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*Research Paper***Changes in soil inorganic phosphorous pools along a precipitation gradient in northern Iran**Mostafa Emadi¹, Majid Baghernejad^{2*}, Mohammad Ali Bahmanyar¹ and Afshin Morovvat²¹Department of Soil Science, Faculty of Crop Sciences, Sari University of Agricultural Sciences and Natural Resources, Sari, I.R. Iran²Department of Soil Science, College of Agriculture, Shiraz University, Shiraz, I.R. Iran*Corresponding author: majidbaghernejad@yahoo.co.uk

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Abstract: This study was undertaken to develop our knowledge relating to the soil inorganic phosphorous (P) pools along a precipitation gradient in calcareous forest soils. The precipitation gradient at Mazandaran province, northern Iran, reflected in the three soil moisture regimes (SMRs) e.g. xeric, ustic and udic SMRs that differed in their annual precipitation (550, 780, and 1250 mm y⁻¹, respectively). The representative soil profiles on the same slope position were selected for the three studied SMRs and the soil samples were collected from the genetic horizons to determine some soil characteristics and soil inorganic P (Pi) pools namely, Ca₂-P, Ca₈-P, Ca₁₀-P, Al-P, Fe-P, and Occluded-P. Increasing available water balance along the precipitation gradient induced greater weathering intensity across this climosequence leading to the pH and EC decline, organic matter accumulation, carbonate loss, and clay formation. Olsen-P and Ca₂-P which are considered as readily available for plants, constitutes a small fraction of total soil Pi for all soils studied and its amounts decreased with depth within all sites. The distribution of soil P fractions across the gradient suggested decreasing Ca-bound P and relatively increasing amounts of occluded P with increasing rainfall. The total Pi was decreased appreciably at udic SMR compared with xeric SMR. The maximum total Pi and Ca-bound P occurred in the upper part of the secondary calcium carbonate horizons when such a zone was present in soils. With increasing precipitation the measured amounts of the Ca₈-P, as pedogenic Ca, and Ca₁₀-P, as primary mineral P (mainly apatite P), decreased about 20 and 2.5 times from the xeric to udic SMR, respectively. Overall, the results herein strengthen our understanding of Pi transformations during pedogenesis along precipitation gradient in northern Iran and provide important insight into P pools distributing within soil solum at different observable SMRs in these regions.

Keywords: soil inorganic phosphorous, precipitation gradient, forest soils, pedogenesis

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Introduction

Phosphorus (P) is one of the major plant nutrients and is of important agronomic interest. P is also a dynamic element in soil genesis. The amount, distribution, and vertical chemical composition of P in the soil profiles are closely related to the soil forming factors like climate (Walker and Syers, 1976; Ippolito et al., 2010), topography (Roberts et al., 1985), parent materials and time (Chadwick et al., 2007; Brandtberg et al., 2010).

Walker and Syers (1976) introduced a conceptual model of soil development and its ecological implications by analyzing transformations in soil P, vegetation, and other ecosystem properties during pedogenesis. This model outlines a conclusion that primary apatite gradually decreased whereas such secondary phosphate as aluminum phosphate (Al-P), iron phosphate (Fe-P) and occluded phosphate increased in content with strengthening of weathering and pedogenesis in soils based on researches along several chronosequences in New Zealand. Thus, over time, P becomes depleted as well as less biologically available, leading to ecosystem level declines in productivity and rates of C and N cycling (Wardle et al. 2004). Cross and Schlesinger (1995) demonstrated that the relative amount of biological soil P increased with increased weathering at the expense of geochemical soil P. Miller et al. (2001) reported that P forms were transformed more commonly and more strongly as precipitation increased.

Selmants and Hart (2010) suggest that, compared to humid climates, reduced inputs of water, energy, and acidity to semiarid ecosystems slow the rate of change in P fractions during pedogenesis, but the overall pattern remains consistent with the Walker and Syers (1976) conceptual model. Furthermore, they implied that pedogenic change may be an important factor controlling the spatial distribution of labile P pools in semiarid ecosystems.

The changes in soil P during pedogenesis have important ecological consequences, because P limitation can become sufficiently intense in the late stages of ecosystem development to cause a decline in forest biomass and productivity (Wardle et al., 2004). The climate-related changes in soil organic and inorganic P can be identified by the chemical fractionations providing potentially the better understanding on soil P dynamics during pedogenesis.

The soil nutrient cycling in Mazandaran province, northern Iran, is affected by the descending precipitation gradient and led to some differences in soil physical, chemical and mineralogical characteristics (Bahmaniar et al, 1999 and Khormali and Kehl, 2011). Although, the climate is the main factor of soil genesis in this region through a variety of direct and indirect processes, however, only a few studies have been done so far concerning the climosequence.

Several sequential chemical fractionations concerning soil P (Hedley et al., 1982; Adhami et al. 2006; Shariatmadari et al. 2007, Emadi et al., 2009) were used to identify the reaction products and inorganic-P fractions in the soils. The Hedley fractionation (Hedley et al., 1982) or similar fractionation schemes, for example Tiessen and Moir (1993), are often used to recognize plant-available and refractory forms of soil inorganic and organic P based on solubility in alkaline and acid extractants applied in a sequential extraction (Cross and Schlesinger, 1995). However, there are not any attempts in the literature to assess the P transformation during the pedogenesis using the fractionation scheme proposed for calcareous soils based on method described by Jiang and Gu (1989) where soil inorganic P pools were divided into six fractions (Ca₂-P, Ca₈-P, Al-P, Fe-P, occluded P, and Ca₁₀-P). Although, Hedley sequential fractionation method has been shown to be a useful tool to examine different forms of soil P (Yang and Post, 2011), however it had not the ability to differentiate the different forms of Ca-bound P in soils especially in calcareous soils. Therefore, the main objective of our research was to study the climate-related changes in soil P fractions by the method of Jiang and Gu (1989) in northern Iran for developing better insights into the P transformation in calcareous soils along a precipitation gradient (550-1250 mm y⁻¹).

Materials and methods

Site and soil descriptions and soil analyses

Sampling sites are located in Mazandaran province, northern Iran, spanning a 700 mm precipitation gradient over 170 km across the province. Figure 1 illustrates the location map of the Mazandaran province and representative soil profiles of these sampling sites (Royan, Ghaemshahr and Behshahr). The mean annual precipitations were 1250, 780 and 550 mm yr⁻¹ for the Royan, Ghaemshahr and Behshahr sampling sites that reflected in udic, ustic and xeric SMRs, respectively. The SMR was determined by the Newhall software program. The mean annual air temperature was the same across the study area (16 °C) and classified as thermic soil temperature regime. All sites have roughly the same elevation as well (150 m asl).

In order to study the effect of climate or precipitation rate on soil formation and P dynamics, other factors of pedogenesis including parent material, relief, vegetation and time must be kept constant. For this purpose, this study was conducted on the soils derived from the calcareous parent material and developed on the summit slope position under the native forest utilization, far above the groundwater table. Soils at these sites were primarily derived from limestone and calcareous sedimentary deposits. Given that forest soils in highland of northern Iran are being degraded and destructed due to extensive agricultural activities (Emadi et al., 2009), this study took the natural forests of Alborz mountain ranges into account. All studied sites were uncultivated and located on summit slope positions. Summit positions are generally quite stable, with minimal erosion or accretion. Dominant natural plants are forest trees including *Fagus orientalis*, *Punica granatum*, *Alnus subcordata*, *Acer insigne*. Anyway, these soils have substantially the same soil forming factors and subsequently their physicochemical and biological characteristics mainly depend on climate parameters. In general, it is assumed that except climate the duration and process of pedogenesis are the same for the studied soils.

At each summit position of the studied SMRs, three representative soil profiles were selected from the several excavated profiles and the soil samples were collected from the genetic horizons. The soils were described and classified according to the Soil Survey Manual (Soil Survey Staff, 1993), Keys to Soil Taxonomy (Soil Survey Staff, 2010), and WRB (2006), respectively. The redness rating (RR) was calculated as (10-H) C/V, where H is the numerical value of YR hue, C is chroma, and V is the value of the Munsell notation (Torren and Barron, 1993). Soil samples were air dried, crushed, and passed through a 2-mm sieve, and some of their characteristics such as texture (pipette method), organic carbon (OC), cation exchange capacity (CEC), calcium carbonate equivalent (CCE), and pH (saturated paste) were determined by the procedure outlined by Sparks et al. (1996). The mean values of above measured soil characteristics and soil P pools were presented in appropriate tables.

Phosphorus sequential fractionation

Inorganic P fractions were measured according to a fractionation scheme proposed for the calcareous soils (Jiang and Gu, 1989). Briefly, the fractionation involved a sequential extraction with (1) 0.25 M NaHCO₃ (pH 7.5) to extract Ca₂-P, (2) 0.5 M CH₃COONH₄ (pH 4.2) to extract Ca₈-P, (3) 0.5 M NH₄F (pH 8.2) to remove Al-P, (4) 0.1 M NaOH-0.1 M Na₂CO₃ to obtain Fe-P, (5) 0.3 M sodium citrate-Na₂S₂O₄-0.5 M NaOH to obtain the occluded P and (6) 0.5 M H₂SO₄ to extract Ca₁₀-P. All of the extraction procedures were performed in duplicate and contents of P were colorimetrically measured in the supernatants by the ascorbic acid method of Murphy and Riley (1962).

Results and discussion

Soil physical and chemical properties

As Table 1 indicates, the differences in precipitation resulted in some pronounced changes in the soil morphological, physical and chemical properties.

Soils' color ranges in xeric and ustic SMRs sites are with the Munsell color index of (moist) 10YR and value and chroma of 3-5 and 2-5, respectively. The soil materials tend to comparatively be redder in udic SMR with the Munsell color hue of (moist) 7.5YR compared with other two sites. Amongst the three studied SMRs, the soils investigated at the area with udic SMR had the higher values of the redness rating (RR). The RR is well correlated with hematite content in the soils (Torrent and Barron, 2002). The rubification i.e. pedogenic hematite formation follows the soil decalcification because the presence of calcite in soils hinders the weathering of Fe-bearing primary minerals. This process occurs at a place similar to that of clay translocation. Apparently, hematites which tend to be associated with silicate clay particles are transported to the argillic horizon (Bt) at the wettest sampling site, Royan, reflecting the soil matrix redder than other two sites. Moreover, a soil with a high RR can also contain goethite, but because of the dominance of the red color of hematite, the RR does not allow estimation of the amount of goethite in a sample (Duiker et al., 2003). Thus, based on RR in Table 1, the Bt1 horizon of the soils studied at udic SMR had the highest hematite content, followed by Bt2, BC and other studied soil horizons.

Despite a considerable variation within soil profiles, the pH, EC and CCE contents gradually decreased and clay content, OC and CEC increased in soils across precipitation gradient. As seen in Table 1, the pH values in the A horizons of the soils in Behshahr, Ghaemshahr and Royan were 7.61, 6.73 and 6.2, respectively. In contrast, CCE content in the A horizons of the soils from Behshahr was higher (9.6 %) than other two wetter sites and increased with depth within all sites. The OC content in the soil solum increased in this precipitation gradient. In this context, Lutzow et al. (2006) described the stabilization of OM in temperate soils through the following mechanisms: (1) selective preservation due to recalcitrance of OM, (2) spatial inaccessibility of OM from decomposers due to occlusion, intercalation, hydrophobicity, encapsulation and interaction with mineral surfaces (Fe, Al, Mn oxides, phyllosilicates) and metal ions.

Overall, subsurface horizons contained greater amounts of CCE at all sampling sites, which decreased with increasing precipitation although effervescence with cold 1 N HCl was absent throughout the Royan soil profile. The greater leaching and effective precipitation in areas of ustic and udic SMRs with higher rainfall compared with xeric SMR were slightly promoted the deeper carbonate accumulation and basic cation removals. Leaching of soluble salts (EC) in ustic SMR leads to an eluvial horizon underlain by phyllosilicate-enriched illuvial horizon above the secondary accumulations of calcium carbonate (and other soluble salts) in the parent material. The depth to this horizon can be inferred as the depth to effective precipitation (Jenny, 1941; Birkeland, 1999).

The clay and CEC contents of soils increased from the xeric to the udic SMR. This could be attributed to the conditions are suitable for humification, decalcification and clay illuviation, and also clay neoformation and transformation through weathering of coarser fractions. Increasing soil available water and a relative leaching environment for the release of K⁺ from micaceous minerals (illite) in the calcareous environment provide favorable conditions for the formation of smectite and vermiculite through clay transformation (Khormali and Abtahi, 2003) containing higher cation exchangeable sites.

The soil classifications of the studied soils according to the WRB (2006) and Keys to Soil Taxonomy (2010) are shown in Table 1. The soil classifications of the xeric SMR are mainly classified as Typic Calcixerepts with cambic and calcic horizons showing the initiation of brunification and structure formation as soil forming processes. An outstanding characteristic of studied soils in xeric SMR, Calcisols, is a prominent horizon of calcium carbonate accumulation near the soil surface. No argillic horizon was found in the area with xeric SMR.

Soils of the ustic and udic SMRs classified as Calcic Haplustalfs and Mollic Halpudalfs (Keys to Soil Taxonomy, 2010) or Calcic Luvisol and Haplic Luvisol (WRB, 2006), respectively, indicating the conditions were favorable for the downward decalcification and the subsequent clay illuviation and formation of moderately to strongly developed argillic horizons. Lavkulich and Arocena (2010) stated that lessivage is the dominant soil-forming process in Luvisols like studied soil in ustic and xeric SMRs, and has significant influence in the ecosystem functions of

soils. The accumulations of phyllosilicates in the Bt horizons provide inorganic colloidal materials with large surface area and high amounts of negative charges that are conducive to the retention of water, metals and OC.

Table 1. Classification and main characteristics of the soils at the three investigated sites of northern Iran¹

Sampling Sites	SMR ^a	Horizon	Depth (cm)	Color (Moist)	RR ^b	Struct ^c	Ef ^d	Sand %	Silt %	Clay %	Tex ^e	pH (paste)	OC ^f %	CCE ^g %	CEC ^h Cmol(+) kg ⁻¹	EC ^k dS m ⁻¹
Fine, mixed, superactive, nonacid, thermic, Mollic Halpudalfs (Haplic Luvisol)																
Royan	Udic	A	0-14	10YR 3/2	0	m1 abk	-	25	35	29	CL	6.2	2.55	1.1	55.5	0.07
		Bt1	14-74	7.5YR3/4	3.3	m3 abk	-	4	38	58	C	6.4	2.1	2.4	48.2	0.11
		Bt2	74-109	7.5YR3/3	2.5	c3 abk	-	4	34	62	C	6.7	0.9	2.4	55.0	0.11
		BC	109-150	7.5YR6/6	2.5	f1 abk	e	14	41	45	SiC	7.2	0.2	12.6	33.2	0.2
Fine, mixed, superactive, nonacid, thermic, Calcic Haplustalfs (Calcic Luvisol)																
Ghaemshahr	Ustic	A	0-11	10YR 3/2	0	m1gr	-	24	41	35	CL	6.73	2.14	5.5	38.6	0.13
		Bt1	11-33	10YR3/4	0	m2abk	-	10	38	52	C	6.67	1.51	6	39.8	0.21
		Bt2	33-89	10YR 4/3	0	m2abk	-	15	30	55	C	6.71	0.62	7.9	39.0	0.29
		Bck	89-145	10YR 5/4	0	m	ev	20	38	42	C	7.36	0.21	29.7	25.8	0.41
Fine, mixed, superactive, calcareous, thermic, Typic Calcixerepts (Haplic Calcisols)																
Behshahr	Xeric	A	0-17	10 YR3/4	0	f1 abk	es	17	43	39	SiCL	7.61	1.23	9.6	25.8	0.51
		Bw	17-45	10YR 4/4	0	m1 abk	es	14	44	42	SiC	7.87	0.62	11.6	20.3	0.61
		Bk	45-110	10YR 5/5	0	f2 abk	ev	18	44	38	SiCL	7.81	0.34	29.7	17.3	0.72
		C	+110	10YR 5/5	0	f1 abk	ev	16	46	38	SiCL	8.1	0.25	22.5	18.2	0.77

¹ Symbols applied according to Soil Survey Manual (Soil Survey Staff, 1993) and the values in the tables are the mean of three soil samples

^a Soil Moisture Regime, ^b Redness rating=(10-Hue)×Chroma/Value, ^c Structure, ^d Effervescence with cold 1 N HCl, ^e Texture, ^f Organic Carbon, ^g Calcium Carbonate Equivalent,

^h Cation Exchange Capacity; ^k Electrical Conductivity

Inorganic phosphorus fractionation in soils

The amount of soil Pi pools at all sites studied is shown in Table 2. Results show that different soil P forms affected by the climate as the most important soil forming factor in these soils.

Table 2. Amounts of different inorganic P fractions (mg kg⁻¹) sequentially extracted from soil samples

Sampling sites ^a	Horizon	Olsen-P	Ca ₂ -P	Ca ₈ -P	Al-P	Fe-P	Occluded-P	Ca ₁₀ -P	Total-Pi
Mollic Halpudalfs (Haplic Luvisol)									
Royan	A	14.2(3.3)	9.8(2.3)	8.5(2.0)	93.1(21.6)	77.8(18.1)	117.3(27.2)	124.4(28.9)	430.9
	Bt1	9.7(2.4)	5.3(1.3)	7.5(1.8)	101.7(24.8)	82.1(20.0)	115.6(28.1)	98.8(24.0)	410.9
	Bt2	3.3(0.8)	4.0(1.0)	7.9(1.9)	92.7(22.5)	81.4(19.8)	101.4(24.6)	124.6(30.2)	412.0
	BC	5.2(1.1)	6.3(1.4)	6.5(1.4)	98.9(21.3)	84.9(18.2)	99.6(21.4)	169.3(36.4)	465.4
Calcic Haplustalfs (Calcic Luvisol)									
Ghaemshahr	A	13.3(2.7)	10.4(2.1)	44.4(8.9)	76.8(15.4)	52.6(10.6)	107.5(21.5)	206.5(41.5)	497.8
	Bt1	8.7(2.0)	7.8(1.8)	17.3(3.9)	74.2(16.8)	59.3(13.5)	82.3(18.7)	199.5(45.3)	440.4
	Bt2	3.1(0.6)	3.4(0.6)	19.2(3.6)	122(23.0)	95.5(18.0)	107.1(20.3)	182.6(34.4)	530.3
	Bck	3.4(0.5)	2.8(0.4)	16.6(2.6)	89.9(14.1)	73.4(11.5)	83.4(13.1)	371.6(58.3)	637.7
Typic Calcixerepts (Haplic Calcisols)									
Behshahr	A	10.3(1.6)	8.3(1.6)	164.6(26.0)	48.2(8.9)	56.2(7.6)	51.5(8.1)	305.5(48.2)	634.3
	Bw	4.5(0.8)	4.1(0.8)	135.2(24.5)	24.9(7.2)	39.8(4.5)	51.3(9.3)	295.3(53.6)	550.7
	Bk	6.2(0.9)	6.2(0.9)	134.8(20.6)	31.0(7.6)	49.6(4.7)	61.1(9.3)	371.8(56.8)	654.0
	C	2.6(0.4)	2.5(0.4)	116.6(19.1)	29.4(7.8)	47.5(4.8)	56.4(9.2)	357.8(58.6)	610.2

^aNumbers in parentheses present the percentage of total inorganic P found in each fraction

Olsen-P and Ca₂-P which are considered readily available for plants, constitutes a small fraction of total soil inorganic P (Pi) for all soils studied. This is likely due to rapid uptake by plants and microorganisms or due to the formation of the secondary mineral phases. The Olsen-P contents in the A horizons of soils in xeric, ustic and udic SMRs were 10.3, 13.3 and 14.2 mg kg⁻¹, respectively. Soil available P decreased with depth within all sites. This is due to the biocycling that increase P available concentrations in the soil surface as plants access nutrients from deeper horizons (Carreira et al., 1997; Chadwick et al., 2007). Ippolito et al. (2010) related the soil surface P accumulation to increased biocycling and biological mining as well as eolian input. It is apparent that the soil available P increased with increasing rainfall (Table 2). Our results herein are inconsistent with findings of Yang and Post (2011) who stated that the mean labile P, readily available soil P, ranges from around 100 mg P kg⁻¹ in slightly weathered soils to about 20 mg P kg⁻¹ in highly weathered soils, decreasing with the weathering stages of the soils. This may be due to the moderately weathered soils of the ustic and udic SMRs sites showing the relatively sufficient available P in soils.

The Ca₂-P, Ca₈-P and Ca₁₀-P contents in the A horizons of the xeric SMR were 8.3, 164.6, 305.5, of the ustic SMR were 10.4, 44.4, 206.5, of the udic SMR were 9.8, 8.5, 124.4 mg kg⁻¹, respectively. The Ca₂-P, Ca₈-P and Ca₁₀-P contents in the wettest site, udic SMR, appreciably were lower than other two sites. With increasing precipitation the measured amounts of the Ca₈-P, as pedogenic Ca in the soils, and Ca₁₀-P, as primary mineral P (mainly apatite P), decreased about 20 and 2.5 times from the xeric to udic SMR, respectively. Therefore, most of the pedogenic Ca, Ca₈-P, in the surface horizons disappeared at the wettest site. Given leaching of roughly all CCE from the soil profiles the relative abundance of Ca-bound P pools constituted about 32 % of total Pi in the surface horizons of udic SMR. The relative abundance of mean inorganic P pools in the soil solum were in the order of Ca₁₀-P >> Ca₈-P > Occluded-P = Al-P = Fe-P > Ca₂-P in xeric SMR sampling site, of Ca₁₀-P > Occluded-P > Al-P = Fe-P > Ca₈-P > Ca₂-P in ustic SMR sampling site and of Occluded-P = Ca₁₀-P > Al-P > Fe-P >> Ca₈-P = Ca₂-P in udic SMR sampling site (Table 2). Adhami et al. (2006) also fractionated inorganic P in highly calcareous soils of southern Iran in the order Ca₁₀-P > Ca₈-P > Occluded-P > Al-P > Fe-P > Ca₂-P. Emadi et al. (2009) found that the relative abundance of inorganic P fractions in the selected heavily fertilized soils of northern Iran were in the order of Ca-P > Al-P > Fe-P >> Occluded-P > soluble-P.

The Al-P, Fe-P and occluded P contents at the A horizons of the xeric SMR were 48.2, 56.2, 51.5, of the ustic SMR were 76.8, 52.6, 107.5, of the udic SMR were 93.1, 77.8, 127.3 mg kg⁻¹, respectively. Overall, the Al-P, Fe-P and occluded P comprised about 22, 20 and 25 % of total Pi at the udic SMR, respectively, whereas at Behshahr site comprised 8, 7 and 8 % of total Pi, respectively. These results showed general increases in Al-P, Fe-P and occluded P contents with increasing precipitation in soils. With the progression of weathering and the increase of Al and Fe oxide minerals and the decrease of soil pH, P mineralized from organic matter adsorbs to the surface of minerals and may further become encapsulated inside of Fe and Al minerals, becoming occluded P. Lindsay (1979) reported that a decrease in soil pH coupled with a loss of basic cations shifted systems dominated by Ca-phosphates to Fe- and Al-phosphates. The observed P weathering patterns across the soils studied also compared well with findings of Carreira et al. (1997) who found that under conditions of low, intermediate, and high weathering the most

inorganic soil P was Ca-bound, Al- and Fe-bound, and occluded, respectively. Consistent with our observations at Royan sampling site having the highest weathering evidences, Ippolito et al., (2010) showed that occluded P increased along the weathering sequence.

Mean total Pi by summing all sequentially measured inorganic forms in soil solum were 612, 526 and 429 mg kg⁻¹ in xeric, ustic and udic SMRs, respectively. Therefore, the total Pi was markedly decreased at the wetter sites. The amount of total Pi in all soils studied at ustic and udic SMRs were high near the surface, decreased to a minimum within Bt horizons, and increased to a maximum beneath the argillic horizons and parent materials (Table 2). The maximum total Pi and Ca-bound P (sum of sequentially measured Ca₂-P, Ca₈-P and Ca₁₀-P) occurred in the upper part of the secondary calcium carbonate horizons when such a zone was present. Apparently, the P pools had been leached from the upper horizons and reprecipitated as Ca-bound P in the drier calcareous horizons and layers.

The vertical distribution pattern of the various P pools for each site is shown in Figure 2. At Behshahr sampling site with xeric SMR, the Al-P, Fe-P and occluded P pools changed little with depth. Ca-bound P varied with depth, containing 434–476 mg P kg⁻¹ in the Bw and C horizons; higher amounts were found in calcic horizons (Bk). Furthermore, the maximum measured Ca-bound P was observed at the Bck and BC horizons in the ustic and udic SMRs, respectively. The soils at Behshahr site with xeric SMR were dominated by Ca-bound P throughout the profile, but its dominance in other two wetter sites decreased appreciably (Figure 2). From xeric to udic SMRs, maximum concentrations of total Pi were found in the horizon with maximum carbonate concentrations demonstrating that downward P movement may be limited by the mean depth of water movement and further impeded by precipitation of Ca-phosphates (Honeycutt et al., 1990; Ippolito et al., 2010).

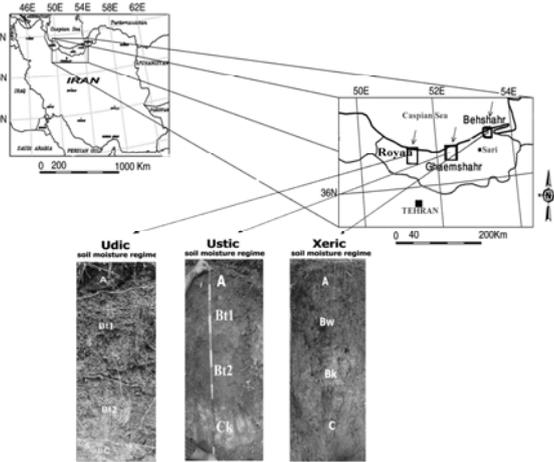


Figure 1. The location map of the study area and the representative soil profiles for three sampling sites

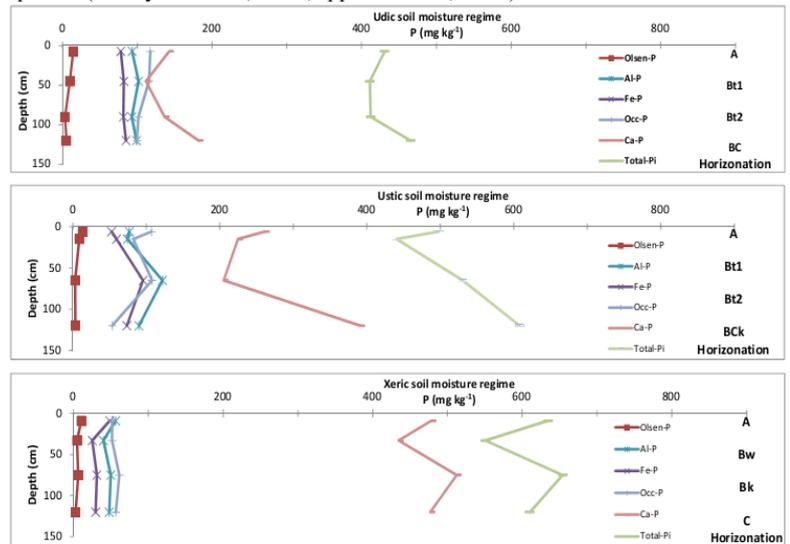


Figure 2. Vertical distribution of soil inorganic P forms at three sampling sites

P retention altered between secondary and primary mineral precipitates in the surface and subsurface at all soil studied. Subsurface Ca-bound P contents increased in parallel with highly observed CCE contents (Table 1). Our results revealed that even in soils with a fairly low CCE, about 1 % of CCE in soil surface at wettest site, the secondary precipitation of Ca–P minerals have broad ecosystem implications for the retention of P in udic SMR (Carreira et al., 2006). Moreover, this could be attributed to this fact that the small remained amounts of the CCE in the soil profiles at the wettest site are apparently enough active to precipitate and/or adsorb the P from soil solum. At udic SMR, in the upper horizons the CCE content is low and Ca-bound P trends within these horizons do not appear to follow that of organic C, suggesting that secondary Ca–P minerals most likely control P availability in the upper horizons (Ippolito et al., 2010).

Slightly weathered Inceptisols at the xeric SMR have a high percentage of Pi in apatite (approximately 50 %), while in intermediately weathered Alfisols at the ustic and udic SMRs, apatite P only accounts for about 40 and 25 % of total soil Pi (Table 2). This is due to drier climate condition and the generation of secondary calcium phosphate in Inceptisols, where the high concentrations of calcium carbonate leads to the chemical reaction between released P from primary apatite P and calcium minerals under neutral or alkaline conditions (Cross and Schlesinger, 1995; Lajtha and Schlesinger, 1988). In contrast to apatite P, occluded P increases with the weathering stage of soils. Occluded P makes up about 9 % of total soil Pi in slightly weathered Typic Calcixerepts, while it constitutes 20 % and 25 % of total soil P in intermediately weathered Calcic Haplustalfs and Mollic Halpudalfs. In the lower subsurface horizon i.e. C, Bck and BC horizons, Ca-bound P increased from the xeric to udic SMR and occluded P followed an opposite trend (Table 2 and Figure 2).

Shifts in the control of P availability, from reactions with Ca in drier climates, xeric SMR, to Al and Fe in wetter climates i.e. ustic and udic SMRs, is a common occurrence observed in soil studied where transformations result from increased weathering intensity. Several reports state that Fe- and Al-oxyhydroxides can overwhelm the role of carbonate minerals in forming P precipitates (Carreira et al., 1997; Pena and Torrent, 1990) even in soils with a basic pH. Ippolito et al., (2010) have noted that within mollic epipedons across the semi-arid US central Great Plains, the Ca-bound P dominates all fractions yet inorganic C content, or CaCO₃, is low or absent like the same saturation in soils of udic SMR in this study. Given the weathering intensity in our study area, it is unlikely the steady state conditions of soil P proposed by Walker and Syers (1976) and Turner et al. (2007), implying dominance of occluded P and organic P in the soils profiles, have been achieved.

Conclusions

The variability in soil P transformations in light of potentially climate-driven changes during pedogenesis was studied in this research. Increasing available water balance along the precipitation gradient induced greater weathering intensity across the climosequence leading to the pH and EC decline, organic matter accumulation, carbonate loss, and clay formation. The soils in xeric, ustic and udic SMRs classified as Typic Calcixerepts, Calcic Haplustalfs and Mollic Halpudalfs, respectively. Slightly weathered Inceptisols at the xeric SMR have a high percentage of Pi in apatite (approximately 50 %), while in intermediately weathered Alfisols at the ustic and udic SMRs, apatite P only accounts for about 40 and 25 % of total soil Pi. In contrast to apatite P, occluded P increases with the weathering stage of soils. Occluded P makes up about 9 % of total soil Pi in slightly weathered Typic Calcixerepts, while it constitutes 20 % and 25 % of total soil P in intermediately weathered Calcic Haplustalfs and Mollic Halpudalfs, respectively. The results revealed that even in soils of udic SMR with a fairly low CCE in the soil surface, about 1 %, the secondary precipitation of Ca–P minerals constitutes about 25 % of total Pi demonstrating the broad ecosystem implications for the retention of P by soil carbonate and calcium compounds. Given the weathering intensity in our study area, it is unlikely the proposed steady-state conditions for soil Pi have been achieved. The results reveal that although P is often assumed to be relatively immobile in soils, significant redistribution occurs during pedogenesis in study area.

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