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Relationships between phosphorus adsorption isotherms and properties of calcareous soils and determination of phosphorus fertilizer requirement from the isotherms

Veli UYGUR[1]* and **Tuba İNCE**[1]

[1]Iğdır University, Agricultural Faculty, Department of Soil Science and Plant Nutrition

Abstract

Phosphorus is one of the nutrient elements in soils having difficulties in the managements with some environmental consequences. Strong reactions with soil components such as precipitation with Fe (iron) and Al (aluminium) in acid soils and Ca (calcium) in alkaline soils rapidly reduce phosphorus availability to plants in soil solution. Phosphorus fertilizer suggestions relying solely on soil analysis have problematic aspects due to differences in phosphorus adsorption characteristics of soils. Thus, total of 71 surface layer (0-20 cm) soil samples were taken from 20 series of Atabey Plain, Isparta. Phosphorus adsorption isotherms of the soils were determined with the batch sorption technique by equilibrating 1.00 g soil samples with 20 mL of 0, 5, 10, 20, 30, 40, 60, and 80 mg P L^{-1} in 0.01 M $CaCl_2$ background solution. The conformation of the data to Freundlich model was tested by regression analysis. Fertilizer requirement (FR) of soils calculated from Olsen P and equilibrium concentrations of 0.2 and 0.11 mg L^{-1} of the isotherms. Paired-t test revealed that $FR_{0.2}$ values were significantly different than either FR calculated from Olsen P or $FR_{0.11}$. The current plant cover at soil sampling had an influence the calculated FR values and adsorption isotherm parameters. In general, negative fertilizer requirements were due to the agricultural lands with high fertilizer input history such as fruit orchards. It can be concluded that using adsorption isotherms, which consider soil P buffering capacity and P input management background, for calculating the P fertilizer requirement is suggested for environmentally and economically feasible farming in the region.

Key words: Freundlich isotherm, phosphorus requirement, soil properties, plant cover, principal component

Introduction

Phosphorus (P) is ultimately deficient essential nutrient element for plants due to the some soils properties especially pH, Ca, CaCO3 and clay (Turan and Horuz, 2012). Therefore, it should be carefully managed for ensuring high crop yield and quality and avoiding environmental consequences of excessive fertilization. Complex reactions of P with different soil components hinder to maintain its availability throughout growth season (Delgado et al. 2002; Uygur 2009). Nutrient supply, including P, to plant roots is largely induced by capacity and intensity factors of soils (Lindsay 1979, 2001). In other words the partitioning of the added fertilizer nutrient between solid and solution phases have detrimental role in P availability to plants. This partitioning is also sensitive to time and environmental conditions including soil characteristics (Huang 1998; Leytem and Mikkelsen 2005). The amount of plant available P should be kept at optimum level to grantee optimal crop performance (Grant et al. 2005) without posing any risk of environmental pollution. This has been mainly maintained via soil tests by supplying P up to critical level (25 mg kg^{-1} for Olsen-P). Fertilization above the critical level decreases the efficiency of P and cause accumulation of P in soils with some serious environmental consequences. As farmers in Turkey do not practice yearly soil analysis and apply same rate of fertilizer repeatedly, the P concentration in soils of Atabey Plain reached an Olsen-P level exerting environmental pollution risks. In contrast, there are some sites suffering from the inadequate P (Durgun 2016).

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*Corresponding author e-mail: vuygur@yahoo.com

This indicates that fertilizer recommendations need to be soil-specific and crop situations on scientifically sound-basis. Due to different physico-chemical properties of any particular soil can exert variation in the P buffering capacity. This means the quantities of P fertilizer needed to increase the soil solution P to a desired level for optimal or targeted crop yield are largely soil-specific. Phosphorus sorption isotherms could explain the partition of added fertilizer between soil solution and sorption sites. The P sorption isotherms are scientific and powerful tool for predicting the amount of P-required to maintain soil solution P about a level which plants perform optimal for maximum yield. Moreover, its usage for assessing P requirement is fast and efficient method (Fox and Kamprath 1970). On the other hand, it can be regarded as economically feasible and environmentally friendly due to application of the most exact amount of P for a specific goal (Kumar, 2015). This sort of fertilizer requirement prediction simultaneously takes in to account the factors determining the standard P requirement (SPR) such as pH, P fixing and buffering capacity (PBC) of the soil, including the residual effects of past fertilizations. It is generally accepted that an equilibrium P concentration of 0.2 mg L^{-1} in soil solution is suggested for optimal growth and crop yield (Beckwith 1965, Fox and Kamprath 1970). The external P required to reach about 0.2 mg L^{-1} P concentration in soil solution is therefore accounted for the standard P requirement (SPR) of a soil in question (Fox 1981; Duffera and Dobarge 1999; Jalali 2007; Hussein et al. 2010). However, there are some other equilibrium concentrations used in the literature. The range (0.03-0.25 mg L^{-1}) changes depending on the soil properties and plant type (Plenchette and Morel 1996; Adetunji 1997; Rashid and Iqbal 2011, 2012). On the contrary, adsorption/desorption isotherms enable to characterize not only plant available and labile soil-P but also the excessive and environmentally undesirable P levels (Jaszberenyi and Loch 1996).

In this context the approach of estimating P requirement of soil for crop production has been successfully employed in changing soils and agro-ecosystems throughout the world. Therefore the aims of this study were to compare the P requirement of calcareous soils from standard soil test and Freundlich isotherm at differing equilibrium concentrations and to reveal the effect of soil properties and land use type on standard P requirement values calculated by different methods and equilibrium concentrations.

Material and Methods

Site description

The Atabey Plain has total of 8,584 ha ag-land and situated between latitude of 30°37’30”-30°45’00” E and longitude of 37°52’30”-38°00’00” N. The soils of Atabey Plain have been formed on different physiographic units such hills and slopes, colluvium, alluvium, old stream beds, bajadas, lowlands, and young stream beds (Akgul et al. 2001). Holocene alluviums which were carried by water and gravitation forces from the surrounding Mesozoic limestones are common in the study area. There are 20 soil series, “a subdivision of a family and consisting of soils that are similar in all major profile characteristics” (Brady, 1990) in the study area under typical transition climate between the Mediterranean to continental types with 524.3 mm average annual precipitation, 12.4°C average temperatures, and about 1000 m elevation from the sea level (Akgul et al. 2001).

The soils are “Xeric” and “Mesic” regarding the moisture and temperature regimes, respectively, according to Soil Taxonomy (Akgul et al. 2001). Soil fertility is generally maintained with mineral fertilizers (50–200 kg N, 30–60 kg P, and 90-150 kg K_2O ha^{-1} per cropping season) and animal manure in a very limited area. Fertigation is very common practice in fruit orchards. Bordeaux mixture usage is also very common for winter pest management and Zn containing fungicides during the growth season in fruit orchards mainly sweet cherry, peach, plum and apple. Crop /land use type of the sampling nodes were: fallow/non cropping land (FA), corn (CR) wheat (WH), ground nut (GN), sun flower (SF), apple (AP), sweet cherry (SC), plum (Pl), pear (Pe), peach (PR), walnut (WN), forest mainly pine and/or juniper (PI), annual vegetables such as tomatoes (DO) and eggplant (AB).

Soil sampling

Completely random pattern in each soil series was established for soil sampling. The locations of sampling nodes were illustrated in Fig. 1. At least five surface (0–20 cm) soil sub-samples from each node were taken by means of a soil-sampling auger to get a representative composite soil samples. Total of 71 soil samples, at least three of them belongs to a soil series, were collected. Then soil samples were air-dried and passed through a 2 mm sieve for physico-chemical analyses, including the adsorption studies.

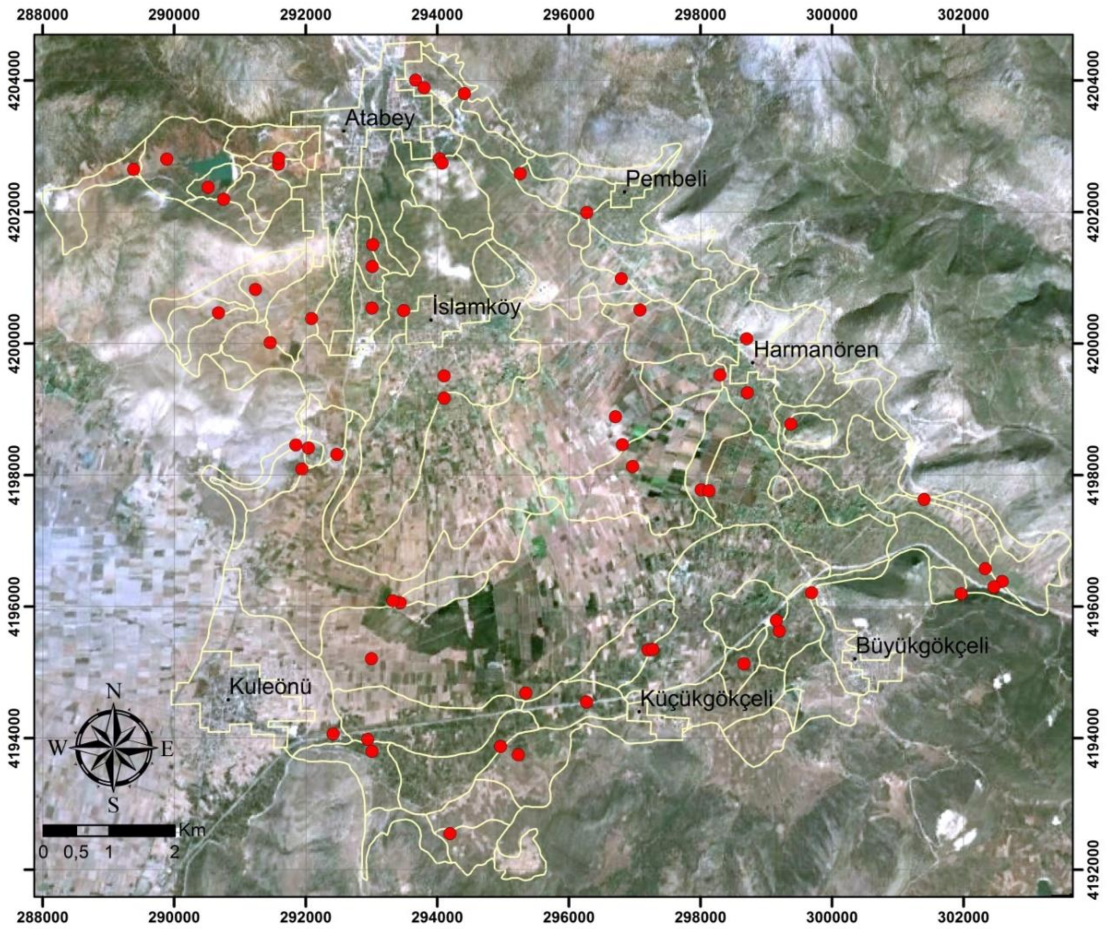

Figure. 1 Study area and sampling nodes

Soil Analyses

Physico-chemical properties of the soil samples were determined by following the procedures of common methods used for calcareous soils (Sparks, 1996): pH and EC in 1:2.5 (W/V) soil : distilled water suspension, organic matter with K_2CrO_7 wet oxidation method, calcium carbonate equivalent (CCE) by a manometric method, cation exchange capacity (CEC) by replacement of saturated Na on exchange sites for molar ammonium acetate at pH 7.0, plant available potassium (K), sodium (Na), magnesium (Mg) and calcium (Ca) by extraction with molar ammonium acetate, available P by extraction with 0.5 M $NaHCO_3$ at pH 8.5. The soil textures were determined by a hydrometer method (Gee and Bauder 1986),

Soils were digested with HNO_3:HCl mixture (3:1, V/V) for total iron (Fe), manganese (Mn) and zinc (Zn) determination (Hossner 1996). Free Mn oxides were solubilized with 0.1 M hydroxylamine hydrochloride (NH_3OHCl) at pH 3.5 (Shuman 1985; Parat et al. 2003). Residue from the removal of free Mn oxides were reacted with 10 mL 0.2 oxalate buffer for 4 h in dark (Shuman 1985) for extraction of amorphous Fe and Mn oxides and subsequently with 0.1 M ascorbic acid prepared in the oxalate buffer for crystalline Fe and Mn oxides. The Fe, Mn, and Zn concentrations of the obtained supernatants were determined by ICP-OES (Perkin Elmer, Optima 2100).

Adsorbed P fraction in soils was extracted with 0.1 M NaOH and 1 M NaCl (Kuo 1996) and the supernatant was wet combusted with $HClO_4$ + HNO_3 mixture (1/4, V/V) and total P in the digests were spectrometrically analysed by molybdate colour reagent (Murphy and Rilley 1962).

Adsorption studies and determination of fertiliser requirement

Scoops of 1.000 g soil samples in triplicates were equilibrated with 20 mL of 0, 5, 10, 20, 30, 40, 60, 80 mg L^{-1} P containing solutions prepared in 0.01 M $CaCl_2$ background solution. After an equilibrium time of 24 h the supernatants were obtained by means of centrifugation at 3000 rpm for 10 minutes. If necessary the supernatant was filtered through Whatman 42 filter paper. Then the P concentration of equilibrium solution was spectrometrically determined by ascorbic acid method at 880 nm wavelength (Murphy and Rilley 1962). The adsorbed P fractions by soil samples were calculated from the equation given below:

$$\boldsymbol{Si} = \frac{(\boldsymbol{Co} - \boldsymbol{Ce}) \times \boldsymbol{V}}{\boldsymbol{W}}$$

where *Si* the amount of P sorbed by unit mass of soil sample (mg kg^{-1}), *Co* the initial P concentration (mg L^{-1}), *Ce* equilibrium P concentration (mg L^{-1}) and *W* soil weight (g) in suspension. Then the sorption and equilibrium concentration data were fitted to modified log-based Freundlich equation as fallow:

$$\text{Log}\,(Sm) = \text{Log}\,K_f + n \log C_e$$

where *Sm* is modified P sorption (available P + NaOH extractable P + Si), *Kf* is coefficient related to intercept at “0” equilibrium concentration and *n* is the slope of the isotherm. Available-P and NaOH-P were included into the calculated sorption values unless otherwise 0.01 M $CaCl_2$ extracted P results in negative sorption data that reduced the determination coefficient of the regression line and it was not possible to reasonably evaluate sorption isotherms between 0 and 5 mg L^{-1} initial P concentrations.

The log Sm values were calculated from the sorption isotherm of each soil for 0.2 and 0.11 mg L^{-1} equilibrium concentration and then the Olsen and NaOH-P were subtracted from the calculated *Sm* to compute the isotherm based FRs. Soil test based FR calculated from the difference of upper limit of adequate P level (25 mg kg^{-1}) and soil test value.

Statistical analyses

The physico-chemical properties of the soil were tested for normal distribution. If necessary the data were transformed to obtain the most possible normal distribution. Then the relationships between the fertilizer requirements (FRs) calculated by varieties of the methods and soil properties were revealed through Pearson correlation analysis. The difference between FRs obtained by different methods were compared by paired *t* test. Then the normalised data set were used in principal component analysis (PCA) in order to reveal the possible roles of soil physico-chemical properties in determination of FRs. Factor analysis, principal component extraction with varimax rotation, was performed in SPSS 17.0 for Windows (Berkman and Reise 2012).

Result and Discussion

Soil characteristics

Descriptive statistics of the experimental soils were given in Table 1. The soil texture ranged in a very large scale from clay to sand. The variation in the texture reflects the differences in pedotranfer function mainly related to physiographic units that soil formed on Holocene alluviums originating from the surrounding Mesozoic limestone (Akgul et al. 2001). Texture plays a preeminent role in adsorption phenomena in soils by influencing the surface area. The studied soils were slightly acidic to alkaline in reaction, where the pH values measured in water suspension was varied from 6.78 to 8.04. The range of CCE was 0.66% to 41.5% as a result of calcareous parent material and dominant calcification soil processes in soil forming under semiarid climate. The soils were different in organic matter content and majority of soils highly rich in available phosphorus. There are extreme variations in terms of sesquioxides fractions in soils. NaOH extractable total P of the soils also had considerable variation mainly depending on the fertilization background of the sampling field which is closely related to the cultivated plant.

Table 1. Descriptive statistics of physico-chemical properties of the soil samples (Durgun, 2016)

Parameters	Min	Max	Mean	Std. Err	Variance	Scewness*		Kurtosis*	
TZn (mg kg^{-1})	27.28	90.51	60.74	1.284	117.1	-0.120	-0.120	1.810	1.810
OM (%)	0.510	6.94	2.067	0.116	0.949	2.224	-0.121 a	8.625	1.452a
CCE (%)	0.660	41.53	11.13	1.274	115.2	1.177	-0.272 a	0.555	-1.175a
CEC (cmol kg^{-1})	11.2	62.93	33.68	1.247	110.5	0.573	0.106 b	0.342	0.115b
pH (1:2.5)	6.78	8.03	7.687	0.034	0.084	-1.563	-1.563	1.691	1.691
EC (1:2.5, dS cm^{-1})	105.2	762	294.6	14.27	14450	1.027	-0.192 a	2.062	-0.163a
Ca (cmol kg^{-1})	6.90	42.0	25.32	0.954	64.6	-0.385	-0.385	-0.157	-0.157
K (cmol kg^{-1})	0.41	3.60	1.589	0.095	0.636	0.864	-0.015 a	-0.092	-0.567a
Mg (cmol kg^{-1})	1.20	15.84	5.485	0.368	9.630	1.138	-0.158 a	1.111	-0.256a
Na (cmol kg^{-1})	0.05	2.15	0.610	0.032	0.070	2.318	-0.518 b	16.14	5.348b
P (mg kg^{-1})	2.50	368	43.19	6.289	2808	3.998	-0.048 a	20.95	0.289a
NaOH-P (mg kg^{-1})**	26.7	360.0	99.05	7.129	6308	1.794	-0.049a	4.115	0.110a
Sand (g kg^{-1})	5.70	694.5	384.9	19.39	26695	-0.181	-0.181	-0.425	-0.425
Silt (g kg^{-1})	118	667	247.4	11.37	9188	1.450	0.790 b	3.931	1.004b
Clay (g kg^{-1})	147	703.6	367.7	14.87	15708	0.584	0.157 b	0.159	-0.264b
MnOx (mg Mn kg^{-1})	53.0	239	154.3	5.159	1890	-0.035	-0.035	-0.408	-0.408
AMnOx (mg Mn kg^{-1})	8.00	3317	134.9	45.70	148267	8.290	0.523 a	69.46	8.467a
TMnOx (mg Mn kg^{-1})	191	3652	499.6	54.45	210513	5.621	-0.382 a	34.83	0.562a
AFeOx (g Fe kg^{-1})	0.666	8.44	2.25	0.177	2220.2	2.290	0.651 a	5.870	0.571a
TFeOx (g Fe kg^{-1})	8.57	28.49	17.60	0.450	14393	0.018	0.018	0.136	0.136

* a log and b square root transformation were performed to approximate normal distribution. CEC cation exchange capacity, CCE calcium carbonate equivalent, TZn total zinc, MnOx free Mn oxides, AMnOx amorphous Mn oxides, TMnOx total Mn oxides, AFeOx amorphous Fe oxides, TFeOx total Fe oxides. Standar error for Scewness is 0.285 and for kurtosis 0.563. ** the data were adapted from Durgun (2016) besides this parameter

Adsorption isotherms

The Freundlich isotherm parameters of the experimental soils were given in Table 2. As the sorbed P (Si) calculated from the equilibrium P concentration for respective initial concentrations used, the determination coefficient of the isotherm for some soil samples were highly poor. The available P and NaOH-P were included in the Si value and the determination coefficient were improved to a level satisfactorily describing the sorption processes in soils. It was then the determination coefficient of the isotherms reached 0.818 and 0.99 ranges. The main reason for such behaviour was likely to be related to simultaneous occurrence of both adsorption and precipitation reactions and excessive P fertilization (Table 1) in those soil samples. However both reactions can be described, to some extent, by sorption isotherms (Uygur 2009; Veith and Sposito 1977).

The log Kf coefficient of the isotherms ranged between 1.956 (FA7) and 4.113 (PI1) whereas the slope of the isotherm between 0.118 and 1.721. Log Kf values up to 1.87 (Jalali 2007), 2.05 (Uygur 2009), 2.18 (Bertrant et al. 2003) and 3.23 (Singh and Gilkes 1991) were reported in the literature. Our Kf values are considerably higher than those reported in the abovementioned literature due to inclusion of Olsen P and NaOH-P which resulted in upward shift up to 1.48-2.83 log units. As these relatively mobile fractions subtracted from the calculated Kf the data are highly similar.

The *n* parameter of the Freundlich isotherm is generally smaller than 1 but the adsorption sites on soil colloids were likely to be near the maximum adsorption due to excessive fertilization of some experimental soils. For this reason the added P in the batch sorption was precipitated and the slope become over one. Uygur (2009) similarly reported that the *n* value for calcareous soils were 0.50-0.85. However, those soils had relatively poor P fertilization history.

Fertilizer requirement

The FR calculated from Olsen-P concentration of soils ranged between -343 to 22.5 mg P kg^{-1} with an average of -18.04 mg kg^{-1} (Table 3, 4). The results indicated that over fertilization in 40 soils have being practiced and the available P concentration of the soils were over upper limit of sufficiency level (25 mg kg^{-1}). It can be also said that these soils show differing degrees of environmental risk of eutrophication nearby surface or ground water sources. Olsen P show readily extractable amounts of P with 0.5 M NaHCO$_3$ however it does not provide sufficient information about the magnitude of potentially plant available but non-NaHCO$_3$ extractable P forms and P buffering capacity (PBC) of soils. Thus, FR computed from the sorption isotherms considers PBC and it can be regarded as soil-specific. The FR of the soils calculated from the fitted Freundlich equation can be treated as an estimate of P sorption potential (Jackman et al. 1997; Wang et al. 2000). It was pointed out that the FR at 0.2 mg P L^{-1} in soil solution (FR$_{0.2}$) is sufficient FR for most crops (Fox and Kamrath 1970; Fox 1981; Afif et al. 1993), even in calcareous soils (Jalali 2007). However there are very large range of equilibrium P concentration used for calculating the FRs for changing soil and crops in the literature (Ylihalla 1991; Rashid and Iqbal 2011, 2012). Thus, 0.11 and 0.2 mg L^{-1} were used in this study due to very large maximum adsorption capacity of calcareous soils. On the other hand, the negative values obtained for FR$_{0.2/0.11}$ in this study can be related to excessively practiced P fertilizer in soil management. The average FR$_{0.2}$ value was 82.4 mg kg^{-1} with a range of -462 to 860 mg kg^{-1} (Table 3, 4). There are total of 29 negative FR$_{0.2}$ values in the soil samples. This indicated that additional 11 soil samples need extra P fertilization to reach 0.2 mg L^{-1} equilibrium concentration comparing to FR calculated from the Olsen-P test. FR$_{0.11}$ which may be used for low P requiring crops had an average of -1.536 mg kg^{-1} which varied from -505 to 795 mg kg^{-1}. FR$_{0.11}$ indicated that 41 soil samples show negative fertilizer requirement (Table 3, 4). Using 0.2 mg L^{-1} equilibrium concentration resulted in 29 soil samples with negative FR$_{0.2}$ between -0.89 and -462.8 mg kg^{-1} (Table 3). These values indicate that some of the soils have previously been exposed to excessive phosphorous fertilizer, whereas some soils have extremely high phosphorus adsorption capacity.

Table 2. Log-based Freundlich adsorption parameters of soil samples

Soil No*	n	Log Kf	R^2	Soil No*	n	Log Kf	R^2
SC1	0.3112	2.4501	0.931	SC9	1.2385	2.9212	0.980
SC2	0.3662	2.2154	0.966	Pl2	1.1341	2.8670	0.961
CR1	1.0792	2.9501	0.989	FA9	0.9391	3.4385	0.869
SC3	0.5867	3.0276	0.978	FA10	0.6931	3.1939	0.910
WN1	0.4500	2.3300	0.920	PE2	1.0229	3.3066	0.950
PO	0.8970	3.0088	0.906	PI1	1.7212	4.1125	0.830
SF	0.2977	2.4223	0.904	PI2	1.1681	3.5233	0.942
SC4	1.0024	3.0565	0.907	PI3	0.9904	3.3803	0.881
FA1	0.4480	2.3148	0.899	SC10	0.7613	2.5838	0.950
PR1	0.3411	2.3716	0.916	FA11	0.8569	2.8808	0.903
SC5	1.0168	2.9512	0.934	FA12	0.5954	1.9611	0.918
PR2	0.3806	2.2677	0.977	ALM	0.9170	2.9592	0.960
SC6	0.4373	2.2930	0.878	FA13	0.8655	2.9412	0.976
AP1	0.1910	2.6973	0.872	FA14	0.9669	3.1260	0.818
DO	0.3998	2.2459	0.879	FA15	0.8969	3.1723	0.909
SC7	1.1062	2.8938	0.906	CR2	0.2843	2.4844	0.966
PR3	1.0706	2.8853	0.951	FA16	0.9409	3.2527	0.971
FA2	0.9907	2.9348	0.957	WH4	0.9848	2.8532	0.990
WH1	0.5022	2.3927	0.962	WY	0.3070	2.3636	0.973
WH2	0.9084	3.2406	0.920	AP4	0.8781	3.0064	0.936
WH3	1.2190	3.4912	0.867	SC11	0.5250	2.0400	0.919
FA3	1.1005	3.0590	0.908	FA17	1.0348	2.7402	0.967
AP2	1.0520	3.3461	0.874	WH5	0.8802	3.0654	0.973
WN2	0.2857	2.4477	0.915	AP5	0.3551	2.3113	0.932
FA4	0.3613	2.3424	0.929	PR5	1.0611	2.9322	0.897
AB	0.4214	2.3020	0.978	SC12	0.3457	2.3480	0.902
AP3	0.9181	2.9615	0.982	CR3	0.3740	2.5850	0.955
GN	0.3368	2.3940	0.963	CR4	1.5637	2.6149	0.929
SC8	0.9721	2.9462	0.937	FA18	0.3223	2.3488	0.975
FA5	0.5825	2.0589	0.963	FA19	0.7205	3.1157	0.945
Pl1	1.1380	2.7297	0.952	WH6	0.9938	3.0646	0.878
Pe1	0.3802	2.2857	0.984	PR6	0.1180	3.0657	0.938
PR4	0.7715	2.5300	0.843	WN3	0.4864	2.3814	0.989
FA6	0.9298	2.8804	0.956	SC13	1.5088	2.5987	0.939
FA7	0.6572	1.9563	0.862	FA20	1.0854	3.3754	0.882
FA8	1.4004	3.5757	0.923				

* Different letters indicate plant cover at soil sampling and the numbers are sample number for the respective cover plant. SC sweet cherry, CR corn, WN walnut, PO poplar, SF sun flower, FA fallow/no cover plant, PR peach, AP apple, DO tomatoes, WH wheat, AB eggplant, GN ground nut, Pl plum, PE pear, PI forest, ALM almond, and WY wine yard.

Table 3. Fertilizer requirement of soil samples calculated by differing methods

Soil No*	FR** (mg kg^{-1})	FR$_{0.2}$** (mg kg^{-1})	FR$_{0.11}$** (mg kg^{-1})	Soil No*	FR (mg kg^{-1})	FR$_{0.2}$ (mg kg^{-1})	FR$_{0.11}$ (mg kg^{-1})
SC1	-22.83	-64.95	-93.95	SC9	-44.92	-24.25	-83.68
SC2	-30.67	-63.45	-81.35	PI5	-62.00	-58.52	-116.93
CR1	-20.42	-48.21	-122.81	FA9	17.92	523.55	263.48
SC3	1.92	182.71	60.10	FA10	15.08	338.50	164.77
WN1	-16.08	-27.68	-52.12	Pe2	16.33	350.77	172.16
PO	0.92	129.65	29.68	PI1	22.50	781.23	259.66
SF	-85.50	-81.12	-107.82	PI2	18.50	455.53	199.69
SC4	14.17	122.58	20.31	PI3	20.33	407.44	189.62
FA1	-88.33	-135.24	-158.82	SC10	14.50	75.41	34.24
PR1	-6.42	19.04	-6.02	FA11	-9.92	31.99	-44.71
SC5	-2.25	86.06	6.83	FA12	21.92	-0.89	-11.39
PR2	-4.17	13.41	-7.02	ALM	4.58	94.74	6.94
SC6	-18.50	-14.33	-36.67	FA13	-25.75	70.91	-16.69
AP1	-63.75	-58.47	-97.99	FA14	10.50	222.21	98.46
DO	-10.75	-36.49	-56.17	FA15	8.17	280.22	134.54
SC7	-36.58	-140.00	-203.86	CR2	-10.08	7.46	-22.71
PR3	-41.75	-25.45	-90.24	FA16	-17.25	213.47	44.17
FA2	6.25	128.01	49.93	Wh4	-43.75	-131.86	-196.89
Wh1	18.42	66.29	37.75	WY	-68.17	-94.26	-117.89
Wh2	10.75	318.56	149.58	AP4	11.33	188.17	87.32
Wh3	13.25	369.56	144.15	SC11	-1.67	-16.77	-29.45
FA3	-44.92	40.28	-53.66	FA17	-20.00	-31.26	-79.22
AP2	4.58	357.87	167.38	Wh5	2.83	196.67	81.32
WN2	-1.67	21.72	-6.07	AP5	-17.42	-22.58	-44.69
FA4	-19.92	0.59	-23.30	PR5	-31.58	2.09	-70.74
AB	5.67	3.27	-19.38	SC12	-13.58	-52.85	-76.70
AP3	3.67	120.68	32.49	CR3	-343.00	-462.80	-505.00
GN	11.33	41.41	15.14	CR4	-111.42	-262.89	-283.09
SC8	-7.50	73.79	-7.65	FA18	18.92	46.80	23.51
FA5	13.58	-17.34	-30.52	FA19	-2.83	275.86	132.62
PI4	-18.75	-69.72	-112.14	Wh6	-0.33	141.74	36.75
Pe1	6.92	-5.46	-26.74	PR6	6.25	860.52	795.00
PR4	-191.25	-348.36	-384.53	WN3	-2.75	-22.18	-49.93
FA6	-20.50	34.90	-37.59	SC13	-67.42	-150.33	-171.13
FA7	10.75	-43.19	-53.39	FA20	17.50	341.89	144.41
FA8	16.00	323.73	99.63				

* Different letters indicate plant cover at soil sampling and the numbers are sample number for the respective cover plant. SC sweet cherry, CR corn, WN walnut, PO poplar, SF sun flower, FA fallow/no cover plant, PR peach, AP apple, DO tomatoes, Wh wheat, AB eggplant, GN ground nut, Pl plum, Pe pear, PI forest, ALM almond, and WY wine yard. ** FR Olsen P requirement, FR$_{0.2}$ and FR$_{0.11}$ are fertilizer requirement from 0.2 mg L^{-1} and 0.11 mg L^{-1} equilibrium P concentration of the Freundlich isotherm.

The FR determination of soils from the adsorption isotherm considers fertilization history of any field in question the excessive fertilization practices can also be quantified. Roy and De Datta (1985) found that the soil fertilizer requirement for 0.2 mg L^{-1} equilibrium solution was 160-540 mg P kg in heavy textured soils with differing clay mineralogy. These results are particularly similar to experimental soils with high adsorption capacity or high P buffering capacity. Mihoub et al. (2016) reported FR$_{0.2}$ values as small as 57.4 and 33.4 mg P kg^{-1} for light textured soils and their FR$_{0.2}$ increased along with the $CaCO_3$ addition up to 106 and 93.6 mg kg^{-1}. Indeed the higher clay and carbonate content can result in higher FR$_{0.2}$ values, as observed in this study. FR$_{0.2}$ calculated for calcareous soils with relatively lower CCE and clay contents showed a range from 4 to 102 mg kg^{-1} (Jalali 2007) which is much smaller than the maximum FR$_{0.2}$ value in this study. The soils of the Atabey plain have formed on calcareous parent materials therefore contain CCE up to 41.53% (Table 1) as well as very high clay content (max 703.6 g kg^{-1}). These extreme conditions promote the adsorption by soil clay minerals and carbonate minerals and cation exchange sites supply enough Ca (Table 1) to scavenge the added P as Ca precipitates (Uygur and Karabatak 2009).

Table 4. Some descriptive statistics for calculated fertilizer requirements

Parameters		FR	FR$_{0.2}$	FR$_{0.11}$
Mean		-18.04	82.40	-1.536
Std. error		6.299	26.00	19.27
Median		-2.750	21.70	-16.69
Mod		-44.92[a]	-462.8[a]	-505.0[a]
Minimum		-343.0	-462.8	-505.0
Maximum		22.50	860.5	795.0
%	5	-97.57	-195.4	-235.6
	10	-66.69	-124.3	-151.6
	25	-22.83	-36.49	-79.22
	50	-2.750	21.72	-16.69
	75	10.75	188.2	60.10
	95	19.48	482.7	223.7
	100	22.50	860.5	795.0

a. There are more than one mod values. The smaller one is shown.

The relationships between Freundlich parameters and the soil properties of P FRs calculated by different methods are given in Table 5. The Freundlich *n* parameter, the slope of the linear isotherm, indicating the intensity of adsorption did not give any significant correlation with any of the soil properties. The higher the slope in this case, the more phosphorus added to the surface reacts with or indicates that it has precipitated as a solid phases. The Freundlich *Kf* parameter showed the highest correlation with FR$_{0.2}$ (0.734**) and followed by FR$_{0.11}$ (0.550**) and FR (0.314**) (Table 5). In previous studies, fertilizer requirements corresponding to different equilibrium concentrations of isotherm were tested by growing plants. It has been determined that a substantial portion of the studies carried out can yield a fraction of 80-95% of the maximum yield with fertilization practiced at an equilibrium concentration of 0.2 mg L^{-1}. In this context, Fox and Kamprath (1970) found that 0.2 mg L^{-1} for millet; Plenchette and Morel (1996) 0.148 and 0.11 mg L^{-1} for barley and soybean; Adentuji (1997) 0.19 mg L^{-1}; Jalali (2007) 0.2 mg L^{-1}; Rashid and Iqbal (2011) determined 0.22 mg L^{-1} and Rashid and Iqbal (2012) 0.25 and 0.23 mg L^{-1}. In this study, the *Kf* parameter gives information about the amount of P previously adsorbed by the soils. The aforementioned reports are in line with our findings. *Kf* parameter showed significant positive correlations with the amount of free Mn oxides (MnOx) (0.287*) and the TFeOx (0.373**) contents of soils; whereas there were negative correlations with the Olsen-P (-0.392**) and the ammonium acetate extractable K (-0.244*) due to possible significant contribution of NaOH-P to *Kf* values.

Significant positive correlations were found between FR value calculated from Olsen test and clay content (0.265*) and MnOx (0.377**) of soils; adsorbed P (-0.664**), available K (-0.295*), TZn (-0.234*), EC (-0.235*), organic matter (-0.482**), and available P (-0.279*). FR$_{0.2}$ values were negatively correlated with K (-0.272*), Olsen-P (-0.719**) and NaOH-P (-0.495**); positively with clay content (0.243*), free MnOx (0.291*) and TFeOx (0.313**). In general FR$_{0.2}$ and FR$_{0.11}$ showed relations to similar soil parameters except for clay and TFeOx which were only correlated with FR$_{0.2}$ (Table 5). The relatively high correlation coefficient between NaOH-P and FR$_{0.11}$ indicates that the FR value is induced by increasing the amount of P retained by the oxide minerals. The NaOH-extractable inorganic P fraction is regarded as a moderately labile fraction (Tiessen et al. 1984) or low-energy-bound P in soils. Thus, it can have very high influence on the FRs calculated by any means.

When the relationships between the FRs values compared, the FR values calculated from the Olsen-P gave higher correlations with the FR calculated from decreasing equilibrium solution (FR$_{0.2}$ 0.624**, FR$_{0.11}$ 0.692**). The FR values calculated from the isotherms were highly correlated in fact their calculation from the same equation (0.945 **).

The available P contents of soils were positively related with soil organic matte r (0.337**), EC (0.325**), K (0.376**), Mg (0.276 *), NaOH-Pt (0.635**); whereas negatively with AMnOx (-0.351**), MnOx (-0.389**) and TFeOx (-0.298*). This indicated that the higher clay minerals, free Mn oxides, and total Fe enhancing P adsorption resulted in the smaller availability of P; organic matter and freshly precipitated amorphous MnOx on which P adsorbed as moderately mobile NaOH extractable fraction (Tiessen et al. 1984; Uygur and Karabacak 2009) mediated the plant availability in the soils. On the other hand, the organic matter especially humic/fulvic acids and low molecular organic acids are to compete with P for adsorption sites in favour of organic acids and/or to retard the reaction of fertilizer P with soil components (Moradi et al. 2012; Taghipour and Jalali 2013; Wang et al. 2016).

Table 1. Relationships between the Freundlich parameters and the calculated fertilizer requirements and soil properties (N 71)

Variable	n	Kf	FR	$FR_{0.2}$	$FR_{0.11}$	TZn	OM	CCE	CEC	pH	EC	Ca	K
n		0.620**	-0.024	0.196	0.066	0.200	0.111	0.055	0.142	0.055	0.062	0.135	-0.019
Kf	0.620**		0.314**	0.734**	0.550**	0.001	-0.063	-0.189	0.095	-0.196	-0.055	0.037	-0.244*
FR	-0.024	0.314**		0.624**	0.692**	-0.234*	-0.482**	-0.169	-0.002	0.100	-0.279*	0.065	-0.295*
$FR_{0.2}$	0.196	0.734**	0.624**		0.945**	-0.062	-0.221	-0.168	0.046	-0.176	-0.207	0.051	-0.272*
$FR_{0.11}$	0.066	0.550**	0.692**	0.945**		-0.081	-0.269*	-0.093	0.005	-0.018	-0.189	0.081	-0.246*
Olsen P	0.055	-0.392**	-0.785**	-0.719**	-0.697**	0.200	0.337**	0.226	-0.087	0.213	0.325**	-0.070	0.376**
NaOH-P	-0.202	-0.205	-0.664**	-0.495**	-0.534**	0.103	0.257*	-0.216	-0.312**	-0.247*	0.065	-0.459**	0.004

	Mg	Na	Olsen P	NaOH-P	Sand	Silt	Clay	MnOx	AMnOx	TMnOx	AFeOx	TFeOx
n	0.066	0.088	0.055	-0.202	-0.095	0.069	0.068	0.080	0.072	0.045	0.115	0.195
Kf	-0.118	0.114	-0.392**	-0.205	-0.182	0.019	0.205	0.287*	-0.024	-0.103	0.094	0.373**
FR	-0.152	-0.179	-0.785**	-0.664**	-0.230	0.025	0.265*	0.377**	-0.233	0.094	-0.009	0.217
$FR_{0.2}$	-0.211	-0.021	-0.719**	-0.495**	-0.199	-0.015	0.243*	0.291*	-0.183	-0.155	-0.038	0.313**
$FR_{0.11}$	-0.181	-0.052	-0.697**	-0.534**	-0.162	-0.017	0.195	0.260*	-0.219	-0.110	-0.073	0.229
Olsen P	0.276*	0.202		0.635**	0.218	0.107	-0.351**	-0.389**	0.254*	0.037	0.085	-0.298*
NaOH-P	0.068	0.326**	0.635**		0.430**	-0.192	-0.425**	-0.329**	0.233	-0.115	0.170	-0.218

Significant at * $P < 0.05$, ** $P<0.01$ (two-tailed). CCE calcium carbonate equivalent, TZn total zinc, MnOx free Mn oxides, AMnOx amorphous Mn oxides, TMnOx total Mn oxides, AFeOx amorphous Fe oxides, TFeOx total Fe oxides. FR Olsen P requirement, $FR_{0.2}$ and $FR_{0.11}$ are fertilizer requirement from 0.2 mg L^{-1} and 0.11 mg L^{-1} equilibrium P concentration of the Freundlich isotherm.

The amount of phosphorus that can be extracted with NaOH in the soil samples were a function of OM (0.257*), Na (0.326**), Olsen P (0.635**) and sand (0.430 **) in a positive way; CEC (-0.312**), pH (-0.247*), Ca (-0.456**), clay (-0.425**) and MnOx (-0.329**) in a negative way. Interestingly, soil properties which cause an increase in the amount of NaOH-P were factors that may cause P adsorption to decrease or to be weaker in the soil. On the contrary, in the soil with high exchangeable Ca concentration, this phosphorus fraction declined considerably, in which case the precipitation reactions of phosphorus with Ca become dominant. The majority of fertilizer P can precipitate as poorly soluble Ca phosphates in low-P-containing calcareous soils (Delgado and Torrent, 2000) and even high P containing soils (Uygur and Karabacak 2009). The contribution of exchangeable Ca ions to Ca phosphate precipitates was higher than that of $CaCO_3$ (Akinremi and Cho 1991a, b; Tunesi et al. 1999) but the role of carbonates in replenishing Ca in either soil solution or exchange sites and calcification process dominated soil formation should not be discarded.

Significant correlation of both clay content and exchangeable Ca concentrations could be an indication of P adsorption on to clay surfaces through Ca bridges (Tan 2011) which in turn may decrease this fraction. The significant negative correlation between MnOx and TFeOx and NaOH-P indicates that Mn and Fe oxides strongly bind P and P adsorbed such mechanism cannot be extracted by NaOH. Because these oxide fractions consist of the occluded P which in turn virtually none extractable or plant available (Walker and Syers 1976).

Phosphorus fertilization requirements of soils calculated by different methods were compared with paired *t* test (Table 6). As seen in Table 6, the *t* test between the values of FR and $FR_{0.11}$ shows no significant difference. On the other hand, $FR_{0.2}$ values are significantly higher than the values calculated by other methods.

Table 6. Paired samples t-test of the phosphorus requirements of soils calculated by different methods

	Paired Differences							
				95% confidence interval of the difference				
Pairs	Mean	Standard deviation	Standard error of means	Alt	Üst	t	df	P (2-tailed)
FR – $FR_{0.2}$	-100.4	190.4	22.59	-145.5	-55.38	-4.446	70	0.000
FR – $FR_{0.11}$	-16.51	131.2	15.58	-47.57	14.56	-1.060	70	0.293
$FR_{0.2}$ – $FR_{0.11}$	83.93	84.19	9.99	64.01	103.9	8.400	70	0.000

Chemometric relations between FRs and soil properties

Principal component (PC) analysis isolates underlying coherence in the relationships shown between the different FR determination methods as a function of other measured soil parameters. Total of 6 components were extracted using the correlation matrix with varimax rotation routine in SPSS environment. The rotated components (PC1-6) with eigenvalue above one explained individually 18.822, 16.356, 13.550, 11.450, 8.279, and 7.633% of variance, respectively, with 76.089% of total variance in the soils (Table 7). 4 out of the 6 routinely extracted components corresponded closely to clear conceptual groupings of the detrimental soil properties influencing the behaviour of the soils whereas 2 of them were likely to be related to the respective FRs with some soil attributes: PC 1 represents CEC, EC, Ca, K, Na, texture fractions, free MnOx, TMnOx and AFeOx; PC 2 Kf, FRs, OM, Olsen-P, free MnOx; PC 3 mainly oxide fractions, CCE, TZn and Mg; PC 4 and 6 variety of soil properties; PC 5 isotherm parameters, $FR_{0.2}$, OM and Na (Table 8). The PCs may extract, to some extent, information about possible effects of soil properties on FRs in the soils.

Table 7. Explained variations by original and rotated principal components (PCs)

	Initial eigenvalues			Rotation sums of squared loadings		
PCs	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
1	5.565	23.188	23.188	4.517	18.822	18.822
2	4.777	19.905	43.093	3.926	16.356	35.178
3	3.448	14.366	57.459	3.252	13.550	48.728
4	1.883	7.847	65.306	2.748	11.450	60.178
5	1.571	6.545	71.851	1.987	8.279	68.457
6	1.017	4.238	76.089	1.832	7.633	76.089
7	0.910	3.792	79.881			

Table 8. Loadings between the rotated components and soil properties

	Components					
Parameters	1	2	3	4	5	6
n					0.780	
Kf		0.463			0.784	
FR		0.838				
$FR_{0.2}$		0.849			0.408	
$FR_{0.11}$		0.898				
TZn			0.401			0.656
OM		-0.538			0.334	
CCE			-0.525	0.690		
CEC	0.853					0.342
pH				0.933		
EC	0.502			0.399		0.385
Ca	0.735			0.507		
K	0.450					0.627
Mg			0.351	0.503		
Na	-0.516				0.356	
Olsen P		-0.802				
Sand	-0.903					
Silt	0.462			0.477		-0.370
Clay	0.854					
MnOx	0.481	0.399	0.512			
AMnOx			0.721			0.529
TMnOx	0.321		0.689	0.335		
AFeOx	-0.328		0.767			
TFeOX			0.739			

Extraction method: Principal component analysis, rotation method: varimax with Kaiser Normalization. Loadings below 0.3 were supressed.

The type of cover plant/ land management system is important in terms of assessing the inherited effects of agricultural practices in long term for the corresponding soil properties. In this context, the scatter diagram of the PCs obtained by factor analysis were utilised to examine how the properties of each individual soil responded to crop-induced management systems. Figure 2 shows the scatter diagram between the PC 1 and PC 2. In general, it was observed that a large number of soils tended to gather in the centre which indicates that the PC 2 and related soil attributes are not very helpful to reveal the reason of such scattering for these soils, but some lands are still distinctly fall apart. SC12, SC3, PR3, FA7, and Wh4 clearly stand out from the other soils in relation to soil properties giving negative loadings with PC 1 (Table 8). These soils are typical with light-texture and high extractable Na and AFeOx contents. The AP5, FA17, Wh1 etc. located at the right end of the respective axis were scattered due to soil attributes such as high clay content, CEC, and extractable Ca that giving positive loadings with PC 1. PC 2 explains the variation in the values of FR values in the soil. Bottom site of the Y axis are typical small FR values whereas the upper site higher FR values. For example, the FR value of PR6 soil was determined to be 860 mg kg^{-1} and 795 g kg^{-1} for $FR_{0.2}$ and $FR_{0.11}$, respectively, in possibly relation to soil attributes having negative loading with PC 1 and positive loading with PC2 (Table 8) . CR3 and CR4 distinctly fall apart depending on the soil properties giving negative loadings with PC 2.

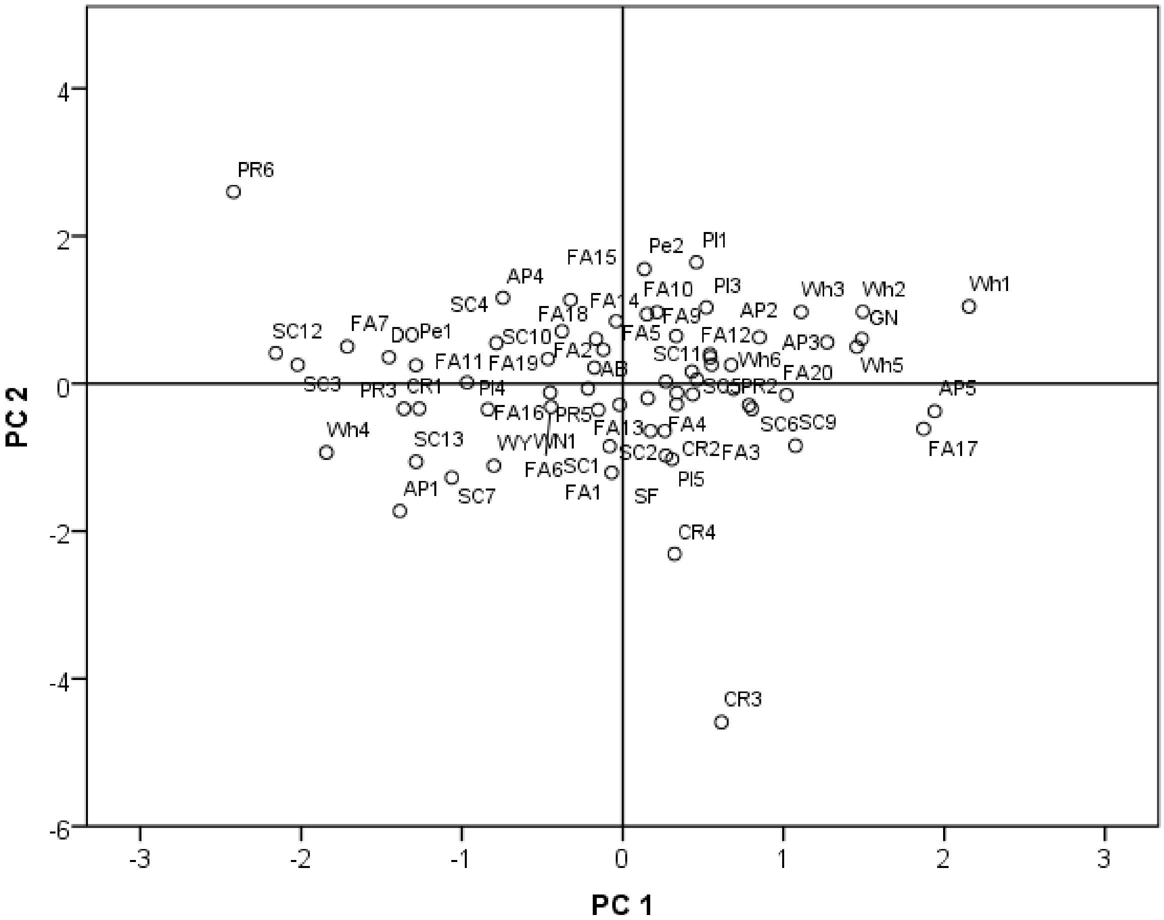

Fig 2. Scatter diagram for PC 1 vs. PC 2. Different letters indicate plant cover at soil sampling and the numbers are sample number for the respective cover plant. SC sweet cherry, CR corn, WN walnut, PO poplar, SF sun flower, FA fallow/no cover plant, PR peach, AP apple, DO tomatoes, Wh wheat, AB eggplant, GN ground nut, Pl plum, Pe pear, PI forest, ALM almond, and WY wine yard.

The scatter diagram of PC 1 vs. PC 5 serves to help visualise the patterns of the soils as a function of some soil phsyco-chemical properties and the Freundlich parameters (Figure 3). SC12, SC3, Wh4, FA7, PR6, AP1 behave differently depending on parameters giving negative loading values with PC1. SC12, DO, FA7 and Pe1 soils also differed in terms of soil attributes revealing negative loadings with PC5. On the contrary, cooperative effects of parameters showing positive and negative loadings with PC 5 and PC, respectively, caused the PR 6 and SC 13 soil to be clearly distinguished. The reason for the different adsorptive behaviour of Wh1, GN, AP5 soils is that the parameters having e negative loadings lower than -0.3 with PC5; and Ca, KDK, and clay those exerting positive loadings with PC1 (Table 8). The effect of the parameters with positive loading value with PC 1 was detrimental for soils taking place on the right of the perpendicular line intercepting the axis at the point 0. From this point of view, the most obvious effect of these parameters can be observed in FA17 soil, which is located at the rightmost axis cutting PC 5 at 0 loading. The FA20, Ap2, Wh3, SC9, Wh5 soils are separated from other soils as a function of soil properties with positive loading values with both PCs.

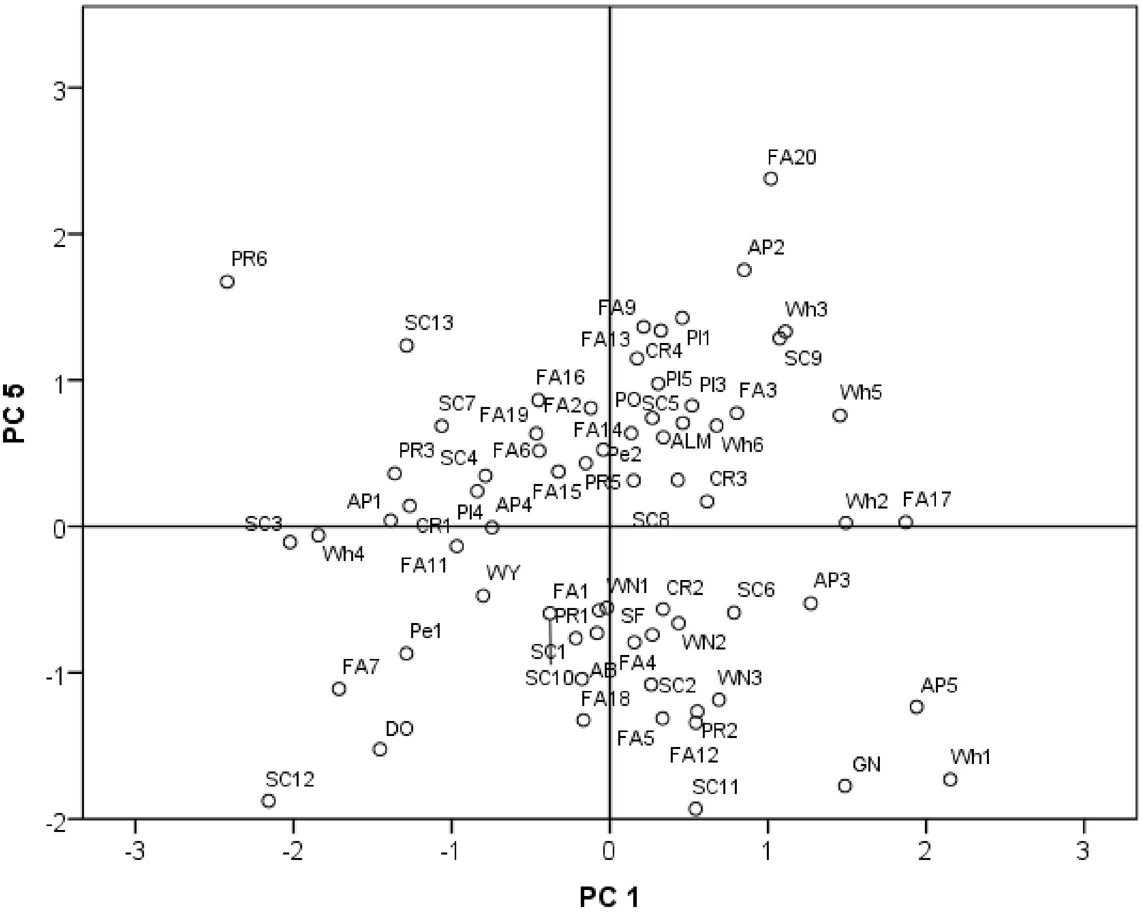

Fig 3. Scatter diagram for PC 1 vs. PC 5. Different letters indicate plant cover at soil sampling and the numbers are sample number for the respective cover plant. SC sweet cherry, CR corn, WN walnut, PO poplar, SF sun flower, FA fallow/no cover plant, PR peach, AP apple, DO tomatoes, Wh wheat, AB eggplant, GN ground nut, Pl plum, Pe pear, PI forest, ALM almond, and WY wine yard.

Conclusions

The study showed that the amount of available phosphorus in majority of the plain's soils were higher than the adequate limit (25 mg P kg^{-1}). This indicates that the soils are contaminated with phosphorus and excessive phosphorus fertilization is performed in the study area. This consequence may lead possible environmental risks in surface and ground water resources.

A considerable proportion of the phosphorus added in the adsorption studies tended to precipitate due to excessive fertilization or low fertilizer input of the soils. This poses a problem in defining the phosphorus adsorption by the Freundlich isotherm model of the soils. This problem may be overcome by inclusion of available and/or NaOH extractable P in the Freundlich equation.

Since sorption isotherms consider P buffering capacity of soil as a function of past fertilization practices and phsyco-chemical properties it can be regarded an environmentally friendly and economically feasible way of FR determination. By this method it can be possible to calculate the amounts of excessively practiced fertilisers. The Pearson correlations indicated that $FR_{0.2}$ can better reflect the fertiliser management background of soils. The $FR_{0.2}$ values were significantly higher than the ones calculated from the standard soil P test. Therefore it can be concluded that isotherm based FR should be used for minimizing the P losses and maximizing the crop yield and quality.

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Conflict of Interest

The authors declare that there are no conflict of interest.

Author Contributions

Veli Uygur designed the experiments, analysed the data, prepared figures and/or tables, and authored the current drafts of the paper. Tuba İnce performed the laboratory works, collected the data and prepared some of figures and/or tables.

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