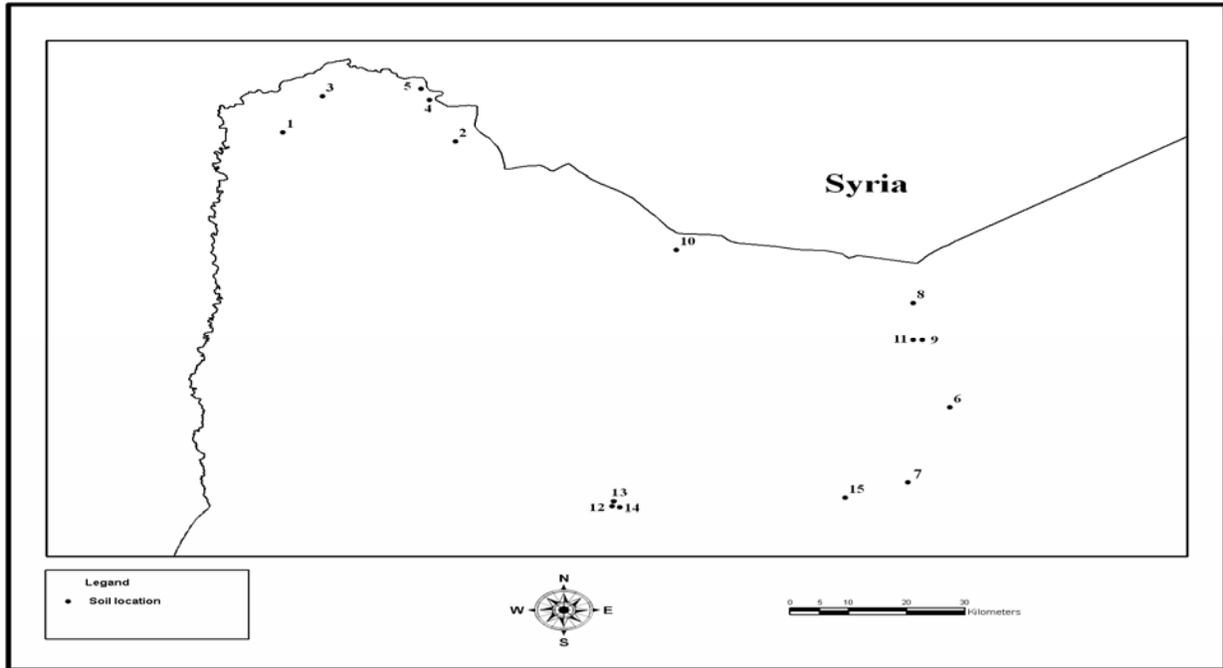


Fig.1. Location of sampled profiles, where numbers correspond to soil numbers in the tables.

Results

Characteristics of Soils

The Vertisols sampled were all calcareous, with CaCO₃ contents ranging from 11.3 to 23.9% (Table 1). Being calcareous soils, they have alkaline reaction as reflected by the high pH values. They have very high clay content, which exceeded 62% in some cases. As a consequence of the high clay content, which is mostly smectite type, the CEC of these soils was also high,

with the lowest value being 41.4 cmol₍₊₎ /kg. With the average rainfall of 300 mm/year, these soils get enough rainfall not to allow salts to accumulate. This is reflected in the very low EC values (Table 1). Organic C was less than one percent in all of the profiles. As these soils are under cultivation, with almost total removal of the crop residues, the organic matter content is low and typical of semiarid areas under rainfed cultivation (Ryan, 1998).

Table 1. Relevant characteristics of Vertisols

Soil	pH	EC (dSm ⁻¹)	CaCO ₃ (%)	Clay (%)	CEC (cmol ₍₊₎ /kg)	Organic C (%)
1. Hakama	7.64	0.45	11.3	48.5	45.8	0.82
2. Ramtha	7.94	0.25	16.4	52.5	42.3	0.61
3. Shajara	7.88	0.28	23.8	58.0	41.4	0.60
4. Amraweh	7.82	0.53	18.6	54.0	48.5	0.50
5. Thnaibeh	7.88	0.30	23.9	62.5	45.8	0.50

The Badia soils were all calcareous with CaCO_3 contents ranging from 20.8 to 29.2% (Table 2). In general, they have higher CaCO_3 contents and higher pH values than the Vertisols, which would be expected because the Badia area receives much lower rainfall (<100 mm/year). The EC values indicate accumulation of salts in the A horizon of some of the profiles; the highest value found was 36.3 dS/m (Table 2), which would preclude any cropping due to excessive salinity in such an area. The rainfall they receive is not enough to leach salts out of the root zone or down the profile. Any

attempt to utilize these soils for agricultural production has to be preceded by salt reclamation using good quality irrigation water followed by normal irrigation. The CEC of the Badia soils was much lower than that of Vertisols for reasons that include the lower clay content, type of clay minerals, and the lower organic matter content. Organic C is generally lower in these soils than in Vertisols largely due to the more arid environment which promotes organic matter mineralization, in addition to the limited natural vegetative cover and lack of input from crop residues.

Table 2. Relevant characteristics of Badia soils

Soil	pH	EC (dS/m)	CaCO_3 (%)	Clay (%)	CEC $\text{cmol}_{(+)}\text{/kg}$	Organic C (%)
6. Tal Hassan	8.9	0.41	22.1	29	21.8	0.29
7. Azraq	8.2	3.20	28.0	61	24.4	0.34
8. Tal Remah	8.7	0.62	20.8	28	24.4	0.71
9. Aretain I	8.6	0.58	29.2	35	21.0	0.51
10. Aretain II	8.9	0.84	23.7	30	25.5	0.49
11. Bishrieh	8.8	1.26	24.7	24	24.9	0.37
12. Muwaqqr I	8.5	0.92	26.9	31	22.5	0.53
13. Muwaqqr II	8.5	0.78	24.1	25	22.5	0.57
14. Muwaqqr III	8.6	1.01	28.0	35	21.7	0.38
15. Shawmari I	7.8	36.3	28.9	40	21.0	0.21

Soil Phosphorus Fractions

The $\text{NaHCO}_3\text{-P}$ (commonly referred to as Olsen P) which is an index of the plant available P, ranged from 4.3 to 15.1 mg kg^{-1} in Vertisols and comprised a very small percentage of the total P varying from 0.65% to 1.50% of total P (Table 3). The values for available P

varied widely. At least three soils had P values higher than the critical values for dryland cropping in the Middle East region, 5-7 mg kg^{-1} , (Ryan, 1997). Clearly, these values were due to a build-up of available P from regular fertilization. Of the others, one soil (Ramtha) had marginal available P and the other (Hakama) slightly

below the critical value. The Olsen P values in the *Badia* soils ranged from 2.9 to 27.1 mg kg⁻¹, comprising a small percentage of the total P in these soils, 0.40 to 3.55% (Table 4). Despite the fact that the *Badia* soils are mostly virgin soils that are not cultivated, and are excessively grazed when there is any natural vegetation

available, nine of the ten soils sampled had Olsen P values in excess of the critical value for cropping. Only one soil (Shawmari I) was deficient in available P. In fact, some values were well in excess of the critical value (e.g., Tal Remah, with 27.1 mg kg⁻¹ Olsen P).

Table 3. Phosphorus fractions in the A horizon of Vertisols (mg kg⁻¹)

Soil	Olsen P	Nonoccluded Al & Fe-P	Occluded Fe-P	Ca-bound P	Organic P	Total P
1. Hakama	4.3	4.3	4.2	522	109	659
2. Ramtha	6.6	1.7	2.4	534	139	682
3. Shajara	14.8	4.2	1.8	1089	33	1193
4. Amraweh	10.4	2.4	1.5	557	109	695
5. Thnaibeh	15.1	4.8	1.4	965	213	1213

Table 4. Phosphorus fractions in the A horizon of Badia soils (mg kg⁻¹)

Soil	Olsen P	Nonoccluded Al & Fe-P	Occluded Fe-P	Ca-bound P	Organic P	Total P
6. Tal Hassan	10.3	10.2	0.9	931	119	1123
7. Azraq	9.6	7.1	0.9	914	104	1089
8. Tal Remah	27.1	16.4	0.5	582	92	764
9. Aretain I	17.9	13.0	1.2	741	88	923
10. Aretain II	13.4	8.0	0.7	829	97	995
11. Bishrieh	17.4	12.5	0.9	832	110	1034
12. Muwaqqr I	9.2	9.8	2.1	729	77	876
13. Muwaqqr II	15.0	16.1	2.8	861	65	1008
14. Muwaqqr III	13.5	12.6	3.5	763	82	943
15. Shawmari I	2.9	0.9	1.4	628	45	729

The combined non-occluded Al and Fe-P and the P occluded within Fe oxides were also a very small fraction of the total P. They ranged in value from 3.9 mg kg⁻¹ to 8.5 mg kg⁻¹ in Vertisols (Table 3), which comprised from 0.50% to 1.29% of total P (Fig.2). The

corresponding values were a little higher in the *Badia* soils where they ranged from 2.3 mg kg⁻¹ to 18.9 mg kg⁻¹ (Table 4) and as a percent of total P they ranged from 0.32% to 2.21% (Fig.3).

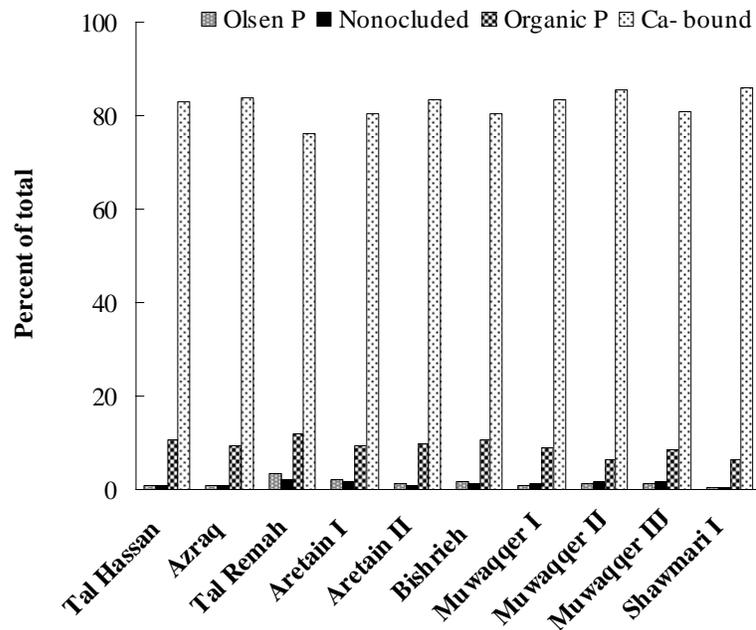
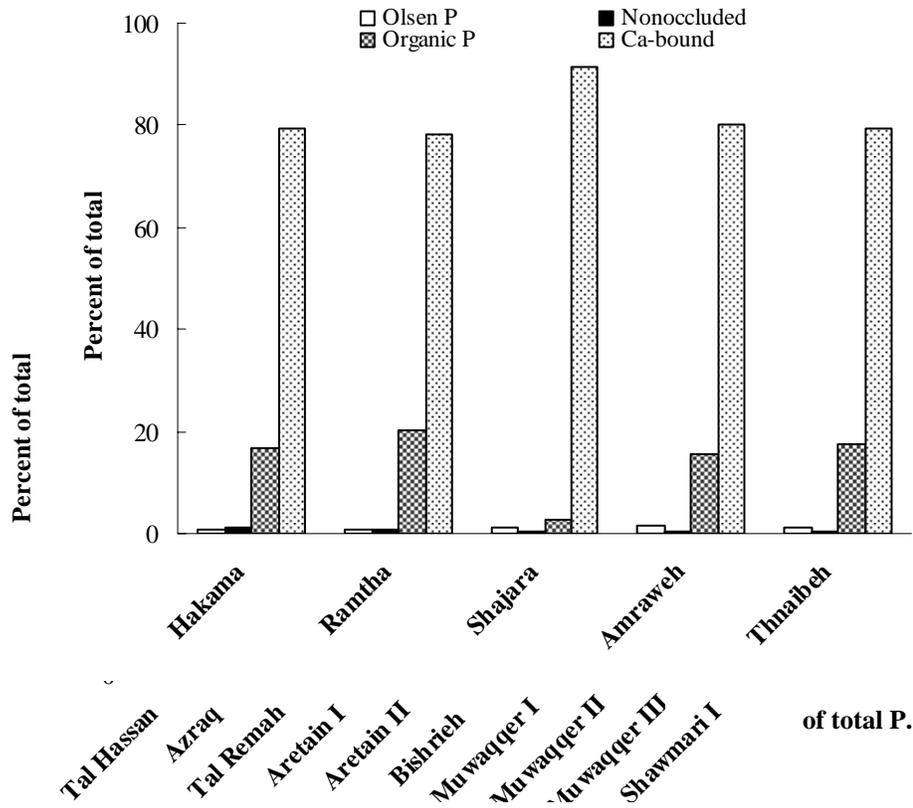


Figure 3. Phosphorus fractions in Badia soils as percent of total P

The largest pool of P fractions by far is the Ca-bound P removed by HCl. This is expected since these soils are dominated by a Ca saturated system, being all calcareous with high content of carbonates. Not only this fraction comprised most of the total P, but the actual values are very high with the minimum value being 522 mg kg⁻¹ and the highest 1089 mg kg⁻¹ in Vertisols, and the range in the *Badia* soils is from 582 to 931 mg kg⁻¹. This fraction comprised 78.3% to 91.3% of total P in Vertisols and 76.2% to 86.1% in the *Badia* soils.

Our results agree with the findings of Carreira et al. (2006), which indicated that pedogenic CaCO₃ (instead of Al and Fe oxyhydroxides) is the primary geochemical agent in arid ecosystems capable of reducing leaching losses of P, through secondary precipitation of Ca-P minerals and/or strong sorption reaction of P with CaCO₃. In a study of the status and distribution of P in six gypsiferous soil profiles collected from Iraq and southern Spain, Ca-P was the dominant form of P in all the samples analyzed, ranging between 61.9% and 78.6% of the total P (Muhammad and Jones, 1992).

Organic P constituted the second largest pool of P fractions in the Vertisols and *Badia* soils after Ca-bound P, ranging from 33 mg kg⁻¹ to 213 mg kg⁻¹ in Vertisols, and from 45 mg kg⁻¹ to 119 mg kg⁻¹ in the *Badia* soils. As a percentage of total P, it ranged from 2.8% to 20.4% in Vertisols (Fig. 1), and from 6.2% to 12.0% in the *Badia* soils (Fig. 2). This indicates the significance of organic P, even under arid conditions.

Total P ranged from 659 mg kg⁻¹ to 1213 mg kg⁻¹ in the Vertisols (Table 3), while it varied from 729 to 1123 mg kg⁻¹ in the *Badia* soils (Table 4). The variation in total P is quite large. Our results approximate the distribution of P among different forms in the surface layers of representative soils from five regions of Saudi Arabia (Bashour et al., 1985), where total P ranged from 182 mg kg⁻¹ to 1088 mg kg⁻¹ and organic P from 0 mg

kg⁻¹ to 90 mg kg⁻¹. Among the fractions of inorganic P, Ca-P was the largest, ranging from 182 to 902 mg kg⁻¹, which accounted for 66 to 100% of total P.

Discussion

This study comprised of two groups of soils in different agro-ecological zones of Jordan, one involving cultivated soils (Vertisols) and the other an uncultivated one in a drier region (*Badia*), sought to characterize total P, organic P, and inorganic P fractions. Some of the findings were anticipated while others were not anticipated. It was clear from the disparities in total P, which is a stable component in soil, that the Vertisols were dissimilar in origin or pedogenesis, as indicated by the high values for the Shajara and Thnaibeh soils compared to other profiles. The total P values in the *Badia* suggest even greater pedogenic diversity. While it is tempting to speculate as to the cause of this variation, the most plausible explanation is enrichment of the soil from P-rich wind-blown dust since Jordan regularly experiences dust storms from the Sahara. Total P values were generally high by comparison with soils elsewhere. The elevated levels of total P were accompanied by relatively high levels of plant-available P. While the enrichment that was apparent in the cultivated Vertisols was obviously due to a build-up from fertilization, the enrichment in the uncultivated *Badia* has to be due to Aeolian deposition.

The sequential extraction of different fractions of P in both groups of soils indicated the dominance of Ca-bound P, which was not surprising since both soil groups were highly calcareous. On average, it constituted over 80% of total P in the two groups of soils (Table 5). The non-occluded Al and Fe-P, and the P occluded within Fe oxides constituted very small fractions of total P. They were a little higher in the *Badia* soils where the average as a percent of total P was 1.29, while it was 0.69% of the total P in the

Vertisols. Again this was expected since these sesquioxide fractions are only significant in acid, highly weathered soils. The wide variation in the values of all P fractions reflected the variation in total P. However, the relative large fraction of organic P was inconsistent with the low levels of

soil organic matter normal to such arid and semi-arid regions. This too may be due to enrichment in the fine wind-blown particles. The average value of this fraction as a percent of total P was 14.6 for Vertisols, while it was 9.2 for the *Badia* soils.

Table 5. P Fractions as an average percent of total P

	Olsen P	Nonoccluded and occluded Al & Fe-P	Ca-bound P	Organic P
Vertisols	1.12	0.69	81.7	14.6
Badia soils	1.47	1.29	82.3	9.2

In summary, the study contributed to the characterization of soils from two major areas of Jordan, semi-arid Vertisols with rainfed cropping, and the arid *Badia* where cropping is prohibited by drought. As anticipated, P forms in both areas were dominated by CaCO₃, but the relatively high organic P was unusual. The influence of man was evident in the buildup of available P in the cropped Vertisols, while the enrichment of P in the *Badia* was evidently due to the

deposition of P-rich Aeolian dust.

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