

# Chemical fractionation of phosphorus in calcareous soils of Hamedan, western Iran under different land use

Mohsen Jalali<sup>1\*</sup> and S. Sajadi Tabar<sup>1</sup>

<sup>1</sup> Department of Soil Science, College of Agriculture, Bu-Ali Sina University, Hamedan, Iran

## Abstract

We investigated the effects of land uses on P distribution and availability in selected calcareous soils under different management practices. KCl-P (labile P), NaOH-P (Fe-Al-bound P), HCl-P (Ca-bound P), and residual P (Res-P) fractions at 0–30 cm depth were determined for soils planted to garlic, orchard, pasture, potato, leafy vegetables, and wheat. Trends in P distribution between chemical fractions were similar between land uses. Ca-bound P was the most abundant P fraction in the soils, constituting between 61% and 78% of the total P, whereas P associated with labile was less abundant (< 2%). Soils under leafy vegetables and wheat along with pasture presented the highest and lowest values in all fractions of P, respectively. Labile P generally was highest for leafy vegetables and potato. Labile P and Fe-Al-bound P comprised < 1.4% and 8% of total P, respectively. Residual P ranged from  $\approx$  14% (potato and garlic) to 31% (pasture). Long-term fertilization increased P allocation to inorganic fractions, as Ca-bound P contained 78% of total P for potato and garlic and 74% for leafy vegetables but 61% for pasture. A strong positive correlation between labile P and Fe-Al-bound P ( $r = 0.534$ ,  $p < 0.01$ ), labile P and Ca-bound P ( $r = 0.574$ ,  $p < 0.01$ ), Ca-bound P and Fe-Al-bound P ( $r = 0.504$ ,  $p < 0.01$ ), Olsen-P and CaCl<sub>2</sub>-P ( $r = 0.821$ ,  $p < 0.01$ ) was found. Principal-component analysis showed that the first four components accounted for most of the variation, 32.5%, 16.9%, 12.9%, and 7.9% of total variation, respectively.

**Key words:** phosphorus / land use / calcareous soils / fractionation

Accepted July 30, 2010

## 1 Introduction

Phosphorus (P) is one of the main limiting plant nutrients in most arid and semiarid soils. Naturally occurring P in arable soil depend on weathering, deposition, sedimentation, and erosion processes, but also on soil variables such as organic matter (OM), oxides, Ca carbonate, and clays. However, normal agricultural practices generally cause enrichment of P (McDowell et al., 2001). Soil P contents of intensively managed agricultural soils have increased in many parts of the world, where P input from fertilizer, manure, and sewage sludge exceeds the withdrawal of P by harvested crops (Sims, 1998; Sharpley and Smith, 1989; Skinner and Todd, 1998; Jalali, 2007a). Continued long-term application of fertilizers can lead to P accumulation in surface horizons and thus increasing the potential for P loss to surface waters and eutrophication (McDowell et al., 2001; Sui et al., 1999).

Phosphorus in soil is considered to be distributed among several geochemical forms that include soil solution and exchangeable phase, OM phase, Ca-bound phase, and Fe- and Al-bound phases (Hedley et al., 1982a, b). The degree of P association with different geochemical forms strongly depends upon physico-chemical properties of the soils due to soil type (Tiessen et al., 1984), climate, and management practices (Motavalli and Miles, 2002). These P fractions have remarkable differences in mobility, bioavailability, and chemi-

cal behaviors in soil and can be transformed under certain conditions (Sharpley et al., 2000). Fractionation technique is used to define them in soils both as qualitatively as well as quantitatively. Such information is potentially valuable for predicting bioavailability, P leachability, and transformations between chemical forms in agricultural and polluted soils (Hedley et al., 1982a, b; Sui et al., 1999). In contrast to analysis of total P, redistribution among various fractions is important for P mobility. Soils with a high proportion of P in labile pools indicate greater potential availability to plants but also greater export by leaching or runoff (Castillo and Wright, 2008). 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 (Castillo and Wright, 2008). The Ca-bound, Fe-Al oxide-, and OM-bound fractions could be considered relatively active depending on the actual physical and chemical properties of soil.

Factors affecting P stability and retention in chemical fractions and distribution in the soil profile may vary between land uses. Sanchez and Porter (1994) stated that P in organic pools is stable under flooded conditions, but may be unstable under drained conditions.



\* Correspondence: Prof. Dr. M. Jalali; e-mail: Jalali@basu.ac.ir

The distribution of P within different fractions provides an indication of the potential stability of P in soil which may differ between land uses. *Castillo and Wright (2008)* studied soil P pools for Histosols under sugarcane and pasture in the Everglades, USA. They found that long-term fertilization increased soil total P for cultivated soil relative to pasture, but plant-available P constitutes < 1% of total P. They indicated that most of the applied P was recovered in the Fe-Al fraction for pasture and the Ca-bound P fraction for cultivated soil. They indicated that the Ca-bound P fraction represented the greatest proportion of total P for sugarcane (41%), but only 12% for pasture.

Over the past four decades, P inputs (superphosphate and  $\text{NH}_4$ -phosphate) to agricultural land in the Iran have increased (*Jalali, 2007a*). Most of the soils in Iran received regular superphosphate applications of 100–300 kg  $\text{ha}^{-1} \text{y}^{-1}$  for > 40 y. Limited information exists concerning the spatial distribution and availability of P in soils in arid and semiarid regions (*Jalali and Ranjbar, 2010*). Hamedan province is very densely populated with intensive agricultural and horticultural production. *Jalali and Ahmadi Mohammad Zinli (2011)* investigated the effects of land-use types on the kinetics of P release under different management practices and the relationship between kinetic parameters and soil physical and chemical properties from calcareous soils. They found that significantly different quantities of P were released under different land use.

While the effects of management systems on P fractions have been studied by a number of researchers, *e.g., Redel et al. (2007, 2008)* in a temperate cropped Ultisol, *Cardoso et al. (2003)* in weathered tropical soils, *Yerokun (2008)* in Alfisols, Ultisols, and Oxisols, limited information on soil P fractions under different land use is available on calcareous soils. This paper contributes to the knowledge of the content and speciation of P in agricultural soils of the Hamedan province, which is a representative area of the calcareous soils found in arid and semiarid regions. A long-term history of fertilization and application of sewage sludge will increase soil total P and P distribution among different fractions for cultivated soil relative to pasture. Thus, the objective of this study was to determine the effect of different land uses on the fractionation and availability of P. The P fractionation in different land uses reflect the rate of fertilizers, manures, and sewage-effluent application in the studied area. To verify this hypothesis, experiments were conducted to determine the effect of different types of land use on the fractionation and availability of P.

## 2 Materials and methods

### 2.1 Site description

Hamedan is located in W Iran (between  $48^{\circ}20'$  and  $49^{\circ}27'$  E;  $34^{\circ}36'$  and  $35^{\circ}15'$  N with a history of > 3000 y. The climate of the study area is considered to be semiarid, the annual precipitation being  $\approx 300$  mm. Rainfall occurs from October to May, with a maximum during November and February of each year. The mean monthly temperatures are varying be-

tween  $-4^{\circ}\text{C}$  and  $25^{\circ}\text{C}$ , and the mean annual value is  $10^{\circ}\text{C}$ . The annual potential evaporation far exceeds the annual rainfall with a mean annual amount of  $\approx 1505$  mm estimated from 1975 to 2001 for Hamedan city (*Sabziparvar, 2003*). Agriculture is a major industry and principal land use in Hamedan. Major crops are winter wheat (*Triticum aestivum* L.), potato (*Solanum tuberosum*), garlic (*Allium sativum*), various nuts, and leafy vegetables (*Jalali, 2005*). However, livestock also substantially contributes to the states agricultural industry. Fertilizers are applied throughout agricultural regions to enhance crop production. The vegetation cover along the study sites is dominated by annual and perennial plants, where the most common are: *Astragalus* spp., *Stipa barbata* Desf., *Euphorbia Aellenii* Rech. F., *Lepidium latifolium* L., *Chenopodium botrys* L., *Chenopodium murale* L., *Acantholimon Festucaceum* Boiss., *Phlomis orientalis* Mill., *Centaurea* spp., *Achillea setacea* Waldst. and Kit., and *Alhagi camelorum* Fich. The soil of the area is mostly classified as Aridisols. The parent rocks are mainly limestone, calcareous shale, and granitic material.

### 2.2 Soil sampling and analysis

The study area covers different land uses including agricultural, orchard (such as apple, *cerasus*, *prunus*, *amygdalus*, *armeniaca*, *juglans*), and uncultivated lands. The six land uses studied included sites under potato cultivation for  $\approx 50$  y, orchard for 75 y, garlic for 30 y, wheat and leafy vegetables (such as lettuce, spinach, parsley, dill) for 60 y, and pasture. The soils are classified according to the USDA Soil Taxonomy (*Soil Survey Staff, 1990*) as Typic Xerofluvents, Typic Calcixrepts, and Typic Xrothents. The average annual application rate of P fertilizer in Iran is currently > 40 kg P  $\text{ha}^{-1}$  (200 kg  $\text{ha}^{-1}$  as superphosphate). In high-yielding crop regions of Iran, P-fertilizer application is usually over 63 kg P  $\text{ha}^{-1} \text{y}^{-1}$ , with accompanying decreases in utilization efficiency. Phosphorous fertilizer is applied in the autumn. Most of the fields are flood-irrigated using poorly managed irrigated systems, resulting in low irrigation efficiency (*Jalali, 2005*). Typical P fertilization for different land uses is indicated in Tab. 2. Normally, a one-time application prior to planting is used. The pasture sites received no historic fertilization or tillage. In leafy vegetables, the land is covered with vegetation most of the year.

To evaluate P fractionation, composite soil samples were taken at 10 or 11 sites for each land use. Samples were collected between May and September 2008. All samples were collected from surface soil (0–30 cm), which is comparable with tillage depth. Grass and OM were removed from the surface of each sampling location before the soil was collected.

The soil samples were air-dried and passed through a 2 mm sieve for laboratory experiments. Soil pH and EC were measured in  $\text{H}_2\text{O}$  using a 1:5 soil-to-solution ratio, after the soil suspension had been equilibrated at  $25^{\circ}\text{C}$  for 1 h on a shaker. Particle-size distribution was determined by the hydrometer method. Organic matter (OM) was determined by dichromate oxidation (*Rowell, 1994*). Calcium carbonate equivalent (CCE) was determined by neutralization with HCl, exchangeable cations were determined using  $\text{NH}_4\text{OAc}$  (*Rowell, 1994*).

Olsen-P was determined using a soil-to-solution ratio 1:20 and 30 min shaking (Olsen and Sommers, 1982) and  $\text{CaCl}_2$ -P 10 using mM  $\text{CaCl}_2$  with a soil-to-solution ratio of 1:10 and 1 h shaking. Phosphorus in extractant was determined using the ammonium molybdate-ascorbic acid method described by Murphy and Riley (1962).

### 2.3 Sequential extractions of P

The distribution of P in soil was determined using a modified version of the Hedley et al. (1982a) procedure as outlined by (Ann et al., 2000; Alvarez-Rogel et al., 2007; Jalali and Ranjbar, 2010): (1) soluble and exchangeable P, (2) Fe- and Al-bound P, (3) Ca-bound P, and (4) residual P. Two grams of each soil sample were weighed into a 50 mL centrifuge tube, and different fractions were extracted by the sequential fractionation procedure: soil extracted with 20 mL 2 M KCl (labile P) for 2 h at room temperature with continuous agitation, residue from the first fraction extracted with 20 mL 0.1 M NaOH (Fe-Al-bound P) for 17 h with continuous agitation, residue

from second fraction extracted with 0.5 M HCl (Ca-bound P) for 24 h with continuous agitation, residue from the last fraction extracted with a 5:2 mixture of concentrated  $\text{HNO}_3$  and  $\text{HClO}_4$  (Res-P) and determining P from the digest (Hedley et al., 1982a). The amount of P in all extractions was determined using colorimetric ascorbic acid method (Murphy and Riley, 1962).

Data on P fractions and physical and chemical soil properties were statistically analyzed using SPSS v. 9.0 program (SigmaPlot).

## 3 Results and discussion

### 3.1 Soil characterization

The descriptive statistics of selected chemical and physical properties of the studied soils for different land uses are summarized in Tab. 1. Significantly higher OM values were observed in soils under orchard and leafy vegetables than

**Table 1:** Statistical summary of Olsen-P,  $\text{CaCl}_2$ -P, and other measured soil properties in different land uses. \*Values followed by the same letter in the column indicate that the effect of land use is not significant at the 5% level, according to Duncan test.

Land use (number of soil samples)	pH	EC	OM	$\text{CaCO}_3$	$\text{Ca}_{\text{ex}}$	$\text{Mg}_{\text{ex}}$	Olsen-P	Clay	Sand	Silt
Garden (10)										
Maximum	7.15	0.168	3.88	9.93	21.20	1.40	44.73	28.48	73.52	34.72
Minimum	6.68	0.125	1.58	3.73	7.00	0.10	4.30	14.48	40.24	4.72
Mean	6.84d*	0.144c	2.65a	6.74b	15.62b	0.42a	27.22c	21.14c	55.29a	23.58a
Garlic (11)										
Maximum	7.47	0.213	2.88	24.48	27.60	4.00	94.77	42.48	71.52	33.44
Minimum	6.31	0.093	0.66	4.23	6.10	0.10	11.59	19.04	25.52	4.72
Mean	7.11bc	0.143c	1.66bc	11.23b	18.64ab	1.52a	50.36b	29.06b	47.00a	23.94a
Pasture (10)										
Maximum	7.61	0.216	4.60	23.65	25.20	4.45	66.27	32.48	79.36	33.44
Minimum	6.22	0.074	0.50	4.08	7.70	0.10	3.72	9.20	39.52	11.44
Mean	7.01cd	0.130c	1.60bc	9.12b	16.60b	1.12a	24.06c	20.44c	55.09a	24.47a
Potato (11)										
Maximum	7.56	0.270	3.05	21.55	24.60	3.90	116.48	46.48	70.44	30.00
Minimum	7.00	0.161	0.26	4.38	11.50	0.20	10.48	13.04	24.24	9.08
Mean	7.33ab	0.213a	1.18c	10.34b	19.74ab	1.68a	73.24a	29.16b	51.35a	19.49a
Vegetables (10)										
Maximum	7.36	0.289	3.53	16.00	22.80	2.35	101.05	32.48	66.24	32.72
Minimum	6.62	0.137	1.16	5.63	12.80	0.05	22.17	17.04	42.24	10.72
Mean	7.09bcd	0.182ab	2.08ab	11.67b	17.71ab	0.96a	73.53a	22.99bc	54.78a	22.23a
Wheat (10)										
Maximum	7.78	0.205	2.58	23.98	25.30	6.45	57.03	45.76	50.24	31.44
Minimum	7.02	0.096	0.46	4.75	10.40	0.10	5.23	33.20	23.52	10.72
Mean	7.43a	0.159bc	1.31bc	18.47a	21.60a	1.62a	21.53c	40.34a	33.64b	26.02a

under other land use, which may be due to the manures and sewage-effluent application and more crop coverage during the year. The lowest  $\text{CaCO}_3$  values were found in soils under orchard and the highest under wheat with significant differences occurring between both. The silt contents did not differ between land uses. For sand contents, significant difference was only observed for soils under wheat, with lower values than the others. The lowest clay values were found in soils under orchard and the highest under wheat with significant differences occurring between both.  $\text{CaCl}_2\text{-P}$  varied from 0.71 to 17.3  $\text{mg kg}^{-1}$  with an average of 4.5  $\text{mg kg}^{-1}$ . Olsen-P varied from 3.7 to 116.0  $\text{mg kg}^{-1}$  with an average of 45.5  $\text{mg kg}^{-1}$ . Olsen-P in different land uses are significantly different (Tab. 1). Greater average Olsen-P in soils occurred under potato and leafy-vegetable (73.2 and 73.5  $\text{mg kg}^{-1}$ , respectively) fields than in pasture and wheat (21.5 and 24.0  $\text{mg P kg}^{-1}$ , respectively) fields which was consistent with other study in Hamedan (Jalali, 2007a). Therefore, it indicates that intensive agricultural practices may cause enrichment of P in surface soil.

### 3.2 Labile P

Characterization of soil P pools by sequential-chemical fractionation methods are somewhat operationally defined, but in general, order of increasing recalcitrance are labile P, Fe-Al-

bound P, Ca-bound P, and Res-P pools (Reddy et al., 1998; Turner et al., 2005). Labile P represents the most biologically available form of P, and these soils had the lowest concentration of all chemical fractions (Fig. 1). The concentrations of labile P varied between land uses (Fig. 2). Labile P was lower for pasture and wheat (averaged 8.5 and 6.9  $\text{mg P kg}^{-1}$ , respectively) than potato (19.1  $\text{mg P kg}^{-1}$ ) and leafy vegetables (21.3  $\text{mg P kg}^{-1}$ ). The labile P was less abundant P fraction in the soils, constituting between 0.9% and 1.3% of the total P. For all land uses, labile P averaged 1.1% of total P (Fig. 3), which was consistent with other studies for canal sediments (Diaz et al., 2006), wetlands (Reddy et al., 1998), and Histosol (Castillo and Wright, 2008). Jimenez-Carceles and Alvarez-Rogel (2008) studied soil P pools for calcareous marsh soils in Spain. They found that KCl-P was very low and insignificant in relation to the total P concentration of the soils.

Castillo and Wright (2008) found that in soils under various managements, most of the P was only slightly available, being mostly bound to Ca-bound or Res-P. Based on average concentration of P ( $\text{mg kg}^{-1}$ ) in the labile fraction, the ranking of labile P for different land use was: leafy vegetables (21.3) > potato (19.1) > garlic (16.4) > orchard (15.4) > pasture (8.1) > wheat (6.9). The ranking reflected the rate of fertilizers, manures, and sewage-effluent application in the studied

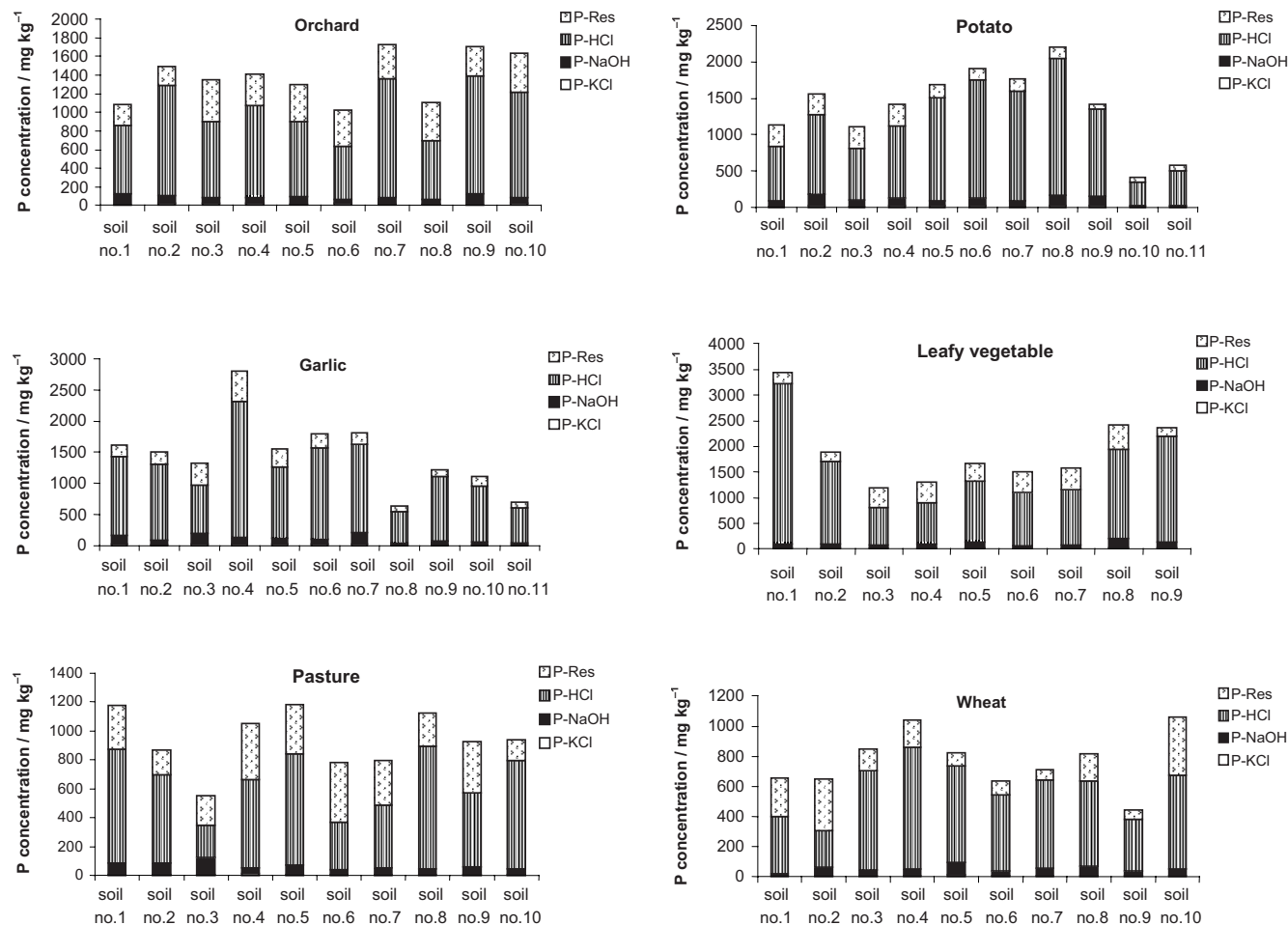
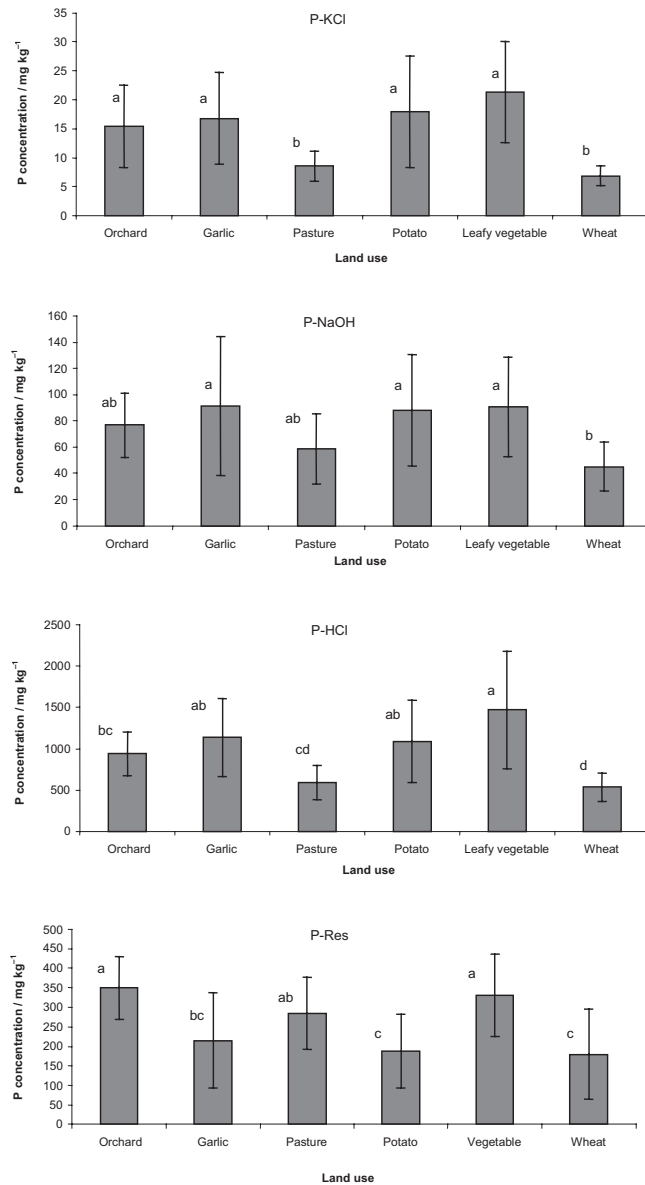
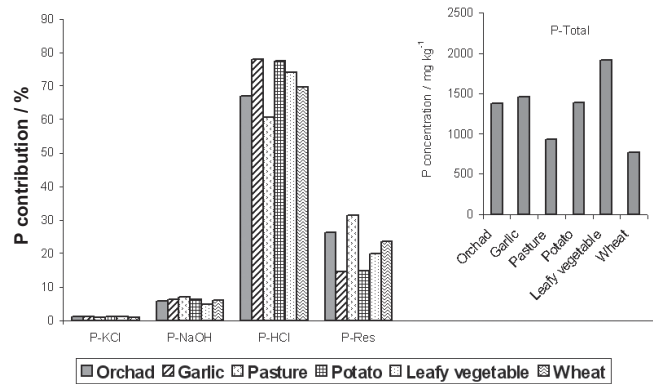


Figure 1: Soil P fractions under different land uses.



**Figure 2:** Soil P fractions in different land uses. Columns are mean values of each fraction under different land use; error bars indicate standard deviation. Values followed by the same letter in the column indicate that the effect of land use is not significant at the 5% level, according to Duncan test.

area. Table 2 compares the amounts of P added to the soil with the crop P uptake in different land uses. These figures do not include the P input from manure, so the total P input could be higher. In leafy-vegetables and potato fields in the study area, the use of 10 t ha<sup>-1</sup> y<sup>-1</sup> of sheep and poultry organic manures is common. The P applied in organic manures would be equal to 200 and 138 kg P ha<sup>-1</sup> based on 2% and 1.38% P in poultry and sheep manures, respectively (Jalali and Ranjbar, 2009). The amount of organic manures applied on orchard and garlic is unknown. Wheat fields and pasture receive no manures. Due to the water shortage in the area, parts of the vegetable fields are irrigated with untreated sewage effluents from Hamedan city since 1970.



**Figure 3:** The percentage contribution of each fractions and average total P content of soil samples under different land uses.

### 3.3 Fe-Al-bound P

The Fe-Al-bound fraction contains P associated with amorphous oxyhydroxide surfaces and crystalline Fe and Al oxides. For all land uses, this fraction had the second-lowest P content of all chemical fractions (Fig. 1). The calcareous nature of these soils tended to promote the sequestration of P into the Ca-bound rather than the Fe-Al-bound fraction. The distribution of Fe-Al-bound P among land uses followed similar patterns as labile P (Fig. 2). The Fe-Al-bound P concentration was higher for garlic, potato, and leafy vegetables than the other land uses (Fig. 2). The P concentration in this fraction averaged 7% of the total P for pasture, but 6.3% and 4.9% of the total P for potato and leafy vegetables, respectively (Fig. 3). In Histosols of Florida, the Fe-Al fraction averaged 2.9% of the total for turf grass and forest, but 11.4% and 9.6% for sugarcane (Wright, 2009). In calcareous marsh soils in Spain, the maximum Fe-Al fraction was 23.9% of the total P (Jimenez-Carceles and Alvarez-Rogel, 2008). The contribution of Fe-Al-bound P to total P was significantly lower than Res-P and Ca-bound fractions. The P contained in this fraction may be unstable with fluctuating redox conditions (Moore and Reddy, 1994), thus there may be considerable movement of P into and out of this fraction depending on environmental conditions for these soils. Since Fe-Al-bound and labile fractions represent the least recalcitrant pools, P in these fractions likely represents recent inputs from fertilizer (Wright, 2009).

### 3.4 Ca-bound P

Concentration of P in Ca-bound fraction in soils under different land uses is presented in Fig. 1. Ca-bound P was the most abundant P fraction in the soils, constituting between 61% and 78% of the total P (represented on average 71.4% of total P), which suggest that a high proportion of P is in stable inorganic form. This result is in accordance with the results obtained for sugarcane by Castillo and Wright (2008). Phosphorus adsorption and precipitation with Ca represents a more stable pool than labile and Fe-Al-bound fractions (Diaz et al., 2006), thus P held in Ca-bound fraction poses less of an eutrophication hazard (Wright, 2009). The major difference in P distribution between land uses occurred with Ca-P bound fraction (Fig. 2). In fact, excess P fertilizer is

**Table 2:** Phosphorus management and applied N and K of the fields in Hamedan province.

Land use	Applied P fertilizer / kg P ha <sup>-1</sup> b	Fertilizer-application method	Average crop yield / t ha <sup>-1</sup> a	Crop P uptake / kg P ha <sup>-1</sup> c	Percentage of P fertilizer applied taken by crop	Applied N fertilizer / kg N ha <sup>-1</sup> b	Applied K fertilizer / kg N ha <sup>-1</sup> b
Wheat	31	broadcast	1.68	4.3 d	14	138	50
Potato	42	broadcast	29	25 f	59	184	100
Leafy vegetables	42	broadcast	7.7	23 i	55	230	70
Garlic	50	broadcast	10	13.3	26.6	170	80
Pasture	0	–	–	–	–	–	–

<sup>a</sup> Iran Ministry of Agriculture (2003).

<sup>b</sup> Recommended by the Soil and Water Research Institute (Malakouti and Gheibi, 2000).

<sup>c</sup> Calculated based on average crop yield and utilization of P by crops (Tisdale et al., 1985).

<sup>d, e, f, g, and h</sup> Including grain and straw, grain and stover, tubers and vines, roots and tops, and fruit and vines, respectively.

<sup>i</sup> Calculated based on a P content of 0.3%.

often sequestered in inorganic fractions, as P concentrations in the Ca-bound fraction were higher for potato and garlic than other land uses (Fig. 2). Potato and garlic were the most intensively managed land use with annual P fertilization, thus the higher contribution of Ca-bound P to total P for potato than other land uses (Fig. 3). Potato and garlic contained 78% of P in the Ca-bound fraction compared to 60.8% for pasture. The pasture had the lowest Ca-bound P concentrations because it was the least disturbed land use. Farming practices increased P sequestration in the Ca-bound fraction under potato, garlic, and leafy vegetables relative to pasture soil, possibly due to higher Ca levels (Sanchez and Porter, 1994; Snyder, 2005). A similar trend was observed for canal sediments in the Everglades (Diaz et al., 2006).

The higher P retention for potato, garlic, and leafy vegetables may have an advantage of minimizing potential for runoff or leaching.

### 3.5 Residual P

The Res-P pool is characterized by stable lignin and organo-metallic complexes (Ivanoff et al., 1998) and generally considered to be a stable and recalcitrant chemical fraction (Turner et al., 2005). The distribution of Res-P among land uses followed similar patterns as Ca-bound P (Fig. 1). Residual-P concentrations were lowest for potato and garlic and highest for pasture and orchard (Fig. 2). The pasture was characterized by the majority of its P in Res-P fraction, while potato had less of its total P in the residual fraction. The proportion of the Res-P to total P was different for all land uses (Fig. 3). Pasture contained 31.3% of P in the Res-P fraction compared to 13.7% for potato. Lower P storage in organic fractions of potato, garlic, leafy vegetables, and wheat soils indicated enhancement of organic-matter decomposition by cultivation, which increased organic-P mineralization and sequestration in inorganic fractions, primarily the Ca-bound fraction (Wright, 2009).

In general, soils under leafy vegetables presented the highest values in all fractions of P considered, while the soils under

wheat and pasture presented the lowest values. Intensive fertilization and management increased P sequestration in inorganic fractions. Other studies have also shown that cultivation increases P retention in mineral-associated pools (McGrath et al., 2001).

In arid and semiarid regions, groundwater is commonly the only source of irrigation, and its quality is usually poor because of limited rainfall and high rates of evaporation (Jalali and Kolahchi, 2009). Thus, a high proportion of low- to medium-quality groundwater is used for irrigation. Such water may contain large quantities of soluble salts, predominately Ca<sup>2+</sup> and Na<sup>+</sup>. The quality of groundwaters in the Hamedan region varies from useable to hazardous (Jalali, 2002). In addition, in the studied area Ca<sup>2+</sup> is the dominant ion in well waters, representing on average 43.6% of all cations (Jalali, 2002). Its concentration in irrigation water in the studied area varies from 0.01 to 11.3 mM (Jalali, 2006; Jalali, 2007b, c). The increasing irrigation of soil by groundwater containing large quantity of Ca<sup>2+</sup> ions encouraged P retention in the Ca-bound fraction, which represents a stable long-term pool under current land use. Land uses with minimal management and no fertilization, such as pasture and to some extent orchard and wheat, had more P in residual fraction. To offset P retention and to maintain plant-available concentrations sufficient for crop production under current land use, higher fertilizer rates in the future would necessitate (Castillo and Wright, 2008).

### 3.6 Correlation between variables

The Pearson correlation matrix was computed (Tab. 3), and the criterion values of probabilities ( $p < 0.05$  and  $p < 0.01$ ) for correlation significance are used. The correlations among the elements are similar to the conclusion drawn from the component loadings (following section), *i.e.*, a strong positive correlation between labile P and Fe-Al-bound P ( $r = 0.534$ ,  $p < 0.01$ ), labile P and Ca-bound P ( $r = 0.574$ ,  $p < 0.01$ ), Ca-bound P and Fe-Al-bound P ( $r = 0.504$ ,  $p < 0.01$ ), Olsen-P and CaCl<sub>2</sub>-P ( $r = 0.821$ ,  $p < 0.01$ ) was observed, which means that these parameters can be considered to be

**Table 3:** Pearson correlation coefficients for the 16 parameters.

	KCl-P	NaOH-P	HCl-P	Res-P	pH	EC	K <sub>ex</sub>	Na <sub>ex</sub>	Ca <sub>ex</sub>	Mg <sub>ex</sub>	CaCl <sub>2</sub> -P	Olsen-P	CaCO <sub>3</sub>	OM	Sand	Silt
NaOH-P	0.534**															
HCl-P	0.574**	0.504**														
Res-P	NS	NS	NS													
pH	NS	NS	NS	NS												
EC	NS	NS	NS	NS	0.474**											
K <sub>ex</sub>	NS	NS	NS	NS	0.605**	0.640**										
Na <sub>ex</sub>	-0.264*	NS	-0.296*	NS	0.469**	NS	0.351**									
Ca <sub>ex</sub>	NS	NS	NS	-0.306*	0.744**	0.386**	0.431**	0.540**								
Mg <sub>ex</sub>	-0.352**	NS	-0.269*	NS	0.321*	NS	NS	0.575**	0.283*							
CaCl <sub>2</sub> -P	NS	NS	NS	NS	NS	0.373**	0.435**	NS	NS	NS						
Olsen-P	NS	NS	NS	NS	NS	0.412**	0.463**	NS	NS	NS	0.821**					
CaCO <sub>3</sub>	NS	NS	NS	-0.314*	0.648**	0.265*	0.326**	0.623**	0.744**	0.415**	-0.348**	NS				
OM	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS			
Sand	NS	NS	NS	NS	0.617**	0.299*	0.394**	0.504**	-0.675**	-0.413**	0.387**	0.363**	-0.799**	NS		
Silt	NS	NS	NS	NS	0.263*	NS	NS	0.302*	0.364**	0.309*	-0.387**	-0.396**	0.460**	0.318*	-0.731**	
Clay	NS	NS	NS	NS	0.617**	0.299*	0.398**	0.504**	0.672**	0.344**	NS	NS	0.744**	NS	-0.847**	NS

<sup>a</sup> \*, \*\* Significant at 5% and 1% level of significance, respectively

strongly correlated. A negative correlation between CaCO<sub>3</sub> and Res-P was found ( $r = -0.314, p < 0.05$ ). A similar correlation was found for calcareous marsh soils in Spain (*Jimenez-Carceles and Alvarez-Rogel, 2008*). There were not any significant correlation between Olsen-P, CaCl<sub>2</sub>-P, and other P fractions with clay, silt, sand, OM, and CaCO<sub>3</sub> parameters. This indicates that variation in P fractions among soils can be related to the P-fertilization management. Other significant correlations are presented in Tab. 2.

### 3.7 Principal-component analysis

Multivariate statistical methods for classification, modeling, and interpretation of large sets may allow the reduction of data set, and analysis of this information may be helpful for soil fertility assessment. The multivariate analysis is suitable to analyses measurements of several variables or characteristics from a set of experimental units. Principal-component analysis was carried out on pooled data of soil solutions in order to better understand their interrelationships and to

**Table 4:** Principal-component loading.

Variable	PC1	PC2	PC3	PC4
KCl-P	0.127	0.044	0.526	-0.121
NaOH-P	0.095	-0.041	0.507	0.164
HCl-P	0.109	-0.011	0.508	0.064
Res-P	0.156	0.037	0.128	0.063
pH	-0.332	-0.167	0.107	-0.154
EC	-0.168	-0.392	0.117	0.169
K <sub>ex</sub>	-0.202	-0.415	0.173	0.079
Na <sub>ex</sub>	-0.310	-0.044	-0.138	0.110
Ca <sub>ex</sub>	-0.354	-0.043	0.135	-0.104
Mg <sub>ex</sub>	-0.243	-0.011	-0.217	0.236
CaCl <sub>2</sub> -P	0.105	-0.507	-0.071	0.040
Olsen-P	0.071	-0.518	-0.078	0.119
CaCO <sub>3</sub>	-0.381	0.071	0.079	-0.042
OM	0.005	0.093	0.007	0.759
Sand	0.374	-0.159	-0.125	-0.016
Silt	-0.225	0.015	0.098	-0.273
Clay	-0.354	0.269	0.102	0.380
Eigenvalues	5.518	2.872	2.196	1.352
% variance explained	32.5	16.9	12.9	7.9
% Cumulative variance	32.5	49.4	62.3	70.2

explore the reduction of the experimental variables. Table 4 shows the principal components, eigenvalues, and associated variance explained in the physico-chemical data and communities. These components all had eigenvalues > 1 (the most significant one) (Miller and Miller, 2000). Four extracted components explain 70.2% of data-set variance. Component 1 explains 32.5% of the total variance, while component 2, 3, and 4 explain 16.9%, 12.9%, and 7.9%, respectively. Component 1 has the highest component loadings of Ca, CaCO<sub>3</sub>, sand, clay, pH, and Na, high component loadings of Mg and silt, and low component loadings for the remaining parameters. This association strongly suggests that PC1 may represent a soil physical and chemical variable. Component 2 has the highest component loadings of P CaCl<sub>2</sub> and Olson-P and high component loadings of K and EC and low component loadings for the remaining parameters, suggesting that PC2 may represent labile P variable. Component 3 has the highest component loadings of labile P, Fe-Al-bound P, and Ca-bound P and low component loadings for the remaining parameters, suggesting that PC3 may represent P fractions variable. Component 4 has the highest component loadings of OM (negative), high component loading of silt, and low component loadings for the remaining parameters, suggesting that PC4 may represent organic-matter variable.

#### 4 Conclusions

The distribution of P among soil chemical fractions differed between land uses, with the highest storage in the Ca-bound fraction for potato and garlic but in the Res-P fraction for pasture. Long-term fertilization increased P retention in mineral-associated fractions, particularly the Ca-bound fraction. Tillage and cultivation decreased organic P, and the incorporation of Ca into soils by irrigation water enhanced P sequestration in the Ca-bound fraction. Continuation of conventional crop-management practices will likely further increase soil Ca levels, leading to greater recovery of P fertilizer in the Ca-bound fraction and lower P availability to plants. The principal-component analysis performed on P fractions and soil physical and chemical properties identified four principal components controlling variability of soil samples: the first PC1 was associated with Ca, CaCO<sub>3</sub>, sand, clay, pH, and Na, Mg, and silt. Thus, this component could be interpreted as linked to soil physical and chemical properties. The second PC2 represents association amongst P CaCl<sub>2</sub>, and Olson-P suggesting that PC2 may represent a labile P variable. Component 3 has the highest component loadings of labile P, Fe-Al-bound P, and Ca-bound P and may be interpreted as P fraction component, and finally PC4 has the highest component loading of OM.

Phosphorous accumulation in irrigated agriculture in some land use should receive considerable attention. The large amount and inadequate management of P fertilization in some fields are mainly responsible for the P accumulation in surface soils. Continuation of conventional crop-management practices will likely further increase soil P. The P fractionation in different land use reflected the rate of fertilizers, manures, and sewage-effluent application in the studied area. Phosphorous-fertilizer recommendation schemes that fail to properly account for differences in P distribution in different land

use could potentially have substantial economic consequences and cause surface and groundwater pollution.

It may be recommended to use organic P fertilizer with limited inorganic P source. The increasing irrigation of soil by groundwater containing large quantity of Ca ions encouraged P retention in the Ca-bound fraction, which represents a stable long-term pool under current land use. In order to reduce Ca-bound fraction in soils, the Ca applied in Ca-rich irrigation water should be taken into account and other irrigation water with low Ca may be considered.

#### References

- Alvarez-Rogel, J., Jimenez-Carceles, F. J., Egea-Nicolas, C. (2007): Phosphorus retention in a coastal salt marsh in SE Spain. *Sci. Total Environ.* 378, 71–74.
- Ann, Y., Reddy, K. R., Delfino, J. J. (2000): Influence of chemical amendments on phosphorus immobilization in soils from a constructed wetland. *Ecol. Eng.* 14, 157–167.
- Cardoso, I. M., Janssen, B. H., Oenema, O., Kuyper, T. W. (2003): Phosphorus pools in Oxisols under shade and unshaded coffee systems on farmers' fields in Brazil. *Agroforestry Sys.* 56, 55–64.
- Castillo, M. S., Wright, A. L. (2008): Microbial activity and phosphorus availability in a subtropical soil under different land uses. *World J. Agric. Sci.* 4, 314–320.
- Diaz, O. A., Daroub, S. H., Stuck, J. D., Clark, M. W., Lang, T. A., Reddy, K. R. (2006): Sediment inventory and phosphorus fractions for Water Conservation Area canals in the Everglades. *Soil Sci. Soc. Am. J.* 70, 863–871.
- Hedley, M. J., Stewart, J. W. B., Chauhan, B. C. (1982a): Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubation. *Soil Sci. Soc. Am. J.* 46, 970–976.
- Hedley, M. J., White, R. E., Nye, P. H. (1982b): Plant-induced changes in the rhizosphere of rape (*Brassica napus* var. Emerald) seedlings. III. Changes in L value, soil phosphate fractions and phosphatase activity. *New Phytol.* 91, 45–56.
- Ivanoff, D. B., Reddy, K. R., Robinson, S. (1998): Chemical fractionation of organic phosphorus in selected histosols. *Soil Sci.* 163, 36–45.
- Jalali, M. (2002): Composition of irrigation waters in west of Iran. Proc. 17<sup>th</sup> World Congress of Soil Science, Bangkok, Thailand, August 14–21, pp. 2184-1–2184-4.
- Jalali, M. (2005): Nitrates leaching from agricultural land in Hamedan, western Iran. *Agric. Ecosyst. Environ.* 110, 210–218.
- Jalali, M. (2006): Chemical characteristics of groundwater in parts of mountainous region, Alvand, Hamedan, Iran. *Environ. Geol.* 51, 433–446.
- Jalali, M. (2007a): Phosphorous status and sorption characteristics of some calcareous soils of Hamedan, western Iran. *Environ. Geol.* 53, 365–374.
- Jalali, M. (2007b): Assessment of the chemical components of Famenin groundwater, western Iran. *Environ. Geochem. Heal.* 29, 357–374.
- Jalali, M. (2007c): Salinization of groundwater in arid and semi-arid zones: an example from Tajarak, western Iran. *Environ. Geol.* 52, 1133–1149.
- Jalali, M., Ahmadi Mohammad Zinli, N. (2011): Kinetics of phosphorus release from Iranian calcareous soils under different land use. *J. Plant Nutr. Soil Sci.* 174, 38–46.



- Jalali, M., Kolahchi, Z. (2009): Effect of irrigation water quality on the leaching and desorption of phosphorous from soil. *Soil Sediment Cotamin.* 18, 576–589.
- Jalali, M., Ranjbar, F. (2009): Rates of decomposition and phosphorus release from organic residues related to residue composition. *J. Plant Nutr. Soil Sci.* 172, 353–359.
- Jalali, M., Ranjbar, F. (2010): Aging effects on phosphorus transformation rate and fractionation in some calcareous soils. *Geoderma*, 155, 1–106.
- Jimenez-Carceles, F. J., Alvarez-Rogel, J. (2008): Phosphorus fractionation and distribution in salt marsh soils affected by mine wastes and eutrophicated water: a case study in SE Spain. *Geoderma* 144, 299–309.
- McDowell, R., Sharpley, A., Brookes, P. H., Poulton, P. (2001): Relationship between soil test phosphorus and phosphorus release to solution. *Soil Sci.* 166, 137–149.
- McGrath, D. A., Duryea, M. L., Cropper, W. P. (2001): Soil phosphorus availability and fine root proliferation in Amazonian agroforests 6 years following forest conversion. *Agric. Ecosyst. Environ.* 83, 271–284.
- Miller, N. J., Miller, J. C. (2000): Statistics and chemometrics for analytical chemistry. 4th edn., Pearson Education, Englewood Cliffs, NJ.
- Motavalli, P. P., Miles, R. J. (2002): Soil phosphorus fractions after 111 years of animal manure and fertilizer applications. *Biol. Fertil. Soils* 36, 35–42.
- Moore, P. A., Reddy, K. R. (1994): Role of eH and pH on phosphorus geochemistry in sediments of Lake Okeechobee, Florida. *J. Environ. Qual.* 23, 955–964.
- Murphy, J., Riley, J. P. (1962): A modified single solution method for determination of phosphate in natural waters. *Anal. Chim. Acta* 27, 31–36.
- Olsen, S. L., Sommers, L. E. (1982): Phosphorus, in Page, A. L., et al., eds.): Methods of soil analysis, part 2. 2nd edn., Agron. Monogr. No.9, ASA and SSSA, Madison WI, pp. 403–427.
- Redel, Y. D., Rubio, R., Rouanet, J. L., Borie, F. (2007): Phosphorus bioavailability affected by tillage and crop rotation on a Chilean volcanic derived Ultisol. *Geoderma* 139, 388–396.
- Redel, Y., Rubio, R., Godoy, R., Borie, F. (2008): Phosphorus fractions and phosphatase activity in an Andisol under different forest ecosystems. *Geoderma* 145, 216–221.
- Reddy, K. R., Wang, Y., DeBusk, W. F., Fisher, M. M., Newman, S. (1998): Forms of soil phosphorus in selected hydrologic units of the Florida Everglades. *Soil Sci. Soc. Am. J.* 62, 1134–1147.
- Rowell, D. L. (1994): Soil Science: Methods and Applications. Longman Group, Harlow, p. 345.
- Sabziparvar, A. A. (2003): The analysis of aridity and meteorological drought indices in west of Iran. Research report. Bu-Ali Sina University, Hamedan, Iran.
- Sanchez, C. A., Porter, P. S. (1994): Phosphorus in the organic soils of the EAA, in Bottcher, D. B., Izuno, F. T. (eds.): Everglades Agricultural Area (EAA). Univ. Press of Florida, Gainesville, FL, pp. 62–84.
- Sharpley, A. N., Smith, S. J. (1989): Prediction of soluble phosphorus transport in agricultural runoff. *J. Environ. Qual.* 18, 313–316.
- Sharpley, A. N., Foy, R. J., Withers, P. J. A. (2000): Practical and innovative measures for the control of agricultural losses to water: An overview. *J. Environ. Qual.* 29, 1–9.
- Sims, J. T., Simard, R. R., Joern, B. C. (1998): Phosphorus losses in agricultural drainage: Historical perspective and current research. *J. Environ. Qual.* 27, 277–293.
- Skinner, R. J., Todd, A. D. (1998): Twenty-five years of monitoring pH and nutrient status of soils in England and Wales. *Soil Use Manage.* 14, 162–169.
- Snyder, G. H. (2005): Everglades Agricultural Area soil subsidence and land use projections. *Soil Crop Sci. Soc. Fl. Proc.* 64, 44–51.
- Soil Survey Staff (1990): Keys to Soil Taxonomy. SMSS Technical Monograph No. 19, 4th edn., Virginia Polytechnic Institute and State University, USDA-SMSS.
- Sui, Y., Thompson, M. L., Mize, C. W. (1999): Redistribution of biosolids-derived total P applied to a Mollisol. *J. Environ. Qual.* 28, 1068–1074.
- Tiessen, H., Stewart, J. W. B., Cole, C. V. (1984): Pathways of phosphorus transformations in soils of differing pedogenesis. *Soil Sci. Soc. Am. J.* 48, 853–858.
- Turner, B. L., Cade-Menun, B. J., Condon, L. M., Newman, S. (2005): Extraction of soil organic phosphorus. *Talanta* 66, 294–306.
- Wright, A. L. (2009): Soil phosphorus stocks and distribution in chemical fractions for long-term sugarcane, pasture, turfgrass, and forest systems in Florida. *Nutr. Cyc. Agric. Sys.* 83, 223–231.
- Yerokun, O. (2008): Chemical characteristics of phosphorus in some representative benchmark soils of Zambia. *Geoderma* 147, 63–68.