

## Phosphorus status and sorption characteristics of some calcareous soils of Hamadan, western Iran

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**Abstract** Phosphorus (P) application in excess of plant requirement may result in contamination of drinking water and eutrophication of surface water bodies. The phosphorous buffer capacity (PBC) of soil is important in plant nutrition and is an important soil property in the determination of the P release potential of soils. Phosphorus sorption greatly affects both plant nutrition and environmental pollution. For better and accurate P fertilizer recommendations, it is necessary to quantify P sorption. This study was conducted to investigate available P and P sorption by calcareous soils in a semi-arid region of Hamadan, western Iran. The soil samples were mainly from cultivated land. Olsen's biocarbonate extractable P (Olsen P) varied among soils and ranged from 10 to 80 mg kg<sup>-1</sup> with a mean of 36 mg kg<sup>-1</sup>. Half of the soils had an Olsen P > 40 mg kg<sup>-1</sup> and >70% of them had a concentration >20 mg kg<sup>-1</sup>, whereas the critical concentration for most crops is <15 mg P kg<sup>-1</sup>. Greater average Olsen P in soils occurred under garlic (56 mg kg<sup>-1</sup>) and potato (44 mg kg<sup>-1</sup>) fields than in dry-land wheat farming (24 mg kg<sup>-1</sup>), pasture (30 mg kg<sup>-1</sup>), and wheat (24 mg P kg<sup>-1</sup>) fields. A marked increase in fertilizer P rates applied to agricultural soils has caused P to be accumulated in the surface soil. Phosphate sorption curves were well fitted to the Freundlich equation. The standard P requirement (SPR) of soils, defined as the amount of P sorbed at an equilibrium concentration of 0.2 mg l<sup>-1</sup> ranged from 4 to 102 mg kg<sup>-1</sup>. Phosphorus

buffer capacity was relatively high and varied from 16 to 123 l kg<sup>-1</sup> with an average of 58 l kg<sup>-1</sup>. In areas of intensive crop production, continual P applications as P fertilizer and farmyard manure have been used at levels exceeding crop requirements. Surface soil accumulations of P are high enough that loss of P in surface runoff and a high risk for P transfer into groundwater have become priority management concerns.

**Keywords** Phosphorous adsorption · Phosphorous buffer capacity · Calcareous soils · Groundwater quality

### Introduction

Phosphorus (P) in soils is important because adequate availability of this nutrient is required for plant growth and crop production. Phosphorous application has become an essential part of crop production systems in order to provide adequate food and fiber for human consumption. The importance of maintaining an adequate P supply to crops in order to maximize agricultural output has long been recognized and the routine application of P fertilizers to agricultural land have become an integral part of developed countries' agriculture (Withers et al. 2001). Phosphorus is often considered the most limiting nutrient for plant growth in soils. One method to raise soil available P to the critical crop level is by addition of P fertilizer. However, continued long-term application of fertilizers can lead to P accumulation in surface horizons greater than that required for optimum plant growth, thus increasing the potential for P loss to surface waters and eutrophication (McDowell et al. 2001; Sui et al. 1999).

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Phosphorous fertilizer is used annually and plant uptake and microbial immobilization cannot remove the entire P from the solution. Long-term fertilization of coarse- to medium-textured soils could increase downward P mobility (Campbell and Racz 1975; Mozaffari and Sims 1994; Zhang et al. 1995). High P application to soils can lead to deterioration of surface water quality as a result of eutrophication. Eutrophication of lakes can be initiated by concentrations of P as low as  $0.01 \text{ mg l}^{-1}$  (Sharpley and Smith 1989). Therefore, the loss of small amounts of P from soil to surface waters and by subsurface drainage waters can lead to a deterioration of water quality (Foy and Withers 1995; Sharpley et al. 2000). Some agricultural soils can now be classified as overfertilized due to a steady increase in available P resulting from application of fertilizer P in the past (Sharpley and Smith 1989). National surveys in the UK showed that soil P fertility on many farms is at a level where research suggests fertilizer and manure P inputs need no longer exceed crop P removal, or can be reduced (Skinner and Todd 1998; Sinclair et al. 1989).

Most of the current management strategies rely on measuring P availability by leaching the soil with an extractant (Hansen and Strawn 2003). The most common index used on calcareous soils is the Olsen's bio-carbonate extractable P (Olsen P) value, which is estimated to be the fraction of soil P available for plant uptake (Kuo 1996) and is an indicator of plant available P in calcareous soils. Kuo (1990) found that the Olsen P test is highly dependent on P sorption capacity.

Sorption reactions and phosphorous buffer capacity (PBC) of soils play an important role in both agronomic and environmental aspects of P management. Sorption isotherms are much used to characterize the retention of P and the PBC of soil (Yli-halla et al. 2002). The capacity of the soil to sorb P greatly influences plant responses to applied P fertilizers and the calibration of soil tests for P (Bolland et al. 1996; Amrani et al. 1999). Therefore, knowledge of the ability of the soil to adsorb P fertilizer is required to provide an accurate estimate on the P fertilizer requirements of soils. In calcareous soils, phosphate sorption is greatly affected by the adsorption and precipitation reactions at calcium carbonate mineral surfaces (Freeman and Rowell 1981). Sorption-isotherm techniques have been widely used to compare the sorption of P by different soils.

In Iran there are concerns that soil P has now reached excessive levels and is having a negative impact on surface water quality. The extent and intensity of agriculture in Hamadan, western Iran, leading to high annual rates of fertilizer application has had a

strong influence on water quality (Jalali 2005b). Phosphorous accumulation in irrigated agriculture should receive considerable attention, because of possible eutrophication of water. Large amounts of P fertilizer and poorly managed irrigated systems may lead to P accumulation and pollution of surface and ground water. The objectives of this study were to determine the P status of surface soils of some intensively cropped sites and evaluate P sorption characteristics of some calcareous soils of Iran, in order to identify areas where P applications in fertilizers and manures should be controlled to protect water quality.

## Materials and methods

### Study area

This study was conducted in Hamadan, about 400 km from Tehran, western Iran. The study area lies between longitudes  $48^{\circ}27'36''$  and  $48^{\circ}35'24''$  E and latitudes  $34^{\circ}46'48''$  and  $35^{\circ}4'12''$  N (Fig. 1). The climate of the region is semi-arid with a mean annual precipitation of 300 mm and a mean annual temperature of  $10^{\circ}\text{C}$ . Agriculture is a major industry and principal land use in Hamadan. Major crops grown in Hamadan are winter wheat (*Triticum aestivum* L.), potato (*Solanum tuberosum*) and garlic (*Allium sativum*) (Jalali 2005b). Fertilizers are applied throughout agricultural regions of Hamadan to enhance crop production. Most of the agricultural land in Hamadan is cropland and pasture. However, livestock also substantially contributes to the state's agricultural industry.

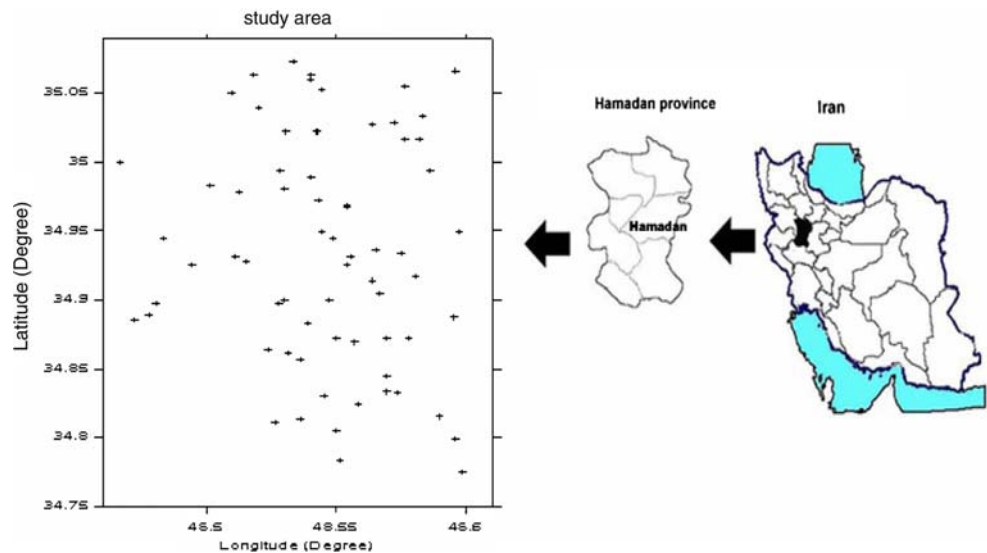
The Hamadan area is characterized by the predominance of metamorphic rocks of both sedimentary and magmatic origins (Sepahi 1999) and the presence of the Alvand huge granitoid complex. The metamorphic rocks constitute an assemblage of high to low metamorphic grade issued from sedimentary sequences that have been affected by a more or less developed tectonometamorphic event (Baharifar et al. 2004).

Soils resulting from the weathering of these rocks are generally sandy to clayey in texture and mostly classified as Aridisols and are calcareous. Mineralogically, most of the soils are dominated by illite, smectite, chlorite and vermiculite (Jalali 2005a), typical for most arid and semi-arid soils.

### Soil sampling

Soil samples (0–30 cm) were collected from 66 calcareous soils, which are located in different agricultural areas with diverse crops in Hamadan, western Iran

**Fig. 1** Study area showing location of soil samples



(Fig. 1). Sample sites included fields with wheat, potato, garlic, and dry-land wheat farming, and also a pasture that received no P fertilizer application. These areas (except pasture) have received various quantities of P fertilizer over the past 40 years. The soil samples were air-dried and passed through a 2-mm sieve for laboratory analysis.

**Soil analysis**

Olsen P (1:20 solid:solution ratio, by volume, in 0.5 M NaHCO<sub>3</sub> at pH 8.5) was extracted according to the method of Olsen and Sommers (1982) and analysed by the ascorbic acid method of Murphy and Riley (1962). The rationale for this soil test is that it is the calibration method for West Asia and North Africa (Afif et al. 1993) and the Olsen P values are the most common index used on calcareous soils (Kuo 1996). In addition, extractable Olsen P has previously been shown to be a useful indicator for P leaching (Heckrath et al. 1995).

Particle size was determined by the pipette method, organic carbon was determined by dichromate oxidation (Rowell 1994), and soil pH and EC were determined in a soil–solution ratio of 1:5 using a combination electrode and electrical conductivity meter. Cation exchange capacity (CEC) was determined by saturation with 1 M NH<sub>4</sub>OAc at pH 7. Calcium carbonate equivalent was determined by the acid neutralization method (Rowell 1994).

**Sorption isotherm**

Phosphorous sorption was determined in ten of the soil samples (Table 1). Phosphate sorption curves were obtained by shaking 2.5 g of soil in a 50 ml centrifuge

tube with screw cap to which was added an equilibrating solution of KH<sub>2</sub>PO<sub>4</sub> containing 0, 4, 8, 20, 50, 100, 150 and 200 mg P l<sup>-1</sup>. The equilibrating solution included 0.01 M CaCl<sub>2</sub> that simulated soil pore water in calcareous soils (Robbins et al. 1999) and the soil solution ratio was 1:10. The suspensions were shaken for 30 min and left for 24 h at 24–25°C and then shaken for another 30 min. At the end of the incubation period, the tubes were centrifuged for 10 min. The P concentration in the supernatant was determined by the ascorbic acid method of Murphy and Riley (1962). Sorbed P was calculated from the difference between the concentration of soluble P added in the initial solution and P in the solution at equilibrium. The procedure was performed in duplicate. The set of initial dissolved P concentrations used in the sorption experiments reflected the high concentration of water-soluble P that can occur in soils to which P fertilizer is added.

The sorption isotherm of P was modelled with the Freundlich equations. The Freundlich equation has the form

$$X = K_f C^n \tag{1}$$

where *X* is the quantity of P adsorbed (mg kg<sup>-1</sup>), *C* is the equilibrium concentration of P (mg l<sup>-1</sup>) and the quantities *K<sub>f</sub>* and *n* are constants relating to the sorption capacity and the linearity of the sorption isotherm, respectively. The linear regression of log *C* against log *X* gives a regression coefficient, a slope of *n*, and an intercept of log *K<sub>f</sub>*. The standard P requirement (SPR) of soils, defined as the amount of P to be added to attain an equilibrium solution concentration of 0.2 mg P l<sup>-1</sup> (Abekoe and Sahrawat 2001) was calculated from the fitted Freundlich equation.

**Table 1** Chemical and physical properties of the ten selected soils selected for sorption determination

Soil no.	Soil classification	pH <sup>a</sup>	EC (dS m <sup>-1</sup> ) <sup>a</sup>	CCE (%) <sup>b</sup>	CEC <sup>c</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	Extractable P (mg kg <sup>-1</sup> )	OM <sup>d</sup> (g kg <sup>-1</sup> )	Clay	Silt	Sand
1	Typic calcixerepts	6.9	0.48	3.3	16.5	30	15.5	107	516	376
2	Typic calcixerepts	7.2	0.40	18.2	21.5	80	13.1	232	514	254
3	Typic haploxerepts	7.3	0.34	14.2	19	24	12.7	147	484	368
4	Typic xerofluvents	7.9	0.51	21.4	22	30	10.7	210	430	360
5	Typic xerofluvents	7.4	0.25	16.4	22.2	40	7.1	226	393	381
6	Typic calcixerolls	7.1	0.32	4.9	16.2	51	5.9	75	315	610
7	Typic xerofluvents	7.3	0.27	10.2	20.8	44	5.2	164	394	443
8	Typic calcixerepts	7.3	0.30	5.1	16.3	25	4.7	127	312	562
9	Typic calcixerepts	7.6	0.24	9.3	16	50	3.5	179	371	450
10	Typic xerofluvents	7.4	0.65	19	23.4	17.5	1.9	205	631	164

<sup>a</sup> 1:5 solution ratio<sup>b</sup> CCE = CaCO<sub>3</sub> equivalent<sup>c</sup> CEC = cation exchange capacity<sup>d</sup> Organic matter

## Results and discussion

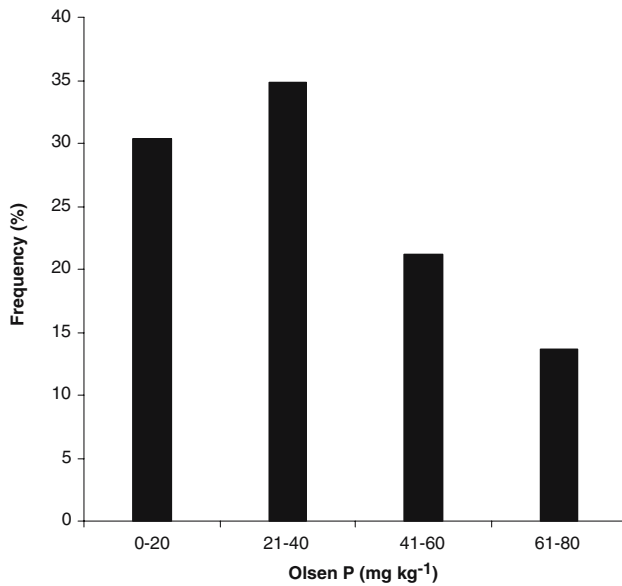
Selected chemical and physical properties of the ten soils selected for isotherm sorption determination are shown in Table 1. Clay contents in these soils averaged 148 g kg<sup>-1</sup> and ranged from 75 to 232 g kg<sup>-1</sup>. The CEC ranged from 16.0 to 23.4 cmol<sub>c</sub> kg<sup>-1</sup>. Calcium carbonate contents varied from 3.3 to 21.4%. Table 1 was arranged according to decreasing organic matter content. The first group of five soils has the high organic matter content (7.1–15.5 g kg<sup>-1</sup>).

Olsen P concentration (66 soil samples) varied from 10 to 80 mg kg<sup>-1</sup> with an average of 36 mg kg<sup>-1</sup>. Olsen P is above 20 mg kg<sup>-1</sup> in 70% and above 40 mg kg<sup>-1</sup> in 50% of the soil samples (Fig. 2). Olsen P in soils under garlic (56 mg kg<sup>-1</sup>) and potato (44 mg kg<sup>-1</sup>) fields was higher than in dry-land wheat farming (24 mg kg<sup>-1</sup>), pasture (30 mg kg<sup>-1</sup>) and wheat (24 mg kg<sup>-1</sup>) fields. High rates of fertilizer P rates applied to garlic and potato fields have caused P to be accumulated in the surface soil. Phosphorous fertilizer is usually recommended when Olsen P soil test levels are below 15 mg kg<sup>-1</sup>, and large, economical yield increases are expected from applied P when soil tests are below 10 mg kg<sup>-1</sup> (Havlin et al. 1999). Of 16 soil samples collected from fields under potato crop, only 2 samples had P contents less than 20 mg kg<sup>-1</sup>. None of the samples (10) collected from garlic fields had P content less than 24 mg kg<sup>-1</sup>. However, of 24, 10 and 6 soil samples collected from fields under wheat, dry-land wheat farming and pasture 7, 3, and 1 samples had a P content less than 20 mg kg<sup>-1</sup>, respectively.

The average annual application rate of P fertilizer in Iran is currently over 40 kg P ha<sup>-1</sup> (200 kg ha<sup>-1</sup> as superphosphate). In high-yielding crop regions of Iran, P fertilizer application is usually over 63 kg P ha<sup>-1</sup> yr<sup>-1</sup> (Malakouti and Gheibi 2000), with accompanying decreases in utilisation efficiency. Table 2 compares the

amounts of P added to the soil with the crop P uptake in several crops in the Hamadan area. It is apparent that the P input is higher than the P requirement. Thus, fertilizer use efficiency is low, even if the application rates of P fertilizer were made according to the soil and water research institute recommendations. These figures do not include the P input from manure, so the total P input could be higher. Most of the soils were sampled from cultivated fields that received regular superphosphate applications of 100–300 kg ha<sup>-1</sup> year<sup>-1</sup> for more than 40 years and additional, unknown rates of farmyard manure. In vegetable and field crops in the study area, the use of organic manure (in potato fields about 10 t ha<sup>-1</sup> year<sup>-1</sup>) is common (usually poultry manure) (Jalali 2005b). Some parts of the studied area have been irrigated with sewage effluent since 1970. The wastewater receives no prior treatment and the irrigated area with wastewater has been growing as sewage volume increases. Presently, farmers do not use any system at all, and fertilize according to experience (Jalali 2005b). Nearly all vegetables (including potato and garlic) growers in these areas apply more P fertilizer than the recommended rate. Framer surveys indicate that excessive P application is often up to two times the recommended rate in field crops. Phosphorous fertilizer is applied in autumn. Most of the fields are flood-irrigated using poorly managed irrigated systems, resulting in low irrigation efficiency (Jalali 2005b). The large amount and inadequate management of P fertilization coupled with a low irrigation efficiency are mainly responsible for the P accumulation in surface soils. This has resulted in environmental pollution and economic and natural resource wastage.

High nitrate concentrations are found in groundwater in some parts of the study area, the origin of which are indicated to be from agricultural fertilizer application (Jalali 2005b). The long-term, repeated application of P fertilizers and farmyard manure have



**Fig. 2** Frequency distribution of Olsen P in studied soils

resulted in a general increase in the high-P status of these calcareous soils. These soils are subject to P losses either by runoff or leaching. Phosphorus leaching can occur in sandy soils (Guertal et al. 1991; Weaver et al. 1988) and other types of soils with high P levels due to continuous P application (Heckrath et al. 1995). Field studies have shown that P losses by erosion, surface runoff, and leaching are greater when soil-test P values are above the agronomically optimum range (Beauchemin et al. 1998; Heckrath et al. 1995; Pote et al. 1996; Sims et al. 1998). The results from recent soil tests in Delaware showed that 92% of the agricultural soils tested from Sussex County are now optimum or excessive in soil-test P (Sims et al. 1998).

The results of soil-test P can be used to identify areas where P applications in fertilizers and manures should be controlled to protect water quality (Sibbensen and Sharpley 1997; Sims et al. 1998). Phosphorus losses in water leaching from disturbed soils were evaluated using 22 soils of studied area that had a wide range in soil-test P (unpublished data). The P concentration in the leachate ranged from 4.5 to 7.5 mg l<sup>-1</sup>. Thus, sub-surface pathways can play an important role in agricultural P losses in the Hamadan area that can decrease surface water quality.

Cadmium (Cd) is one of the heavy metals that can be potentially toxic to human health. There is an increasing concern over the use of Cd-containing P fertilizer for crop production because Cd uptake by plants can be one possible avenue of Cd entry into the human food chain through the consumption of plants directly or indirectly by man (Mortvedt 1996). Assuming that applications of single superphosphate contained an average of 350 mg Cd kg<sup>-1</sup> P (McLaughlin and Singh 1999), the amount of Cd added to the soils from P fertilizer applications (40 kg P ha<sup>-1</sup> or 200 kg ha<sup>-1</sup> as superphosphate) can be estimated to be about 14 g Cd ha<sup>-1</sup> yr<sup>-1</sup>. Cd accumulation in soil and Cd uptake from annually applied P fertilizers at the rate currently being used could be an environmental issue after long-term applications of P fertilizers. Recently, field experiments conducted in Australia have shown that increased chloride (Cl) content greater than 450 mg l<sup>-1</sup> in irrigation waters could have a high risk of producing crops with high Cd concentration (McLaughlin et al. 1997; Smolders et al. 1998; Weggler-Beaton et al. 2000). Other researchers have also reported that Cd and Cl can form soluble complexes that result in a decrease in Cd adsorption by soil minerals

**Table 2** Average crop yield, applied P-fertilizer and crop P-uptake in Hamadan province

Crop	Average crop yield (t ha <sup>-1</sup> ) <sup>a</sup>	Applied P-fertilizer (kg P ha <sup>-1</sup> ) <sup>b</sup>	Crop P-uptake (kg P ha <sup>-1</sup> ) <sup>c</sup>	Percentage of P-fertilizer applied taken by crop
Wheat	1.68	31	4.3 <sup>d</sup>	14
Barley ( <i>Hordeum vulgare</i> L.)	2.5	31	6 <sup>d</sup>	19
Corn ( <i>Zea mays</i> L.)	8.8	42	18.6 <sup>e</sup>	44
Potato	29	42	25 <sup>f</sup>	59
Sugar beet ( <i>Beta vulgaris</i> )	33	42	7.7 <sup>g</sup>	18
Tomato ( <i>Lycopersicon esculentum</i> )	34	42	15.6 <sup>h</sup>	37
Onion ( <i>Allium cepa</i> L.)	6.14	31	18 <sup>i</sup>	58
Other vegetables	7.7	42	23 <sup>i</sup>	55

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

<sup>b</sup> Recommended by 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)

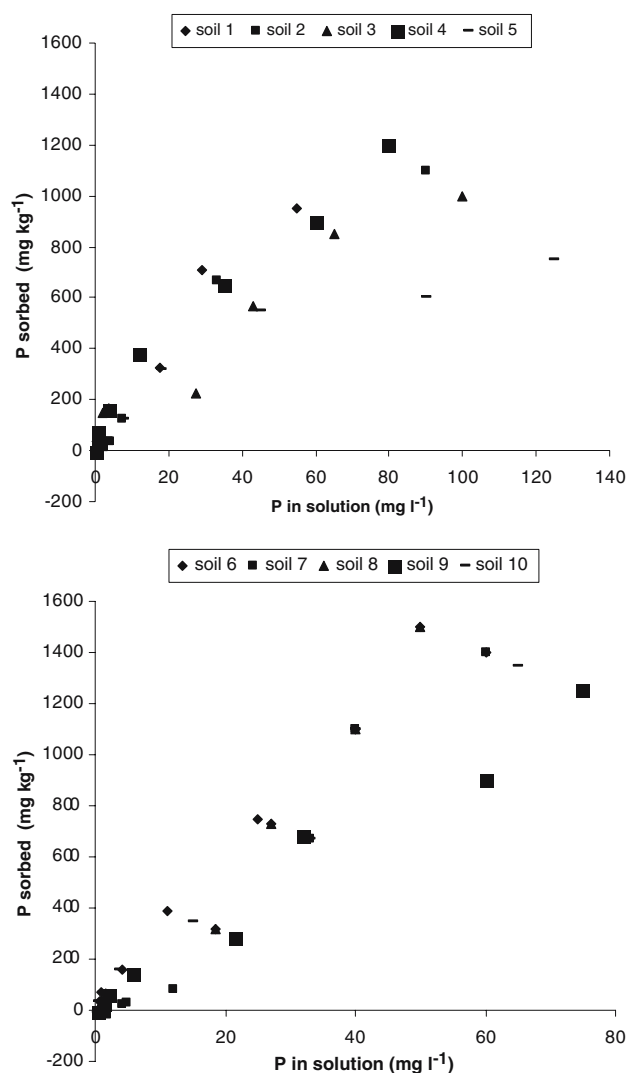
<sup>d, e, f, g, and h</sup> including grain and straw, grain and stover, tubers and vines, roots and tops, and fruit and vines, respectively

<sup>i</sup> Calculated based on 0.3% P uptake

and an increase in Cd uptake by plants (Garcia-Miragaya and Page 1976; Hirsch et al. 1989; Sparrow et al. 1994). The effect of Cl on Cd availability implies that use of irrigation water containing high Cl content with Cd-containing P fertilizers may result in increased Cd uptake by plants. Groundwater studies indicate that 8% of water samples used for irrigation in the studied area contains a Cl concentration above  $450 \text{ mg l}^{-1}$  (Jalali 2002).

The relationships between sorbed P and equilibrium P concentration for the studied soils are shown in Fig. 3. Phosphate sorption is used here to comprise all the processes (mainly surface adsorption and precipitation) resulting in removal of phosphate from the solution (Castro and Torrent 1998). The magnitude of P sorption exhibited by the different study soils varied. Two soil groups have been classified based on their maximum adsorption (Fig. 3). The first group, with maximum P adsorption less than  $1,200 \text{ mg P kg}^{-1}$ , included soils 1–5. The second group with maximum P adsorption, between 1,200 and 1,500 included soils 6–10. These soils have different P sorption capacities, therefore, the P application rates required to increase and maintain P concentration at a given level would probably be different.

Phosphorus sorption increased with increasing P concentration in all soils. The adsorption rate was high for small concentrations of added P. At a low rate of added P ( $4 \text{ mg l}^{-1}$ ), the amounts of P adsorbed were between 15 (62.5% of added P, soil 2) and  $37.5 \text{ mg kg}^{-1}$  (94% of added P, soil 1). At the high added-P rate ( $200 \text{ mg l}^{-1}$ ) however, the amounts of P adsorbed were 750 (62.5%, soil 5) to  $1,500 \text{ mg kg}^{-1}$  (75%, soil 8). This shows that a greater proportion of the added P is sorbed at low P concentrations. In calcareous soils, P sorption is greatly influenced by the adsorption and precipitation reactions at calcium carbonate surfaces (Freeman and Rowell 1981; Amer et al. 1985). Adsorption seems to predominate at P concentrations in solution less than about  $10^{-4} \text{ M}$  ( $3.1 \text{ mg l}^{-1}$ ) (Holford and Mattingly 1975b; Freeman and Rowell 1981; Hamad et al. 1992). Under these conditions, Fe oxides and the edge surfaces of the clay minerals provide P sorption sites of more affinity than  $\text{CaCO}_3$  (Holford and Mattingly 1975a; Pena and Torrent 1990). When P is added to a calcite suspension such that the P concentration in solution exceeds  $10^{-4} \text{ M}$  ( $\sim 3 \text{ mg l}^{-1}$ ) supersaturation with respect to insoluble Ca-P minerals cause a decrease in dissolved P content by precipitation (Freeman and Rowell 1981; Amer et al. 1985). In general, the amount of P needed to achieve this concentration is about  $8 \text{ mg l}^{-1}$  ( $80 \text{ mg kg}^{-1}$ ) (Fig. 3). Therefore, it could be expected that in the present



**Fig. 3** Phosphorus adsorption isotherms for studied soils

study, at a rate of less than  $8 \text{ mg l}^{-1}$  added P the sorption process is dominant, while above this value, the precipitation process prevails. Assuming  $2,500 \text{ t soil ha}^{-1}$  (calculated based on the top 20 cm of soil with a bulk density of  $1.25 \text{ g cm}^{-3}$ ), gives a required input of  $200 \text{ kg P ha}^{-1}$ . In fact, precipitation processes prevail when granular P fertilizers are applied to calcareous soils and large local P concentrations arise as a result (Olsen and Flowerday 1971).

There is an apparent correlation of the P sorption characteristics of the two groups of soils with the different organic matter content. The first group of five soils has the high organic matter (Table 1) and lower P sorption (Fig. 2) and the second group has low organic matter and higher P sorption. In general, organic matter in soils decrease P sorption by the anion replacement of  $\text{H}_2\text{PO}_4^-$  on adsorption sites and the

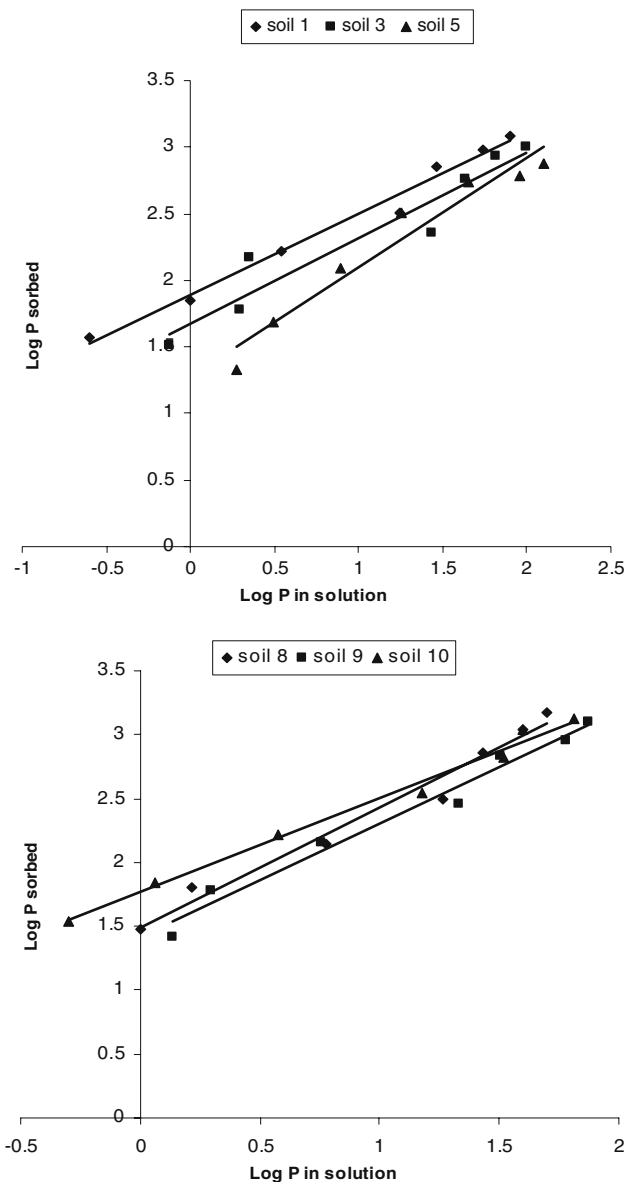
coating of Fe/Al oxides by humus to form a protective cover and reduce P sorption (Havlin et al. 1999).

Phosphorus sorption by the study soils is well described by the Freundlich equation (Fig. 4 and Table 3). The coefficients of determination ( $R^2$ ) ranged from 0.92 to 0.99 (Table 3). Other studies reporting representation of P sorption by soils with the Freundlich equation include Fitter and Sutton (1975), Mead (1981), Polyzopoulos et al. (1985), Yuan and Lucas (1982), Solis and Torrent (1989), Said and Dakermanji (1993) and Zhou et al. (1997). The Freundlich constants  $K_f$  and  $n$ , which represent the intercept and slope of the log-transformed sorption

isotherm, may be taken as measures of the extent of adsorption and the energy of adsorption, respectively. The exponent term ( $n$ ) in the Freundlich relationship describing solid phase P and solution P at equilibrium is more than one for most of the soils (Table 3). This indicates that the relationship is curvilinear and suggests that precipitation of P is controlling solution P concentrations in most of the soils (Bertrand et al. 2003). The Freundlich coefficient  $K_f$  ranged from 2 to 77 (Table 3). These values are relatively low compared with those found by Singh and Gilkes (1991) for the major soil types of south-western Australia, which varied from 1 to 1,681, but are in good agreement with those published by Bertrand et al. (2003) for alkaline soils from southern Australia, which varied from 1 to 151.

The amount of P sorbed at an equilibrium concentration of e.g.  $1 \text{ mg P l}^{-1}$  was between 88 and  $348 \text{ mg kg}^{-1}$  of soil. The SPR of the soils calculated from the Freundlich equation (Table 3) which is an estimate of P sorption potential (Jackman et al. 1997; Wang et al. 2000). Fox (1981) and Afif et al. (1993) indicated that this concentration is an adequate external P requirement for most crops. The value of SPR ranged from 4 to  $102 \text{ mg P kg}^{-1}$  for the Hamadan soils. The average SPR for the first group of soils ( $58 \text{ mg kg}^{-1}$ , samples 1–5) was higher than for the second group ( $37 \text{ mg kg}^{-1}$ , samples 6–10). In general, the SPR of these calcareous soils was less than reported for highly weathered soils ( $42\text{--}175 \text{ mg P kg}^{-1}$ ) in West Africa (Abekoe and Sahrawat 2001).

Phosphorus buffer capacity was obtained for each soil from the slope of the linear equation by plotting P sorbed against P concentration at equilibrium for the adsorption dominated part of the isotherm (up to  $8 \text{ mg l}^{-1}$ ) (Bertrand et al. 2003). The regression coefficient ( $r$ ) was  $>0.78$  for the determination of the PBC. Phosphorous buffer capacity of the soils varied from 16 to 123 and averaged  $58 \text{ l kg}^{-1}$  (Table 3), and was classified according to Moody and Bolland (1999). Their classification defines PBC between 10 and 20 as very low, 20–30 as low, 30–60 as moderate, 60–90 as high, and  $>90$  as very high. Amongst the ten calcareous soils, 30% exhibited a very low PBC, 30% had a moderate PBC, 20% had a high PBC and 20% were considered to have a very high PBC (Table 3). The results are within the range found by Bertrand et al. (2003) for 22 calcareous soils of Australia. They found that 36, 50 and 14% of soils exhibited a moderate, high and very high PBC, respectively. The PBC of a soil is its ability to moderate changes in the P concentration of the solution phase. Phosphorus buffer capacities can be related to both plant nutrition and environmental



**Fig. 4** The P adsorption isotherms as described by the linearised Freundlich equations in soils 1, 2, 4, 8, 9 and 10

**Table 3** Freundlich adsorption parameters and SPR and PBC of studied soils

	Soil no.	<i>n</i>	<i>K<sub>f</sub></i>	R <sup>2</sup>	SPR <sup>a</sup> (mg kg <sup>-1</sup> )	PBC <sup>b</sup> (l kg <sup>-1</sup> )
	1	1.64	77	0.98**	102	71
	2	0.85	8.6	0.93**	15	16
	3	1.58	47	0.92**	63	39
	4	1.46	60	0.98**	82	123
	5	1.22	19	0.95**	27	17
	6	1.26	57	0.97**	81	120
	7	0.62	2	0.97**	4	17
<sup>a</sup> Standard P requirement	8	1.06	31	0.97**	48	54
<sup>b</sup> P buffer capacity	9	1.13	26	0.98**	38	40
**Significant at <i>P</i> < 0.01	10	1.13	26	0.98**	38	40

pollution. The greater the PBC of the soil, the higher the P rate required to increase P concentration in the soil solution.

The PBC values can be used to calculate the proportion of added fertiliser-P that remains in the soil solution (Rowell 1994). The reciprocal of the PBC is the ratio of the amount of added P that remains in solution to the amount that becomes sorbed. For PBC values ranging from 16–123 l kg<sup>-1</sup> and assuming moist soil containing 0.3 l solution kg<sup>-1</sup> soil, the proportion of added P that remains in solution in the studied soils is 2–0.3 percent. Thus 98–99.7% of P applied to the soils is adsorbed or precipitated, of which only a fraction can be extracted by the Olsen P method. Also with time, applied P in a soil becomes increasingly less soluble either by diffusion smaller pores of the soil that are less accessible to extractants or by the P remaining on adsorption sites becoming more tightly bound as in the process of P mineral formation (Freeman and Rowell 1981; Bramley et al. 1992; Javid and Rowell 2002). Jalali (2006) found that on average 79% of applied P becomes non-extractable after 90 days in some calcareous soils in Iran. Javid and Rowell (2002) found that between 45 and 80% of the Olsen P in some Pakistani calcareous soils was no longer extractable after 100 days at 25°C. They concluded that a rapid decrease in Olsen P can occur in the field between the time of fertilizer P application and subsequent crop demand for strongly adsorbing soils. These soils can supply P to crops over long periods of time without P addition. The residual P provides the native P to crops in the coming year. The special value of residual P is probably related to its uniform distribution through the soil (Rowell 1994). After high levels of soil-test P have been attained, considerable time is required for significant depletion. For example, McCollum (1991) estimated that without further P addition, 16–18 years of cropping corn or soybeans would be needed to deplete the soil-test P content (Mehlich III method) of a Portsmouth (north eastern USA) soil (fine sandy over

sandy or sandy-skeletal) from 100 mg kg<sup>-1</sup> to the threshold agronomic level of 20 mg kg<sup>-1</sup>. Obviously, fertiliser-P recommendation schemes that fail to properly account for differences in P status and soil PBC among soils can have substantial economic consequences and surface and groundwater pollution.

## Conclusions

The level of available soil P should meet the demand of crops but should not be much higher than the optimum. The continual long-term application of P fertilizer and manures at levels exceeding crop requirements can raise soil-test P concentration above levels required for optimum crop yields. This study found that the P content of a high percentage of calcareous soils of the Hamadan area of Iran exceeded the optimal range for plant growth and can be attributed to overfertilization with P. Once soil-test P levels become excessive, the potential for P loss in runoff and drainage water is greater than any agronomic benefits of further P applications. Based on P sorption, two groups of soils were recognized in the study area: low P-sorbing soils that require low rates of P additions, high P-sorbing soils that initially need relatively large amounts of P addition. The residual soil P is expected to be greater in the second group of soils. For these soils, small rates of P may now be satisfactory for crops. Phosphorous fertilizer recommendation schemes that fail to properly account for differences in P status and soil PBC among soils could potentially have substantial economic consequences and cause surface and groundwater pollution.

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