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Chemical forms of phosphorous and physicochemical properties of acid soils of Cheha and Dinsho districts, southern highlands of Ethiopia

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Abstract

Background: Soil acidity and low availability of P are among the major problems limiting crop production in the highlands of Ethiopia. The current study was conducted to evaluate the distribution of chemical P forms and selected physical and chemical properties of soils in Cheha and Dinsho districts, southern highlands of Ethiopia. Twelve representative composite soil samples were collected from the surface layer (0–15 cm) and analyzed for selected soil properties. Analysis of available P and oxalate extractable P, Al and Fe, and P fractionation were done following standard procedures.

Results: The pH of soils in the study area ranged from 4.65 to 5.45. In the study area the Mehlich-3 extractable P ranged from 8.90 to 25.75 mg kg⁻¹, while the Bray-I extractable P varied from 8.54 to 22.81 mg kg⁻¹. The studied soils had a total P content that ranged from medium to very high. Mehlich-3 P was positively and significantly correlated with pH, CEC and OM, while it was negatively and significantly ($P \leq 0.01$) correlated with exAc and exAl. Oxyhydroxides of iron and aluminum were dominating the exchange sites of the studied soils. In terms of the relative abundance of P forms, Res-P and HCl-P followed by NaOH-P_o and NaOH-P_i were the dominant P forms in Cheha and Dinsho districts respectively. The total sum of readily available P forms (NH₄Cl-P_i, NaHCO₃-P_i and NaHCO₃-P_o) did not exceed 4% of the total P.

Conclusion: Soils of the study area were acidic in reaction and found to have low available P. Given the presence of considerable amount of total P, low P availability and high soil acidity in the study areas, further research has to be done on adsorption characteristics to determine the P requirements of the soils for better P management.

Keywords: Amendment, Fractionation, Oxyhydroxide, Phosphate, Acid soils, Ethiopian soils

Background

Soil acidity and low availability of phosphorous (P) are among the major problems limiting crop production in the highlands of Ethiopia where high rainfall, nutrient leaching, and soil erosion are more prevalent (Asmare et al. 2015). When soil pH drops below 5, active form of Al becomes soluble and results in reduced nutrient uptake (Achalu 2014). Reports from numerous

experiments in P-deficient soils in the highlands of east Africa indicate that the inorganic form of P assessed by the Olsen method is less than 5 mg P kg⁻¹ soil (Ikerra 2004). Limited availability of P in many tropical soils can be attributed to severe P fixation or retention, which is particularly strong in soils with low P status. In acidic soils, crystalline and non-crystalline oxides of Fe and Al (sesquioxides) are the main adsorbing agents of phosphate (Jiang et al. 2015).

Despite the absence of specific system that offers an adequate solution for generalizing or comprehending the behavior of P in different soils, sequential extraction

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has been used for characterization of complex mixtures that do not lend themselves to conventional chemical analysis (Herlihy and McCarthy 2006). In a review on the use of the Hedley method, contrasting agro-ecosystems of tropical and temperate climates, with different soil use and managements, Negassa and Leinwebe (2009) reported that inorganic and organic fractions of P could act as a source or sink of available P to plants. The Hedley sequential extraction or fractionation of P method has also been used to distinguish labile from non-labile fractions and to rank stable fractions and organic fractions in terms of their availability to plants (Cross and Schlesinger 1995). Based on this extraction method, P can be classified as available to plants or microorganisms (labile P), which includes the sum of inorganic P (Pi) and organic P (Po) extracted by ammonium chloride (NH₄Cl) and sodium bicarbonate (NaHCO₃). The non-labile P includes the sum of the remaining fractions (Pi and Po in hydroxide and in sonicate + hydroxide, Pi in HCl and residual P in sulfuric acid digestion). Accurately characterizing P forms has been proved to overcome the limited information that total P analysis can provide (Zhou et al. 2001). The quantity of P reserve to replenish solution P and the ability of the soil to maintain sufficient solution P concentration are the main factors governing P supply to plants (Buresh et al. 1997) and in the absence of fertilization, solution P is replenished from other soil P pools with different degree of availability.

Even though several works have been done on the relative distribution and forms of P (Duffera and Robarge 1996; Shiferaw 2004; Negassa and Leinwebe 2009; Fisseha et al. 2014; Achalu et al. 2014; Asmare et al. 2015), research related to the different P forms and distribution encompassing organic P in the soils of the study areas is scant. Besides, given the role played by phosphorous in agriculture, knowledge on the status of various P forms, their relative distribution and interaction with other soil attributes that influence P availability in soils of the study area is worth researching. Therefore, this work was initiated to characterize the forms and distributions of P and their relation with selected soil physical and chemical properties in acidic soils of Dinsho and Cheha districts, southern highlands of Ethiopia.

Methods

Description of the study area

The study was conducted in Ethiopian highlands of Dinsho district in Bale zone and Cheha district in Gura-gura zone, Ethiopia (Fig. 1). Dinsho district lies between 6°58'40" and 7°20'0" N, and 39°44'0" and 40°26'40" E. Physiographically, most of the land area of the district is situated above 2000 m above sea level (masl). The district is classified into three agro-climatic zones: highlands (2300–2600 masl), midlands (1500–2300), and lowlands (1200–1500). The district has a bimodal rainfall distribution with mean annual rainfall of about 1150 mm. The

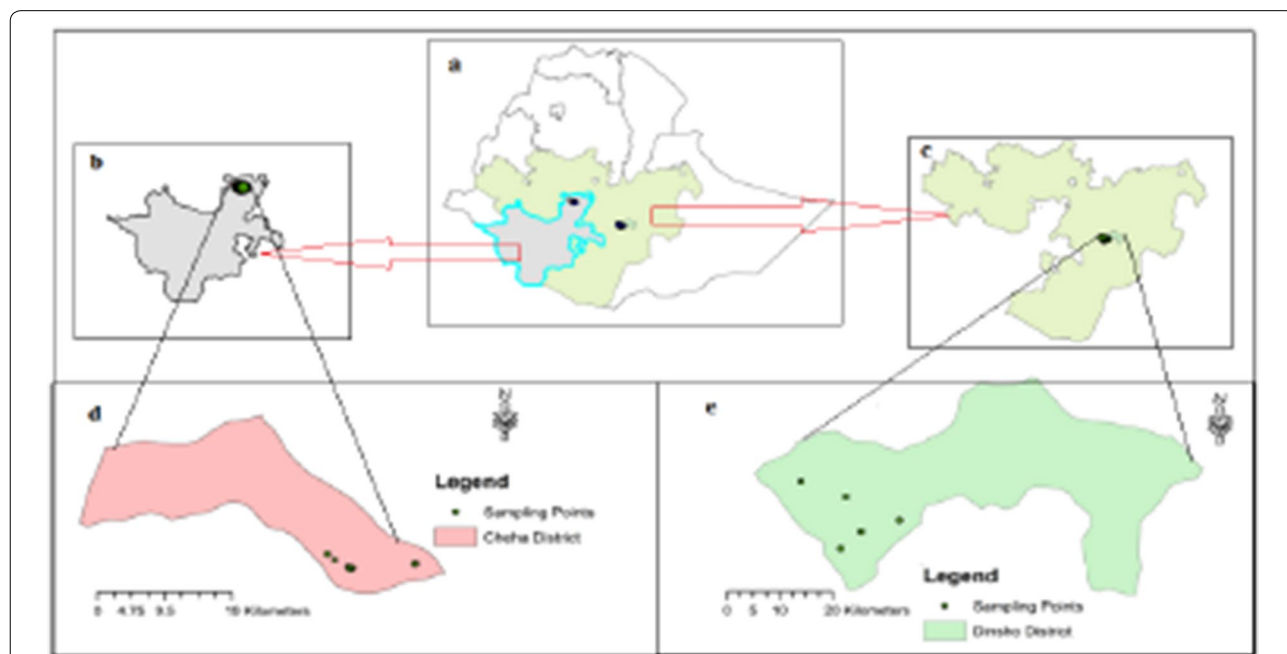


Fig. 1 Location map of the study areas, **a** Oromia and SNNP regions in Ethiopia, **b** Cheha district in SNNP region, **c** Dinsho district in Oromia region, **d** Cheha district, **e** Dinsho district

maximum and minimum mean annual temperatures of the District are 17.5 and 6 °C, respectively. Wheat and barley are some of the major cereal crops grown in the area. The major reference soil groups in the district are Pellic Vertisols, Eutric Cambisols, Eutric Nitisols (now Nitisols), and Chromic Luvisols (FAO Food and Agriculture Organization 1984).

Cheha district is situated between 8°32'0" and 8°20'0"N, and 37°41'20" and 38°2'40"E, at an elevation that ranges from 900 to 2812 masl. EIAR (Ethiopian Institute of Agricultural Research) (2011) classified the area into three agro-ecological zones i.e. highlands (2300–3200 masl), midlands (1500–2300 masl), and lowlands (500–1500 masl) based on the bimodal rain fall system. The 10 years mean annual rainfall of the district is about 1268 mm. The mean annual maximum and minimum temperatures are 24.97 and 10.69 °C, respectively. The dominant soil types are Eutric Nitisols, Leptosols, and Pellic Vertisols (FAO Food and Agriculture Organization 1984).

Site selection, soil sampling, and soil analysis

A preliminary soil survey and field observation was made using topographic map (1:50,000) of the study area. Soil pH (potentiometer), altitude (GPS), and slope (clinometer) were used as criteria for selection of soil sampling sites. Fifteen (15) sub-samples were collected from each sampling site to make one composite sample. Accordingly, twelve composite soil samples (0–15 cm), seven from Cheha district (Goha 1, Goha 2, Goha 3, Aftir, Abret, Kechot, and Moche), and five from Dinsho district (Doyomarufa 1, Doyomarufa 2, Tulu, Weni, and Ketasire) having pH values of less than 5.5 were obtained within an altitudinal range of 2000–3000 masl and slope less than 8% (Table 1). Soil pH was measured at field condition using portable pH meter to select soils having a pH of less than 5.5. The soil samples were put in plastic bag, tagged, and transported to laboratory for analysis during the 2014/2015. Consequently, adequate (about 1 kg) amount of composited soil samples were air dried and ground to pass through a 2 mm sieve for analysis of selected soil chemical and physical properties except organic carbon and total nitrogen in which case the samples were passed through a 0.5 mm sieve.

Analysis of soil physical and chemical properties

Soil particle size distribution was analyzed by the Bouyoucos hydrometer method (Day 1965). Soil bulk density was measured from three undisturbed soil samples collected using a core sampler following the procedure described by Jamison et al. (1950). The moisture retention at field capacity (FC) (−0.33 bar) and permanent wilting point (PWP) (−15 bar) was determined using the pressure plate apparatus method (Gupta

Table 1 Sampling locations and site description

Sampling sites	Longitude (E)	Latitude (N)	Altitude (masl)	Slope (%)
SC1	037°93'891"	08°033'45"	2426	4
SC2	037°94'389"	08°032'35"	2508	3
SC3	037°94'134"	08°030'78"	2498	2
SC4	037°91'180"	08°052'36"	2302	5
SC5	037°92'114"	08°043'58"	2401	3
SC6	038°02'572"	08°038'63"	2603	5
SC7	038°02'377"	08°038'23"	2563	5
SD1	039°51'934"	07°075'65"	2819	4
SD2	039°51'900"	07°072'28"	2832	5
SD3	0390 52'387"	07°066'39"	2790	3
SD4	039°52'450"	07°071'01"	2768	2
SD5	039°52'714"	07°080'40"	2719	5

SC1 Goha 1, SC2 Goha 2, SC3 Goha 3, SC4 Aftir, SC5 Abret, SC6 Kechot, SC7 Moche, SD1 Doyomarufa 1, SD2 Doyomarufa 2, SD3 Tulu, SD4 Weni, SD5 Ketasire

2004). Available water holding capacity (AWHC) was calculated from the difference between moisture content at FC and PWP. Soil pH measured potentiometrically in H₂O and 1 M KCl solution at the ratio of 1:2.5 for soil:water and soil:KCl solutions using a combined glass electrode pH meter (Van Reeuwijk 1992). The soil lime requirement (LR) was determined by Shoemaker, McLean and Pratt (SMP) single buffer procedure (Shoemaker et al. 1961). Cation exchange capacity (CEC) of the soils was determined by making use of the method suggested by Lavkulich (1981). Exchangeable calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) were determined by saturating the soil samples with 1 M NH₄OAc solution at pH 7.0. Then, Ca and Mg were determined by using atomic absorption spectrophotometer (AAS) while exchangeable Na and K were measured by flame photometer from the same extract. Exchangeable acidity was determined by saturating the soil samples with 1 M KCl solution and titrating with 0.02 M NaOH as described by Rowell (1994).

Total nitrogen was analyzed using the micro-Kjeldahl digestion followed by ammonium distillation and titration method (Bremner 1965). Organic carbon was determined by the dichromate oxidation method as described by Walkley and Black (1934). Available P was determined by different techniques: Bray-I P (by shaking the soil samples with an extracting solution of 0.03 M NH₄F in 0.1 M HCl for 1 min (Bray and Kurtz 1945) and Mehlich 3 P (by shaking the soil samples with an extracting solution of 0.2 M CH₃COOH + 0.25 M NH₄NO₃ + 0.015 M NH₄F + 0.013 M HNO₃ + 0.001 M EDTA for 5 min) (Mehlich 1984). Total soil P was determined using the method stated by Olsen and Sommers (1982).

Soil P fractionation

For P fractionation study, 30 ml of 1 M NH_4Cl was added in centrifuge tube containing 0.5 g of soil equilibrated for 16 h followed by centrifugation, and then the inorganic P was determined from the extract. To the remaining soil in the tube, 30 ml of 0.5 M NaHCO_3 was added and shaken for same period as before, in order to determine inorganic P and total P extracted by NaHCO_3 . The soil in the tube was allowed to interact with 30 ml of 0.1 M NaOH . Then the solution was shaken for 16 h, and centrifuged for determination of inorganic P from the extract. In the fractionation scheme total P in the NaOH extract was determined by perchloric acid digestion of the aliquot sample. Subsequently, 30 ml of 0.1 M NaOH was added into the tube containing the soil and sonicated for 2 min at 75 W for the determination of inorganic and total P in the sonicated NaOH extract. The remaining soil was treated with 1 M HCl followed by shaking and centrifugation of the soil containing 30 ml of 1 N HCl in order to determine the inorganic P in the HCl extract. Finally, the soil was digested with a mixture of concentrated HNO_3 and HClO_4 acids in order to determine the residual P. Accordingly, the P fractions were successively extracted with 1 M NH_4Cl (available Pi), 0.5 NaHCO_3 (labile Pi and Po adsorbed on the soil surface), 0.1 M NaOH (moderately labile Pi and Po held more strongly by Chemisorption to surfaces of Al and Fe oxides), Sonicate + 0.1 M NaOH (Pi and Po adsorbed within surfaces of Al and Fe oxides of soil aggregates-occluded P), 1 M HCl (P associated to Ca, derived from primary mineral-apatite) and a mixture of HNO_3 and HClO_4 (residual P-non-labile, stable Po forms and relatively insoluble Pi forms) as described by Hedley et al. (1982) and modified by Chen et al. (2000).

The oxalate extractable P, Al and Fe (P_{ox} , Al_{ox} and Fe_{ox}) were determined with 0.05 M ammonium oxalate [$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, pH 3.3] in the dark (Mckeague and Day 1966). Citrate bicarbonate dithionite-extractable Fe and Al (Fe_{d} and Al_{d}) were determined by the method of Mehra and Jackson (1960). Degree of P saturation was determined from total phosphorous sorption capacity (PSC_t) which is alienated into P occupied sites and remaining P sorption capacity (PSC_r). The amount of P sorbed on the PSC_t was evaluated from PSC_r and oxalate-extractable P (P_{ox}). Likewise, the PSC_r was calculated by multiplying an experimental P sorption capacity (F_r) by a factor of 2.75 (Maguire et al. 2001). Experimental P sorption capacity was determined by the standardized one-point short-term isotherm method (Bache and Williams 1971). Three gram of 2 mm soil was shaken with 60 ml of a 75 mg P l^{-1} as KH_2PO_4 equivalent to 1.5 g P kg^{-1} soil in 0.01 M CaCl_2 solution for 18 h with some drops of chloroform. The sorbed P (F_r) was calculated as the difference

between added P and P remaining in solution. Accordingly, the degree of P saturation (DPS) was determined as the percentage of the ratio of the different forms of P to the oxalate extractable Al and Fe (Al_{ox} and Fe_{ox}) as follows (Van der Zee et al. 1988):

DPS as the percentage of ratio of P_{ox} to PSC

$$\text{DPS } P_{\text{ox}} = (P_{\text{ox}}/PSC) \times 100$$

The P adsorption capacity (PSC, mmol kg^{-1}) of the soil was calculated and estimated by (Börling et al. 2001):

$$PSC = \alpha(Al_{\text{ox}} + Fe_{\text{ox}})$$

where Al_{ox} and Fe_{ox} are oxalate-extractable Al and Fe, and α is a scaling factor.

The α scale factor was estimated by:

$$PSC_t = PSC_r + P_{\text{ox}}$$

$$PSC_r = F_r * 2.75$$

$$\alpha = \frac{P_{\text{ox}} + PSC_r}{Fe_{\text{ox}} + Al_{\text{ox}}}$$

The F_r , PSC_r , PSC_t parameters and α scale factor were determined for the twelve soil samples and the mean α was used to calculate PSC and DPS.

Statistical analysis

Pearson's simple correlation coefficient was executed using Statistical Analysis System (SAS) version 9.1 (SAS (Statistical Analysis System) version 9.1. SAS Institute 2004) to evaluate the magnitudes and directions of relationship between the different P forms and other related soil properties.

Results and discussion

Characteristics of selected soil physical properties

The selected soil physical properties of the studied soils are indicated in Table 2. The textural class of the studied soils is predominantly clay. Generally, the clay content of the studied soils ranged from 36.6 to 49.8% and the highest clay content was recorded from SC3 soil and the lowest was obtained from SD3 soil. This difference in clay content could be attributed to the variability in the degree of weathering of the soils. The bulk density values ranged from 1.11 to 1.32 g cm^{-3} with a mean value of 1.21 g cm^{-3} and the bulk density values of the studied soils were found to be within the normal range suggested for clay soils, which ranges from 1.0 to 1.6 g cm^{-3} (Aubertin and Kardos 1965). The observed variability in bulk density among the studied soils might be due to differences in organic matter content of the soils. Moreover, potential root restriction of the soils is

Table 2 Selected physical properties of the soils studied

Sampling sites	Particle size distribution (%)			Textural class	Bulk density (g cm ³)	Water content at (%)		AWHC (%)
	Sand	Silt	Clay			FC	PWP	
SC1	23.2	28.6	48.2	Clay	1.32	31.00	19.60	11.40
SC2	22.8	32.6	44.6	Clay	1.25	32.25	22.25	10.00
SC3	23.2	27.0	49.8	Clay	1.29	31.00	20.55	9.65
SC4	19.4	34.0	46.6	Clay	1.22	31.95	21.75	10.20
SC5	14.8	37.2	48.0	Clay	1.21	31.65	20.90	10.75
SC6	19.6	37.0	43.4	Clay	1.24	32.90	22.50	10.40
SC7	22.0	33.0	45.0	Clay	1.24	32.70	21.80	10.90
SD1	29.6	32.6	37.8	Clay	1.13	31.60	21.60	10.00
SD2	23.8	32.6	43.6	Clay	1.16	33.00	22.70	10.30
SD3	29.0	34.4	36.6	Clay loam	1.11	39.15	22.20	16.95
SD4	26.8	29.0	44.2	Clay	1.17	38.10	25.11	12.99
SD5	29.2	32.6	38.2	Clay loam	1.16	32.31	20.72	11.59

SC1 Goha 1, SC2 Goha 2, SC3 Goha 3, SC4 Aftir, SC5 Abret, SC6 Kechot, SC7 Moche, SD1 Doyomarufa 1, SD2 Doyomarufa 2, SD3 Tulu, SD4 Weni, SD5 Ketasire

presumed to be less as the bulk densities are less than 1.4 g cm⁻³ (Hazelton and Murphy 2007). The soil water content at FC ranged from 30.2 to 39.2% with mean value of 33.1%. According to the result obtained from FC and PWP measurements, soil samples collected from Dinsho district showed relatively higher water retention compared with soil samples collected from Cheha. This difference could be attributed to the relatively higher organic matter content of the former. The PWP and AWHC ranged from 19.6 to 25.1 and 9.7 to 16.9% with mean values of 21.8 and 11.3%, respectively.

Soil pH, buffer pH and lime requirements

The pH (H₂O) values of the soils varied between 4.65 and 5.45 (Table 3). Based on the rating suggested by Jones (2003), 58% of the sampled soils were found to be very strongly acidic while 42% could be considered as strongly acidic. The pH (KCl) values of the studied soils varied from 3.98 to 4.46. The pH measured in potassium chloride solution was lower than pH measured in water for all the soil samples. The greater amount of exchangeable Al (0.21–1.54 cmol_c kg⁻¹) at the exchange sites might have contributed for the lower pH (KCl) value in solution of the studied soils. The finding of the present

Table 3 Soil pH, buffer pH and lime requirements

Sampling sites	pH			ΔpH	LR (tons CaCO ₃ ha ⁻¹)	
	H ₂ O	KCl	Buffer		KCl	pH (6.0)
SC1	4.65	3.98	5.11	0.66	9.20	11.50
SC2	4.79	4.05	5.41	0.74	7.80	9.60
SC3	4.73	4.04	5.20	0.68	8.70	10.70
SC4	4.81	4.10	5.31	0.71	8.20	10.00
SC5	5.13	4.22	5.61	0.90	6.70	8.20
SC6	4.76	4.12	5.30	0.64	8.20	10.00
SC7	4.91	4.09	5.31	0.82	8.20	10.00
SD1	5.30	4.38	6.20	0.92	3.70	4.60
SD2	5.01	4.21	6.11	0.79	4.10	5.00
SD3	5.12	4.29	6.51	0.83	2.10	2.60
SD4	5.36	4.42	6.31	0.94	3.30	4.00
SD5	5.45	4.46	6.41	0.99	2.80	3.40
Mean	5.00	4.20	5.73	0.79	6.08	7.47

LR lime requirements, SC1 Goha 1, SC2 Goha 2, SC3 Goha 3, SC4 Aftir, SC5 Abret, SC6 Kechot, SC7 Moche, SD1 Doyomarufa 1, SD2 Doyomarufa 2, SD3 Tulu, SD4 Weni, SD5 Ketasire

study concurs with previous reports which described that the pH measured in chloride solution is lower than pH measured in water because of the larger amount of H^+ ion forced to soil solution when Al^{3+} or Fe^{3+} are replaced by K^+ on the exchange sites (Kissel and Vendrell PF Isaac 2004; Asmare et al. 2015). According to USDANRCS (2004) report, the numerical difference in the values of pH measured in KCl and H_2O is referred to as the delta pH (ΔpH). When this difference is negative, the colloid has a net negative charge, and when positive, it has a net positive charge. The ΔpH value obtained for the studied soil samples indicates that the colloid has a net positive charge. The highest difference between pH- H_2O and pH-KCl was found for soil sample SD5 from Dinsho (0.99 pH units) and the lowest (0.66 pH units) was for the soil sample SC1 from Cheha district. The variation in abundance of exchangeable Al which ranged from 0.21 to 1.54 $cmol_c kg^{-1}$ might be a possible rationale for the disparity of ΔpH among soils of the study area.

The hydrogen ion (H^+) concentration that exists on the soil colloids (buffer pH) was evaluated for soil samples and varied between 5.11 and 6.51 pH units. The LR values, as determined by the SMP single buffer method to raise the pH of the soils to target pH values of 6.0 and 6.5 are presented in Table 3. Consequently, the amount of lime required to raise the respective pH values of the studied soils to the target pH of 6.0 and 6.5 ranged from 2.10 to 9.20 t $CaCO_3 ha^{-1}$ and 2.60–11.50 t $CaCO_3 ha^{-1}$ respectively. Therefore, the soils of the study area need substantial amount of lime to alleviate the acidity problem and increase the productivity of acid sensitive crops. Likewise, the output of the correlation matrix in

Table 8 shows a strong significant and negative correlation between pH and LR ($r = -0.88$, $P \leq 0.01$). Hence, the lower the pH value of the soil, the higher is the amount of liming material needed to increase the pH to a suitable range for sustainable production of acid sensitive crops.

Exchangeable cations and exchange properties

The cation exchange capacity of soils of Cheha district (SC1–SC5) showed a relatively lower range (21.15–31.54 $cmol_c kg^{-1}$) than soils from Dinsho district (SD1–SD5) (31.14–36.03 $cmol_c kg^{-1}$) (Table 4). According to Hazelton and Murphy (2007) the CEC of the soils were in the range of moderate to high values. The variation in CEC among the soils might be due to the difference in OM content, clay mineralogy between some soil forms and the pH range in which the soils exist. In agreement with the current study, Peinemann et al. (2000) declared that clay and organic matter are the main sources of CEC and the more clay and organic matter (humus) a soil contains, the higher is its CEC.

As per the ratings suggested by Hazelton and Murphy (2007), the exchangeable Na was in the range of very low to moderate in the study area. Whereas the exchangeable Ca and Mg were in the range of low to moderate for soils from Cheha and moderate to high for Dinsho district. In Cheha district, the variation in concentration levels of exchangeable K among the soils followed the same trend with that of Ca and Mg whereas it was moderate in Dinsho district. Barber (1984) indicated that the critical level of exchangeable K for optimum crop production is 0.38 $cmol_c kg^{-1}$. The status of exchangeable bases in soil from Dinsho was slightly higher than soils from Cheha. The

Table 4 Exchangeable cations and exchange properties

Soil	Exchangeable cations and CEC ($cmol_c kg^{-1}$)									Percent saturation (%)			K/Mg
	Ca	Mg	K	Na	TEB	exAc	exAl	CEC	ECEC	PACs	PAIS	PBS	Ratio
SC1	4.21	0.98	0.20	0.04	5.43	2.61	1.54	19.15	10.56	13.63	8.04	28.36	0.20
SC2	8.45	2.23	0.26	0.09	11.03	2.18	0.82	23.88	17.77	9.13	3.43	46.19	0.12
SC3	4.91	1.11	0.25	0.09	6.36	2.38	1.29	20.88	11.12	11.40	6.18	30.46	0.23
SC4	7.86	1.69	0.28	0.11	9.96	1.57	0.35	26.98	14.09	5.82	1.30	36.92	0.17
SC5	8.95	2.38	0.30	0.11	11.74	1.09	0.42	22.81	15.39	4.78	1.84	51.47	0.13
SC6	6.40	1.42	0.29	0.12	8.25	2.11	0.43	29.54	12.93	7.14	1.46	27.93	0.20
SC7	9.42	2.05	0.32	0.16	11.92	2.29	0.49	25.03	16.77	9.15	1.96	47.62	0.16
SD1	13.30	2.87	0.34	0.25	16.76	0.59	0.28	33.70	18.73	1.75	0.83	49.73	0.12
SD2	9.29	2.14	0.32	0.21	11.97	0.87	0.32	29.80	14.44	2.92	1.07	40.17	0.15
SD3	14.78	4.39	0.41	0.38	19.96	0.62	0.24	34.03	25.95	1.82	0.71	58.65	0.09
SD4	10.87	3.52	0.34	0.20	14.93	0.56	0.22	29.14	17.87	1.92	0.75	51.24	0.10
SD5	12.90	3.77	0.37	0.23	17.27	0.59	0.21	30.66	21.25	1.92	0.68	56.33	0.10
Mean	9.28	2.38	0.31	0.17	12.13	1.46	0.55	27.13	16.41	5.95	2.35	43.75	0.13

TEB total exchangeable bases, exAc exchangeable acidity, exAl exchangeable Aluminum, CEC cation exchange capacity of soil, ECEC Effective cation exchange capacity, PACs percent acid saturation, PAIS percent aluminium saturation, PBS percent base saturation

likely reason for the observed variation in exchangeable bases could be the difference in soil pH and organic carbon content. It has been reported that soil pH and soil OC are regarded as the main factors influencing the variation in exchangeable cations (YuGe et al. 2013). Based on this critical level, except soil from SD3 the entire soil samples from both districts had an exchangeable K concentration of below the optimum level. Other study results have also reported about the insufficiency of K in acidic soils of Ethiopia (Mesfin et al. 2014; Asmare et al. 2015). The persuasive reason for the scarcity of exchangeable K could be attributed to the higher intensity of weathering and intensive cultivation.

The distributions of these basic cations in the exchange complex followed the order of $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$. The variations in the order of distribution of these cations could be related to the charge density in which the divalent cations (Ca^{2+} and Mg^{2+}) have higher affinity towards the colloidal surface than monovalent ions (K^+ and Na^+) (Alemu et al. 2016). Similar order of distribution of these cations was reported by several studies (Teshome et al. 2013; Asmare et al. 2015; Okubay et al. 2015). Antagonistic effects are known to exist between Mg and K (FAO 2006) when disproportionate quantities of the cations are present in soil. In this study, the ratio was evaluated and ranged from 0.09 to 0.23 (Table 4). According to the recommendation noted by Abayneh and Ashenafi (2006), potassium is deficient for field crops (5:1), vegetables (3:1) and fruits (2:1) in soils from Dinsho and Cheha districts. On the other hand, according to the ratio (0.7:1) suggested by Loide (2004), the clay textured soils of the study area showed Mg induced K deficiency. The observed order ($\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$) of cations concentration in the exchange complex could also substantiate the existence of Mg induced K deficiency.

The percentage base saturation (PBS) of the studied soils varied from 25.66 to 55.39% (Table 4). Based on the rating suggested by Hazelton and Murphy (2007), about 50% of the soils had a PBS value that is within the range of low (25.66–34.35%) to moderate (42.64–47.3%). The possible reason for the low PBS value of soils might be the loss of soluble basic cations through leaching and erosion. Research results made on other Ethiopian soils also revealed low values of PBS in acidic soils possibly due to intensive cultivation, enhanced loss of basic cations through leaching and erosion (Getachew and Heluf 2007; Mohammed et al. 2016).

The exchangeable acidity (exAc) and exchangeable aluminium (exAl) of the studied soils were found to be in the range of 0.56–2.61 and 0.21–1.54 $\text{cmol}_c \text{ kg}^{-1}$, respectively (Table 4). Meanwhile, the acid saturation (PACs) and Al saturation (PAIs) ranged from 1.75 to 13.63 and 0.68 to 8.04%, respectively. Variability was observed among soils

of the two districts in terms of exAc and exAl. The disparity in these values between the two locations might be due to the difference in soil CEC. In agreement with the present study, Al Baquy et al. (2017) attributed the difference in exAc and exAl to the difference in soil type, organic matter content and CEC of soils.

The correlation result in Table 8 shows that exAc and exAl were negatively correlated with pH, whereas significant positive correlation was observed between pH and extractable P (Mehlich 3-P). This indicates that the lower the pH of the soil, the higher will be the concentrations of exAl and exAc. Strong and positive correlation was also observed between LR of soils and exAl ($r = 0.71$, $P \leq 0.01$) and exAc ($r = 0.94$, $P \leq 0.01$). The result of this correlation study is concomitant with what was reported by Asmare et al. (2015) and indicates that higher dose of lime is required for soils with higher exchangeable Al and acidity. Therefore, pH, amount of exchangeable acidity and Al can provide preliminary information on LR of soils. Cation exchange capacity (CEC) was negatively correlated with exAc and exAl [$r = -0.78$, $P \leq 0.01$ and $r = -0.83$, $P \leq 0.01$]. This correlation indicates that soils with high exAc and exAl have lower CEC. This could be an indication of weaker desorption of P associated with oxyhydroxides of Fe and Al for soils having higher exchangeable Al and exchangeable acidity. Furthermore, the strong negative correlation between CEC of soil and clay content [$r = -0.67$, $P \leq 0.05$] reveals that the difference in CEC can be explained by the difference in clay contents among some soils (De Kimpe et al. 1979).

Organic carbon, total nitrogen, available and total phosphorus

As the result of soil analysis for OC, total N, C:N ratio, available and total P contents of the studied soils illustrated the percentage of organic carbon and total nitrogen in the soils of Cheha district varied from 1.58 to 2.11 and 0.17–0.19%, respectively and were appeared to be higher values compared to soils of Dinsho district (2.15–2.58 and 0.19–0.22% respectively) (Table 5). In general, as per the rating suggested by Hazelton and Murphy (2007), OC content of soils of the study area were within the range of moderate (1.00–1.80%) to high (1.80–3.00%). Even though soils of the study area have been intensively tilled, the crop residue that is often left after crop harvest, a common practice in the study area, might have contributed to this level of organic carbon in the soils. Furthermore, high clay content, which controls organic matter enrichment ability of soils, could also be another reason for the moderate to high organic carbon content in soils of the study area. The variation in percent clay fraction, management practices and intensity of cultivation might have contributed for the slight disparity in OC matter

Table 5 Organic carbon (OC), total nitrogen (TN), available and total phosphorus (P) OC=organic carbon, TN=total nitrogen, C:N=carbon to nitrogen ratio

Sampling sites	OC (%)	TN	C:N	Mehlich 3 P (mg kg ⁻¹)	Bray 1 P	Total P
SC1	1.58	0.17	9.55	8.90	8.54	648.62
SC2	1.86	0.17	11.24	10.14	9.65	806.55
SC3	1.93	0.19	9.89	9.73	8.95	708.11
SC4	1.97	0.18	11.23	9.15	7.78	728.20
SC5	2.11	0.19	11.38	10.79	7.61	693.18
SC6	2.00	0.18	11.43	13.94	7.90	789.43
SC7	1.91	0.19	10.32	10.38	7.61	736.77
SD1	2.39	0.19	12.89	23.26	19.36	1094.25
SD2	2.37	0.20	11.85	18.33	16.15	1022.80
SD3	2.58	0.22	11.98	24.35	21.41	1175.80
SD4	2.56	0.21	12.17	22.29	20.24	1045.60
SD5	2.52	0.21	12.29	21.34	20.12	1130.15
Mean	2.15	0.19	11.35	14.84	12.59	881.62

SC1 Goha 1, SC2 Goha 2, SC3 Goha 3, SC4 Aftir, SC5 Abret, SC6 Kechot, SC7 Moche, SD1 Doyomarufa 1, SD2 Doyomarufa 2, SD3 Tulu, SD4 Weni, SD5 Ketasire

content of the soils. Many studies confirm that carbon retention in soil is influenced by crop management systems, such as crop rotation (Saljnikov et al. 2004), tillage (Saljnikov et al. 2009), residue management (Rasmussen et al. 1980) and fertilization and fertility (Saljnikov et al. 2005).

In addition to the above-mentioned reasons, the high silt plus clay content of the soils might have contributed to the moderate to high organic carbon content. Numerous studies have described the positive relationship between clay (or clay + silt) content and soil organic matter (OM) in soils from different sites in the tropics (Xie and Steinbergera 2001). These studies have shown that clay-silt content is a relatively important determinant of soil OM or total OC level in soils. As a case in point, studies in Spanish semi-arid Mediterranean bare soils have shown different soil OM mineralization rates for different soil textures (GarcõÂa and HernaÂndez 1996) and indicated the importance of the physical and chemical properties, which might have played an important role in soil water availability. It has also been suggested that fine particles with high surface activity may physically and chemically protect soil OM from decomposition by binding strongly and create physical barrier to protect microbial access (Hassink et al. 1993).

As per the rating suggested by Hazelton and Murphy (2007), the total nitrogen (TN) content of soils in the study area was within the range of medium (0.17–0.22%). However, medium TN level in soils of the study area could not be taken as a guaranty for adequate availability of N to plants. Therefore, in order to maintain or enhance the nitrogen status of the soils imbalanced use of

fertilizers, nutrient mining through intensive cultivation and crop residue removal should be avoided. The slight variation within sites in particular might be associated to the variability of soils OC content.

The C:N ratio of the studied soils varied between 9.54 and 12.89. According to the recommendation made by Newey (2006), 17 and 83% of the studied soils were categorized under soils having very low (<10) and low (10–15) C:N ratio respectively indicating the fast decomposition of OM in the studied soils. Abera and Belachew (2011) investigated soils from cultivated lands of Bale Zone including Dinsho and reported a C:N ratio ranging from 12.57 to 13.53, which is comparable with the findings of the current study.

Total P content in the surface soil samples ranged from 648.62 mg kg⁻¹ in the SC1 soil collected from Cheha farmers' field to 1175.8 mg kg⁻¹ in the SD3 soil collected from the Dinsho district (Table 5).

The amount of P extracted with Mehlich-3 and Bray and Kurtz-1 ranged from 8.90 to 25.75 and 8.54 to 22.81 mg kg⁻¹ respectively (Table 5). However, there was a considerable variation among soils of the districts in terms of available P (Table 5). This may be ascribed to the presence of higher concentrations of oxyhydroxides of Al and Fe which are responsible for fixation of P at the exchange sites for soils of Cheha district compared to soils of Dinsho. As per the rating established by EthioSIS (2014), the Mehlich-3 extractable P of the studied soils in Cheha fall in the very low range (0–15 mg kg⁻¹), whereas soils of Dinsho exhibited low (15–30 mg kg⁻¹) Melich-3 P. Similarly, the rating proposed by Horneck et al. (2011) also indicated the predominantly low available P for

Cheha (<20 mg kg⁻¹ for Bray-1 P) and low to medium P for Dinsho soils (<20 mg kg⁻¹ Bray 1 P 20–40 mg kg⁻¹). The insufficiency may be due to acidic reaction in which free oxides of Fe and Al tend to fix P on the exchange sites. Reports of low available P in many parts of Ethiopian soils have been documented possibly due to the impacts of fixation, abundant loss by crop harvest and erosion (Asmare et al. 2015; Wolde et al. 2015).

The amounts of P extracted from studied soils decreased in the following order: Bray and Kurtz-1 < Mehlich 3. The differences among the P extraction methods probably arose from the fact that plant available P in the soil is not from a prudent fraction but from a continuum of fractions. Thus extracting agents preferentially extract P from different fractions depending on their reactions with soil components involved in P sorption. Furthermore, each extracting solution has a different ability to extract varying segment of soil P because they were embattled at different pools of soil P (Zhang et al. 2004). Extractable P by the Mehlich-3, and Bray and Kurtz-1 in this study were correlated among themselves (Table 8). The correlation coefficient (r) was appeared to be 0.96 indicating that any of these extractants could be used to estimate P extractability (available P) in soils. In spite of the strong positive correlations among these extractants, Mehlich-3 extraction method could be used as a substitute over the former conventional extraction method Bray and Kurtz-1 (1945) because of its capability to generate opportunities for optimization of laboratory management and cheaper procedure (Mesfin et al. 2014).

As per the ratings of Murphy (1968), the studied soils had a total P content that ranges from medium

(501–750 mg kg⁻¹) to very high (>1000 mg kg⁻¹). A gamut of results have been produced by several scholars on the total P contents of several soils of Ethiopia from various localities: 200–800 mg kg⁻¹ (Eylachew 1987), 185 to 1981 mg kg⁻¹ (Tekalign and Haque 1991), 226–1570 mg kg⁻¹ (Duffera and Robarge 1996), 553–976 mg kg⁻¹ (Achalal et al. 2012) and 685–1432 mg kg⁻¹ (Asmare et al. 2015). The result also indicates that the total P content of the studied soils was much higher than 200 mg kg⁻¹ which was the value indicated by Olsen and Engelstad (1972) as the maximum total P value for highly weathered tropical soils. The total P content determined in this study was very far from a report made on soils from northwestern highlands of Ethiopian for which the total P content ranged from 6900 to 24,000 mg kg⁻¹ with a mean value of 12,275 mg kg⁻¹ (Birru et al. 2003). However, the normal range of total P in soils is 100–3000 mg kg⁻¹ (Frossar et al. 2000). Viewing the total P contents of some tropical soils, Asmare et al. (2015) observed that the total P contents of Ethiopian soils were not as poor as the other tropical soils. Surprisingly, despite the medium to high contents of total P, the available P contents of the studied soils were in low to very low range (Table 5).

Inorganic and organic phosphorus fractions

The amount, distribution and sum of various P fractions of the soils studied are presented in Table 6. The relative abundance of P forms was in the following order: Res-P > NaOH-Po > NaOH-Pi > HCl-P > (NaOH-Pi)sn > (NaOH-Po)sn > NaHCO₃-Po > NaHCO₃-Pi > NH₄Cl in soils from Cheha district, whereas

Table 6 Inorganic and organic P fractions and their distribution

Sites	NH ₄ Cl-Pi	NaHCO ₃ -Pi	NaHCO ₃ -Po	NaOH-Pi (mg kg ⁻¹)	NaOH-Po	(NaOH-Pi)sn	(NaOH-Po)sn	HCl-P	Resl-P	Sum ∑P
SC1	1.93	2.43	2.74	135.31	160.41	31.74	35.31	71.32	164.15	606.34
SC2	3.23	3.72	3.91	139.71	196.87	40.93	85.17	86.89	216.25	776.68
SC3	1.69	2.45	2.78	130.45	167.59	33.9	36.28	77.01	185.18	637.33
SC4	2.53	2.06	3.63	129.66	180.82	37.76	76.68	77.88	187.30	698.32
SC5	2.32	2.59	2.97	124.13	168.69	36.33	72.85	75.57	177.55	663.00
SC6	2.59	2.72	4.04	138.82	190.94	44.24	79.32	83.55	213.41	759.63
SC7	2.06	2.11	3.85	131.76	182.48	38.10	77.6	77.95	190.94	706.85
SD1	5.90	7.61	9.35	89.65	154.49	28.28	72.29	379.32	317.24	1064.13
SD2	3.90	5.12	5.63	82.76	144.32	23.42	70.50	354.86	301.16	992.67
SD3	7.40	7.75	8.95	97.37	168.11	30.40	77.76	407.26	340.73	1145.73
SD4	5.90	6.51	6.53	86.63	147.56	27.01	69.03	362.64	303.60	1015.41
SD5	6.90	7.14	7.97	96.12	161.64	31.22	72.71	391.69	324.87	1100.26
Mean	3.86	4.35	5.19	115.20	168.66	33.61	68.79	203.83	243.53	847.20

NH₄Cl-P ammonium extractable P, NaHCO₃-Pi sodium bicarbonate extractable inorganic P, NaHCO₃-Po sodium bicarbonate extractable organic P, NaOH-Pi sodium hydroxide extractable inorganic P, NaOH-po sodium hydroxide extractable organic P, (NaOH-Pi)sn sonicated sodium hydroxide extractable inorganic P, (NaOH-po)sn sonicated sodium hydroxide extractable organic P, HCl-P hydrochloric acid extractable P, ∑P sum of P fractions

HCl-P > Res-P > NaOH-Po > NaOH-Pi > (NaOH-Po) sn > (NaOH-Pi)sn > NaHCO₃-Po > NaHCO₃-Pi > NH₄Cl was the order for soils of Dinsho district. The labile P (Pi in NH₄Cl+Pi and Po in NaHCO₃) varied between 1.1 and 2.2%, the moderately labile P (Pi + Po in NaOH), varied between 22.9 and 48.8%, the occluded P (Pi + Po in Sonicate + NaOH) varied between 9.4 and 16.5%, the P associated to Ca (HCl-Pi) varied between 11.0 and 35.8% and the residual-P varied between 26.8 and 30.3%. It could be concluded that soils of Cheha district are dominated by Res-P (occluded Pi associated with the remaining inorganic minerals and non extractable Po) followed by NaOH extractable P (NaOH-Po and NaOH-Pi). On the other hand, it was HCl-P that dominates P fractions in soils of Dinsho district indicating (Ca)-Pi mineral were very prominent in these soils. Similar work has been conducted by Duffera and Robarge (1996) who characterized organic and inorganic P in the highland Plateau Alfisols of Ethiopia and reported that the relative abundance in cultivated farmers' fields was in the ensuing order: Residual P > NaOH-Po > NaOH-Pi > Sonic-Po > NaHCO₃-Po > Resin-P = Sonic-Pi > NaHCO₃-Pi = HCl-P.

In the studied soils considerable proportions of P (NaHCO₃-P_o) that may be easily mineralized were noticed and ranged from 36.00 to 48.00% indicating the significance of organically bound P as a source of labile, plant available P (Duffera and Robarge 1996). In this regard Cross and Schlesinger (1995) suggested that the bicarbonate Po as a percent of the total labile forms of P (resin Pi, bicarbonate Pi, and bicarbonate Po) represents a minimum index of the proportion of P that may be easily mineralized through biological processes. In clayey soils of Dinsho district, the sum of NH₄Cl-P, NaHCO₃-P

and NaOH-P was smaller than oxalate-P, indicating that the oxalate method extracted some residual P that contained insoluble inorganic P associated with Ca minerals and a highly resistant pool of inorganic occluded P and organic P (Table 6).

The result of the present study also revealed that the studied soils from Cheha district were dominated by moderately labile P fractions, accounting for 43.3–48.8% of the total P, whereas NH₄Cl-P was the lowest in concentration, 0.3–0.4% of the total P. On the other hand, the studied soils of Dinsho district were dominated by HCl-P, 35.6–35.8% of the total P, while NH₄Cl-P was the least in proportion (0.4–0.7%). Residual-P, which accounted for about 29.5–30.3% (Dinsho) and 26.8–28.1% (Cheha) of the total P, was the second higher fraction followed by moderately labile-P (22.9–23.4%) and occluded-P (11.0–16.5%) fractions, respectively (Table 6). The relatively higher abundance of Al and Fe bound P could be associated with the presence of variable Al and Fe contents in soils at various stages of relative development and their reaction with soil P (Kiflu et al. 2017). On the other hand, the P associated to Ca (HCl-Pi) varied between 11.0 and 35.8%, which could be attributed to the difference in Ca content of the studied soils and the residual-P varied between 26.8 and 30.3% (Table 7).

A noticeable variability in proportion of P fractions in the order of their relative abundance in the studied soils of the two districts was observed. The management practices being used by farmers and the extent of weathering of soils might have contributed for the variations in concentrations and distributions of different forms of P. As an illustration, NaOH extractable P in soils of Cheha district, which accounted for about

Table 7 Oxalate and dithionite citrate bicarbonate extractable Al, Fe and P

Sites	Al _{ox} (mmol kg ⁻¹)	Fe _{ox}	P _{ox}	PSC	P _{ox} ^a DPS (%)	Al _d	Fe _d (mmol kg ⁻¹)	Al _d /Al _{ox}	Fe _{ox} /Fe _d	Scaling factor (α)
SC1	152.37	97.70	5.51	133.54	4.13	173.33	633.66	20.6	0.24	0.62
SC2	139.07	78.54	6.17	116.20	5.31	151.85	478.04	12.78	0.29	0.62
SC3	145.96	88.18	5.82	125.03	4.65	164.07	551.61	18.11	0.27	0.57
SC4	130.07	79.96	6.07	112.16	5.41	144.07	456.25	14.00	0.29	0.59
SC5	126.37	77.46	7.07	108.85	6.49	149.26	491.61	22.89	0.26	0.61
SC6	131.85	76.39	7.32	111.20	6.58	161.11	476.61	29.26	0.28	0.62
SC7	134.37	81.75	6.45	115.41	5.59	150.74	498.75	16.37	0.27	0.56
SD1	90.00	66.21	9.74	83.42	11.68	119.26	313.93	29.26	0.29	0.42
SD2	91.85	82.29	8.26	92.99	8.88	112.19	355.54	20.33	0.26	0.45
SD3	71.89	51.75	12.29	66.02	18.62	134.07	281.07	62.19	0.26	0.45
SD4	90.37	59.43	8.39	79.99	10.49	128.52	307.14	38.15	0.29	0.44
SD5	78.15	63.36	10.35	75.56	13.69	124.07	291.43	45.93	0.27	0.44
Mean	115.19	75.25	7.79	101.70	8.46	142.71	427.97	27.52	0.27	0.53

Al_{ox} oxalate extractable Al, Fe_{ox} oxalate extractable P, P_{ox} oxalate extractable P, PSC phosphorous sorption capacity, DPS P saturation with respect to P_{ox}, Al_d dithionite extractable Al, Fe_d dithionite extractable Fe

59.9% of the total P, was in higher proportion compared to the 32.6% in soils of Dinsho district. Likewise, HCl extractable P, which was 11.4% of the total P in Cheha soils, was much lower than the 35.7% in Dinsho soils. This could be due to the dominance of free Fe and Al oxides and higher extent of weathering in soils of Cheha district compared to Dinsho soils as indicated in Table 7.

The dependence of different forms of P upon the physical and chemical properties of the soil was tested using correlation analysis (Table 9). Thus, $\text{NH}_4\text{Cl-P}_i$, $\text{NaHCO}_3\text{-Po}$ and $\text{NaHCO}_3\text{-Pi}$ were positively and significantly correlated with pH, CEC, OC and available P but negatively and significantly correlated with exAc and exAl. The other forms of P, such as NaOH-Po and NaOH-Pi , were negatively and significantly correlated with pH, CEC, OC, and available P (Mehlich 3 P). Furthermore, the present study revealed that $\text{NH}_4\text{Cl-P}_i$ ($r = -0.87$, $P \leq 0.01$), $\text{NaHCO}_3\text{-Pi}$ ($r = -0.85$, $P \leq 0.01$), $\text{NaHCO}_3\text{-Po}$ ($r = -0.89$, $P \leq 0.01$) and HCl-P ($r = -0.82$, $P \leq 0.01$) were negatively and significantly correlated with clay content. It may be inferred that the concentrations and distributions of these P fractions are smaller in soils where there is high clay content. The outcome of the present study was found to be in agreement with the correlation result obtained by Duffera and Robarge (1996) whose result exhibited negative correlation between clay content and the readily available P fractions, the bicarbonate Pi and HCl extractable P for highland soils from Ethiopia.

The P contents in terms of the sum of P fractions in the surface soil samples ranged from 606.3 mg kg^{-1} in the SC1 soil collected from Cheha district to 1145.7 mg kg^{-1} in the SD3 soil collected from the Dinsho district indicating a closer similarity between total P determined through direct digestion technique and summation of the P fractions. In general, the sum of the various P fractions was within 4% of the total P content determined by the Olsen and Sommers (1982) approach, indicating that the fractionation procedure does account for almost all of the P present in the soils.

Oxalate and dithionite citrate bicarbonate extractable Al, Fe and P

The distribution of oxalate and dithionite citrate bicarbonate extractable Al and Fe oxides values of the studied soils are presented in Table 7. Accordingly, considerable variations among the studied soils with respect to DCB and oxalate extractable Al and Fe were observed. The disparity in relative abundance of aluminum and iron oxides in studied soils, which are the most important phosphate adsorbents in weathered acidic soils, might have contributed to the variations observed in extractable Al and Fe.

Substantial differences were observed between dithionite extractable Fe and Al in the soils. This might be due to the fact that the dithionite in the dithionite citrate bicarbonate procedure is a reducing agent and it might have reduced Fe^{3+} to Fe^{2+} and thereby increased the solubility of Fe. However, Al is not a redox sensitive element and hence treatment with reducing agents such as dithionite is not likely to cause much extraction of Al.

The differences between DCB-extractable Fe and Al oxides and oxalate-extractable Fe and Al oxides represent the amounts of extracted crystalline Fe (c-Fe) and Al (c-Al) oxides. There was a large amount of c-Fe (76.9–84.6% of total Fe). In contrast, c-Al content was low (8.4–46.4% of total Al) (Table 7). The observed variation in the amount of crystalline Fe and Al might be ascribed to the amount of organic matter present in the soil. In agreement with the results of the existing study, Kang et al. (2009) reported that organic matter in soil inhibits Al oxides crystallization. The oxalate extractable Al, and Fe values ranged from 1941.03 to 4113.99 mg Al kg^{-1} and from 2898 to 5471.2 mg Fe kg^{-1} were comparable with acid soils of northwestern highlands of Ethiopia that contained 3528–5432 mg Fe kg^{-1} 3699–4779 mg Al kg^{-1} (Asmare et al. 2015). However, these extractable forms were higher than acidic soils of European countries that are characterized by an average of 1835.2 Fe_{ox} kg^{-1} to 2349.8 mg Al_{ox} kg^{-1} (Roberto and Giampietro 2005). The ratio of $\text{Fe}_{\text{ox}}/\text{Fe}_d$ has been taken as an indicator of the maturity or crystallinity of free Fe oxides in soils (Blume and Schwertmann 1969). The value of the $\text{Fe}_{\text{ox}}/\text{Fe}_d$ for the studied soils ranged from 0.24 to 0.29. All the values of $\text{Fe}_{\text{ox}}/\text{Fe}_d$ ratio for studied soil samples were >0.1 , which indicates that poorly crystalline iron oxides are dominant in these soils (Fitzpatrick and Schwertmann 1982).

As it may also be seen in Table 7 the P_{ox} of the studied soils was ranged from 5.51 to 12.89 mmol kg^{-1} and were higher than acidic soils of West African soils which held 0.35 to 3.42 mmol P_{ox} kg^{-1} (Narteh and Sahrawat 1999). The observed difference in P_{ox} of the soils might be attributed to the variation in their poorly crystalline Fe and Al which are the most reactive fractions of soil iron and aluminum oxides.

The correlation matrix (Tables 8 and 9), Table 9 indicates that readily available P fractions (NH_4Cl , $\text{NaHCO}_3\text{-Pi}$ and $\text{NaHCO}_3\text{-Po}$) had a significantly negative relationship with Fe_{ox} [$(r = -0.89$, $P \leq 0.01$), $r = -0.82$, $P \leq 0.01$, $r = -0.84$, $P \leq 0.01$], Al_{ox} [$(r = -0.94$, $P \leq 0.01$), $r = -0.93$, $P \leq 0.01$, $r = -0.92$, $P \leq 0.01$] respectively. This result indicates that soils with high concentrations of free oxyhydroxides of aluminum and iron are deprived of NH_4Cl and NaHCO_3 extractable P. The negative relationship among oxalate and dithionite extractable metal oxides and readily available fractions of P is in agreement

Table 8 Correlation table for some soil properties

	Clay	pH	exAc	exAl	OC	Mehl 3P	Bra P	Fe _{ox}	Al _{ox}	Fe _d	PSC	DPS	P _{ox}
pH	-0.66*												
exAc	0.51	-0.90**											
exAl	0.65*	-0.72**	0.79**										
LR	0.81**	-0.88**	0.94**	0.71**									
OC	0.83**	0.88**	-0.94**	-0.79**									
M 3P	-0.82**	0.81**	-0.86**	-0.86**	0.93**								
Bra P	-0.80**	0.81**	-0.84**	-0.54	0.90**	0.96**							
Fe _{ox}	0.80**	-0.79**	0.81**	0.81**	-0.88**	-0.85**	-0.80**						
Al _{ox}	0.83**	-0.85**	0.93**	0.93**	-0.97**	-0.95**	-0.94**	0.86**					
Fe _d	0.99**	-0.85**	0.92**	0.92**	-0.96**	-0.92**	-0.90**	0.90**	0.97**				
PSC	0.85**	-0.86**	0.92**	0.92**	-0.93**	-0.95**	-0.93**	0.93**	0.98**	0.98**			
DPS	-0.88**	0.73**	0.81**	-0.81**	0.87**	0.91**	0.89**	-0.89**	-0.93**	-0.87**	-0.95**		
P _{ox}	-0.91**	0.75**	-0.82**	-0.82**	0.88**	0.92**	0.88**	-0.88**	-0.94**	-0.88**	-0.95**	0.99**	
CEC	-0.67*	0.66*	-0.78**	-0.78**	0.84**	0.87**	0.77**	-0.87**	-0.83**	-0.91**	0.86**	0.83**	0.86**

LR lime requirements, Mehl 3P Mehlich 3P, Bra P Bray 1 P, Ols P Olsen P, LR lime requirement, exAl exchangeable Al, exAc exchangeable Acidity, OC organic carbon, Alox, Feox, and Pox oxalate extractable Al, Fe, and P, respectively, PSC phosphorous sorption capacity, DPS degree of P saturation, Fed citrate dithionite bicarbonate extractable Fe

*Significant at 0.05 and **Significant at 0.01 probability levels, respectively

Table 9 Correlation table for fractions of P and some soil properties

	Clay	pH	exAc	exAl	OC	M 3P	Fe _{ox}	Al _{ox}	Fe _d	PSC	DPS	P _{ox}	CEC
NH ₄ Cl	-0.87**	0.82**	-0.84**	-0.84**	0.89**	0.94**	-0.89**	-0.94**	-0.93**	-0.96**	0.94**	0.94**	0.82**
NaHCO ₃ pi	-0.85**	0.81**	-0.84**	-0.84**	0.88**	0.96**	-0.82**	-0.93**	-0.90**	-0.92**	0.91**	0.91**	0.80**
NaHCO ₃ Po	-0.89**	0.78**	-0.82**	-0.82**	0.85**	0.95**	-0.84**	-0.92**	-0.91**	-0.92**	0.92**	0.93**	0.89**
NaOH Pi	0.05	-0.81**	0.89**	0.89**	-0.89**	-0.89**	0.64*	0.91**	0.86**	0.85**	-0.74**	-0.75**	-0.72**
NaOH po	-0.23	-0.55	0.60	0.60	-0.55	-0.57	0.19	0.56	0.43	0.46	-0.39	-0.39	-0.26
HCl p	-0.82**	0.81**	-0.87**	-0.87**	0.92**	0.97**	-0.77**	-0.96**	-0.92**	-0.93**	0.88**	0.89**	0.81**

LR lime requirements, Mehl 3P Mehlich 3P, Bra P Bray 1 P, Ols P Olsen P, LR lime requirement, exAl exchangeable Al, exAc exchangeable Acidity, OC organic carbon, Alox, Feox, and Pox oxalate extractable Al, Fe, and P, respectively, PSC phosphorous sorption capacity, DPS degree of P saturation, Fed citrate dithionite bicarbonate extractable Fe

*Significant at 0.05 and **Significant at 0.01 probability levels, respectively

with the general assumption that the higher the value of free oxides of aluminum and iron, the stronger is the binding capacity of the soil for P. Consequently, the amount of P desorbed (NH₄Cl-P, NaHCO₃-Pi and NaHCO₃-Po) from the exchange sites with increasing levels of these free oxides could be decreased. The bicarbonate Po had strong negative [(r = -0.91, P ≤ 0.01)] correlation with Fe_d, as it had positive and significant association [(r = 0.85, P ≤ 0.01) and (r = 0.89, P ≤ 0.01)] with OC and CEC, respectively. The correlation result of the present study is in agreement with what has been found by Tiessen et al. (1984) where organic P fractions were positively related to organic C despite the contrasting correlation result observed from bicarbonate Po and dithionite extractable Fe (Fe_d).

Extent of phosphorus saturation

As shown in Table 7, the degree of phosphorous saturation of the studied soils varied considerably ranging from 4.1 to 6.6 and 8.9–18.6% in Cheha and Dinsho districts respectively. The portions of soil exchangeable sites that were bound with P were greater for soils collected from different sampling sites of Dinsho as compared to soils collected from Cheha which had higher free metallic oxides. The extent at which the potential sites for P adsorption already occupied was designated by DPS (%). Accordingly, the highest DPS (18.6%) was recorded from Dinsho (SD3) and the lowest from Cheha (SC1) sampling site. Recent studies have shown that the degree of P saturation (DPS), as a function of the portion of the soil exchangeable sites that are bound with P (P sorbed) in relation to the number of

sites available for P binding capacity (PBC), is a good indicator of the soil's potential to release P (Hooda et al. 2000). Therefore, the variation in DPS of the studied soils may be attributed to the disparity among these soils in terms of the number of sites available for binding P. In view of the cut off point for loss of P due to runoff (Ige et al. 2005), all the samples showed DPS values lower than 20% indicating no risk of P loss from soil (Table 7). These low values might be attributed to the higher adsorption capacity of these soils.

Extractable P (NH_4Cl , $\text{NaHCO}_3\text{-P}_i$ and $\text{NaHCO}_3\text{-Po}$) was positively correlated with DPS ($r=0.94$, $P\leq 0.01$; $r=0.91$, $P\leq 0.01$; $r=0.92$, $P\leq 0.01$, respectively) and P_{ox} ($r=0.94$, $P\leq 0.01$; $r=0.91$, $P\leq 0.01$; $r=0.93$, $P\leq 0.01$, respectively). This confirms that these soils are characterized by higher amounts of readily available P fractions, larger concentrations of oxalate extractable P (P_{ox}) and greater degree of phosphorous saturation.

Phosphorous determined from NaOH extracts (NaOH-P_i), which is thought to be Fe and Al bound P, was positively correlated with Fe_{ox} ($r=0.64$, $P\leq 0.05$) and Al_{ox} ($r=0.91$, $P\leq 0.01$) despite the fact that it was negatively correlated with DPS ($r=-0.74$, $P\leq 0.01$) and P_{ox} ($r=-0.75$, $P\leq 0.01$). The correlation result substantiate that in the case where higher concentrations of oxalate and dithionite extractable iron and aluminum oxides are observed, the amount of P determined from NaOH extracts is higher. The same result has been found by Adhami et al. (2013) who reported that oxalate extractable iron had positive association with NaOH extractable P. This could be ascribed to the higher Al and Fe oxides on the exchange sites that might have resulted in lower pH at which the concentration of NaOH extractable P would become higher. Furthermore, P fraction determined from the HCl extract had a strong and negative association with Fe_{ox} ($r=-0.77$, $P\leq 0.01$) and Al_{ox} ($r=-0.96$, $P\leq 0.01$) although it was positively correlated with DPS ($r=0.88$, $P\leq 0.01$). Likewise, the correlation result proved that the higher the concentrations of extractable iron and aluminum in soil, the lower the concentrations of P determined from HCl extract. It has been reported by several studies that it is oxyhydroxydes of aluminum and iron in weathered acidic soils rather than Ca that supersede the active surface of soils on which P is adsorbed (Agbenin 2003; Yan et al. 2013; Campos et al. 2016). Therefore, with increasing concentrations of these free oxides, the amount of HCl extractable P decreases. Besides, NaOH and HCl extractable P (NaOH-P_i and HCl-P) could be best predicted from Al_{ox} and therefore put forth considerate information on the abundances and distributions of NaOH- P_i and HCl- P in the studied soils.

Mehlich 3 extractable P was negatively correlated with Fe_{ox} , Al_{ox} and Fe_d ($r=-0.85$, $P\leq 0.01$; $r=-0.95$,

$P\leq 0.01$; $r=-0.92$, $P\leq 0.01$) respectively. It is evident that the higher the concentrations of free oxides of Fe and Al, the lower the pH, which triggers adsorption of P at the exchange sites; in effect Mehlich 3 extractable P (available P) would be decreased. Moreover, the Mehlich 3 extractable P could best be predicted from Fe_{ox} , Al_{ox} and F_{ed} and therefore put forth thought full information on the availability of P in the soils is still lacking.

Conclusions

The soils of the study area were strongly to very strongly acidic in reaction that triggers the fixation of P at the exchange sites in the presence of oxyhydroxides of Fe and Al. Despite the medium to high contents of total P, the Mehlich-3 extractable available P contents of the studied soils is in the low to very low range indicating P deficiency in the study area. Among the different fractions of P, HCl extractable P fraction dominates the soils P pool for soils of Dinsho district, whereas soils' P pool of Cheha district was dominated by res-P. The sum of the labile P fractions ($\text{NH}_4\text{Cl-P}_i$, $\text{NaHCO}_3\text{-P}_i$, and $\text{NaHCO}_3\text{-Po}$) constitutes less than 4% of total P in soils from both districts reflecting very low reserves of crystalline Fe and Al-P. The sum of P fractions, which ranged from 606.3 to 1145.7 mg kg^{-1} , is almost equivalent to the total P determined through fusion method and reveals that the Hedley fractionation procedure could be used for determination of total P. The high content of Al and Fe oxides and hydroxides present in the soil might be responsible for the strong fixation of the native P as well as the applied P. Given the presence of considerable amount of total P, low P availability and high soil acidity in the study areas further research has to be done on adsorption characteristics to determine the P requirements of the soils for better P management.

Authors' contributions

BA: collected, analyzed, interpreted the data and made the final write up which was part of his Doctoral thesis in Soil Science at Haramaya University, Ethiopia. AMT, KK and AM, as co-authors. All authors read and approved the final manuscript.

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