

Research Article

Phosphorus Status, Inorganic Phosphorus Forms, and Other Physicochemical Properties of Acid Soils of Farta District, Northwestern Highlands of Ethiopia

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Soil acidity and low availability of P limit crop production in the highlands of Ethiopia. The objective of this study was to determine the P status, distribution and forms of inorganic P and relate them to selected chemical properties of eight representative acidic surface soil samples from Farta District. Soil pH (H_2O) varied between 4.74 and 5.50. The moderate to high CEC suggests that besides kaolinite, the soils also contain expandable 2:1 clay minerals. Though the total P content was high, the available Olsen P content was very low or low in all soils except one. In most soils, the abundance of inorganic P fractions was as follows: P bound by oxalate extractable iron (Fe_{ox} -P) > reductant soluble Fe-P > occluded Al-Fe-P > P bound by oxalate extractable aluminum (Al_{ox} -P) > calcium bound P (Ca-P). Olsen P had a very strong positive correlation ($P \leq 0.01$) with Al_{ox} -P ($r = 0.98$), Fe_{ox} -P ($r = 0.96$), and oxalate extractable P ($r = 0.94$). Though Fe bound P reserves were quite abundant and the degree of P saturation of Al_{ox} + Fe_{ox} (median 3.3%) was moderate, the extremely low P saturation of Al_{ox} (median 0.5%) explains the P deficiency of the soils.

1. Introduction

Ethiopia has a long history of intensive agriculture and human settlement particularly in the highlands [1]. Misuse of soils, arising from a desperate attempt by farmers to increase production for the growing population, has resulted in soil quality degradation. It is associated with soil nutrient depletion by repeated cultivation with low external inputs of nutrients and soil erosion caused by long-term deterioration of natural vegetation and intensive cultivation [2–4].

Phosphorus (P) deficiency is particularly widespread in rain-fed upland farming systems throughout the tropics and remains a major plant nutrient constraint. In this respect, the Ethiopian soils are similar to the other agricultural soils of the tropics being generally low in P [5–8] and hence P is one of the limiting elements in crop production in the highlands of Ethiopia. Accordingly, P supply is apparently essential in the management and sustainability of upland land use systems in the tropical environment [9–12].

Soil P deficiency can be attributable to the low P content of the parent material, high weathering intensity, long-term anthropogenic mismanagement through imbalance between nutrient inputs and exports, and P loss by soil erosion [11]. Limited availability of P in many tropical soils can be attributed to severe P fixation or retention, which is particularly strong in soils of low P status. In acidic soils, crystalline and noncrystalline oxides of Fe and Al (sesquioxides) are the main adsorbing agents of phosphate [13]. However, noncrystalline forms tend to control the soil adsorption reactions, due to their large specific surface area [14]. Similarly, exchangeable Al in intensely weathered and sesquioxide rich acidic ($pH < 5.5$) soils enters the solution causing P deficiency through precipitation as Al-P [11, 15].

Chemical fractionation provides a method for identifying the predominant individual forms of inorganic P in soils, most commonly easily soluble P, active forms of inorganic P, including P adsorbed on the surface of Al and Fe oxides (Al-P and Fe-P) and associated with Ca (Ca-P) as secondary

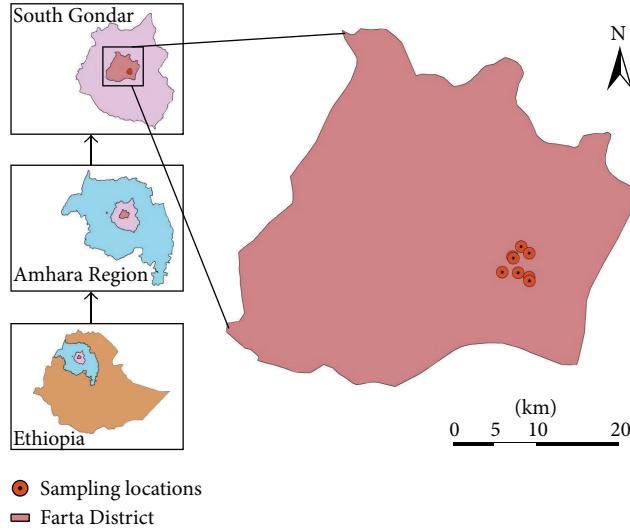


FIGURE 1: Location map of the study area.

precipitation or native minerals such as apatite, and inactive forms of P, including P occluded in the interiors of Al and Fe oxides (occl-Al-Fe-P) and reductant soluble Fe-P (reds-Fe-P) [10]. Paulos [16] indicated that the concentrations of active P forms were related to the degree of chemical weathering. All the forms of P can exist in all soils but P bound by Al and Fe is abundant in highly weathered acidic soils, while Ca-P predominates in young calcareous soils of arid and semiarid areas which usually have high pH. These fractions have remarkable differences in mobility, bioavailability, and chemical behavior in soils and they can be transformed from one form to another under certain conditions. Information of the abundance of the various P forms and their interactions with each other and other factors that influence P availability in the soils of Ethiopia in general and in the study area in particular is crucial for sustainable management of soil P. Therefore, this study was conducted to assess the P status and the amounts and the distributions of the different inorganic P forms and their relationship with other properties and their implications for the future P management strategy of acidic soils of Farta District, Northwestern Highlands of Ethiopia.

2. Materials and Methods

2.1. Description of the Study Area. The study was conducted in Gassay area of Farta District in South Gondar Zone of the Amhara National Regional State (Figure 1). The district lies between $11^{\circ}32'$ and $12^{\circ}03'$ N latitude and $37^{\circ}31'$ and $38^{\circ}43'$ E longitude and covers an area of 1118 km^2 within the altitude range of 1900 to 4035 meters above sea level (masl). In terms of topography, 45% of the total area is gentle slope, while flat and steep slope lands account for 29 and 26%, respectively.

According to the Regional Office of Planning for Northwestern Ethiopia [17], geologically, the study area is covered with thick trap series volcanic rocks which were erupted from fissures during the early and middle Tertiary and from Choke Shield volcanic mountain center during the Miocene

and the Pliocene. The trap volcanic series consists mainly of weathered and jointed basalt. The soils of the study area are developed from the parent materials of volcanic origin, predominantly Tertiary basalt. According to FAO-UNESCO system, Luvisols dominate in Farta District [18]. Luvisols are potentially suitable for a wide range of agricultural uses because of their favorable physical characteristics and moderate chemical fertility [19]. The soils of the study area have not been classified according to U.S. Soil Taxonomy, but tentatively many of them likely fall in the Alfisol order, more accurately Haplustalfs [20].

Considering land use, an estimated 65% of the area is cultivated for different annual and perennial crops, while areas under grazing and/or browsing, forests and shrubs, settlements, and wastelands account for about 10, 1, 8, and 16%, respectively. The natural vegetation in the study area consists of tree species that are remnants of a once dense evergreen forest occurring on slopes and sparse grass complex in various areas. The dominant tree species in the area include *Juniperus procera*, *Olea africana*, and *Hagenia abyssinica*. Currently, refilling or replantation strategy is being implemented in the study area [21]. The rural households are engaged primarily in crop-livestock mixed farming systems. Barley, wheat, teff, sorghum, maize, faba beans, peas, and potatoes are dominant crops while chickpeas and some oil crops are also grown.

The average minimum, maximum, and mean temperatures are 9.3 , 22.3 , and 15.8°C , respectively (Figure 2). The rainfall pattern is unimodal, stretching from May to September. The mean annual rainfall is 1445 mm [22].

2.2. Site Selection and Soil Sampling. The soil sampling sites were selected using the topographic map of the Farta District in South Gonder Zone of the Amhara National Regional State by selecting farm lands with an altitude greater than 2400 masl and slopes less than 15% (Table 1). Based on the field survey, the pH of the soils was measured using portable

TABLE 1: Sampling locations and site description.

Sampling site	Longitude (E)	Latitude (N)	Altitude (masl)	Slope (%)
Ayermarefiya	38°9'22"	11°46'49"	2885	2
Abalomeda	38°9'23"	11°46'34"	2929	10
Kumbelie	38°8'49"	11°48'49"	2783	5
Korekonch	38°9'21"	11°48'24"	2802	2
Agawer I	38°7'33"	11°47'8"	2909	7
Agawer II	38°8'37"	11°47'6"	2898	6
Jura I	38°8'14"	11°48'10"	2834	9
Jura II	38°8'18"	11°48'4"	2830	11

masl = meters above sea level.

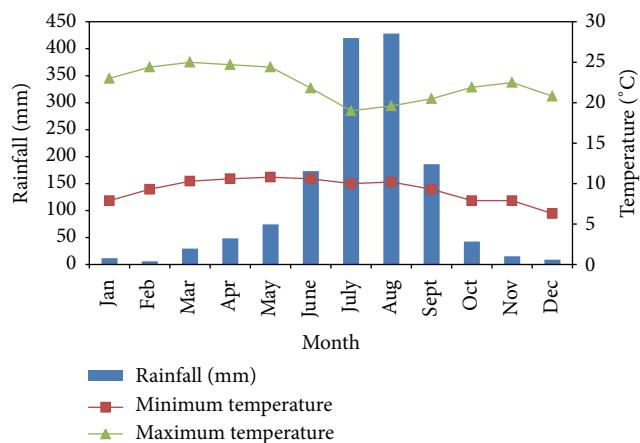


FIGURE 2: Mean monthly rainfall and mean monthly maximum and minimum temperatures of the study area.

digital pH meter under field condition. Three replicate soil samples from the surface (0–20 cm) layers having a pH \leq 5.5 were collected from the eight representative sampling sites. Composite soil samples were prepared after thoroughly mixing the three subsamples. The soil samples were air-dried and ground to pass through a 2 mm sieve for the analyses of physicochemical properties of the soils following standard laboratory procedures.

2.3. Soil Analyses. Water holding capacity (WHC) was measured at $-1/3$ bar for field capacity (FC) and -15 bars for permanent wilting point (PWP) using the pressure plate apparatus method [23]. Particle size distribution was analyzed by the Bouyoucos hydrometer method as described by Day [24] after dispersion with hydrogen peroxide and sodium hexametaphosphate. Soil bulk density was measured from three undisturbed samples collected using a core sampler (2.5 cm radius and 5.0 cm height) as per the procedure described by Jamison et al. [25]. Organic carbon (OC) and total nitrogen (N) contents of the soil samples were determined using the Vario MAX elemental analyzer by dry combustion method. It was assumed that in our acidic soils total C, which is determined by the analyzer, is all organic.

Soil pH was measured potentiometrically in H_2O and 1 M KCl solution at the soil to solution ratio of 1:2.5 using a combined glass electrode pH meter [26] and change in pH was determined by subtracting soil pH (KCl) from soil pH (H_2O). The lime requirement (LR) was determined by the Shoemaker, McLean, and Pratt (SMP) single buffer procedure [27]. Exchangeable calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) were determined by saturating the soil samples with 1 M NH_4OAc solution at pH 7.0. Then, Ca and Mg were determined by using ICP-OES while exchangeable Na and K were measured by flame photometer from the same extract. The potential cation exchange capacity (CEC) of the soil was determined from the NH_4^+ saturated samples that were subsequently replaced by K^+ from a percolated KCl solution. The excess salt was removed by washing with ethanol and the NH_4^+ that was displaced by K^+ was measured using the micro-Kjeldahl procedure [28] and reported as CEC. Total exchangeable acidity was determined by saturating the soil samples with 1 M KCl solution and titrated with 0.02 M NaOH as described by Rowell [29]. From the same extract, exchangeable Al in the soil samples was determined by application of 1 M NaF which forms a complex with Al and releases NaOH, which was back titrated with 0.02 M HCl. The effective cation exchange capacity (ECEC) of the soil was calculated as the sum of exchangeable bases and exchangeable acidity. Cation exchange capacity attributable to the clay fraction (CEC_{clay}) was estimated as follows:

$$\text{CEC}_{\text{clay}} = \frac{[\text{CEC}_{\text{soil}} - (\text{OM} \times 200)]}{\text{clay}}. \quad (1)$$

In the calculation of the CEC_{clay} , the CEC associated with the percent organic matter (OM) was subtracted from the soil (CEC_{soil}) assuming OM has a CEC of 200 $\text{cmol}_{\text{c}} \text{kg}^{-1}$ [30] and mineral fractions coarser than clay do not have significant CEC.

An index of plant available P was determined according to Olsen et al. [31] by shaking the soil samples with 0.5 M NaHCO_3 , pH of 8.5, in 1:20 of soil to solution ratio for half an hour. Total soil P was extracted using microwave assisted aqua regia digestion and the P in the extract was determined by ICP-OES. The inorganic P fractions were successively extracted with 1 M NH_4Cl , 0.5 M NH_4F , 0.1 M NaOH, 0.25 M

TABLE 2: Selected physical properties of the studied soils.

Sampling site	Sand (%)	Silt (%)	Clay (%)	Bulk density (g cm ⁻³)	FC (%)	PWP (%)	AWC (%)	OC (%)	Total N (%)
Ayermarefiya	19.6	29.3	51.1	1.21	35.2	24.7	10.4	1.9	0.17
Abalomeda	14.9	32.1	53.0	1.26	37.3	26.9	10.4	1.8	0.17
Kumbelie	26.3	30.7	43.0	1.30	32.3	21.5	10.8	2.0	0.17
Korekonch	17.5	32.7	49.8	1.26	33.0	21.2	11.8	1.8	0.19
Agawer I	24.0	36.4	39.6	1.12	34.4	24.8	9.5	3.2	0.25
Agawer II	21.4	35.0	43.6	1.47	31.2	19.7	11.4	1.8	0.18
Jura I	19.3	27.1	53.6	1.33	31.5	22.5	9.0	1.8	0.20
Jura II	20.0	35.0	45.0	1.46	27.4	18.4	9.0	1.6	0.17
Mean	20.4	32.3	47.3	1.30	32.8	22.5	10.3	2.0	0.19

FC = field capacity; PWP = permanent wilting point; AWC = available water capacity; OC = organic carbon.

H_2SO_4 , 0.3 M Na-dithionite and Na-citrate solution, and 0.1 M NaOH to estimate easily soluble P, Al-P, Fe-P, Ca-P, reds-Fe-P, and occl-Al-Fe-P, respectively, as described by Chang and Jackson [32] and modified by Hartikainen [33]. The modification here was that the NH_4F had a pH of 8.5 which is higher than in the original Chang and Jackson procedure (pH of 7.0) in order to decrease the dissolution of P bound by Ca in this fraction. The oxalate extractable P, Al, and Fe (P_{ox} , Al_{ox} , and Fe_{ox}) were extracted 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) for two hours in the dark [34]. After centrifuging and filtration through a Whatman filter paper number 42, the extracts were analyzed for P, Al, and Fe by ICP-OES. Citrate dithionite bicarbonate-extractable Fe and Al (Fe_{d} and Al_{d}) were determined by the method of Mehra and Jackson [35]. The extracts were analyzed for Al and Fe by ICP-OES.

The P sorption capacity (PSC, mmol kg⁻¹) of the soil was calculated as the sum of the concentrations of oxalate-extractable metals (Fe_{ox} and Al_{ox} , mmol kg⁻¹) according to Hartikainen et al. [36] as

$$\text{PSC} = \text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}. \quad (2)$$

The degree of P saturation (DPS, expressed as %) was determined as the percentage of the ratio of the oxalate extractable P (P_{ox} , mmol kg⁻¹) to the sorption capacity as follows:

$$\text{DPS} = \left(\frac{\text{P}_{\text{ox}}}{\text{PSC}} \right) \times 100. \quad (3)$$

DPS was also calculated separately for Al_{ox} and Fe_{ox} as

$$\text{DPS Al}_{\text{ox}}-\text{P} = \left(\frac{\text{Al-P}}{\text{Al}_{\text{ox}}} \right) \times 100, \quad (4)$$

$$\text{DPS Fe}_{\text{ox}}-\text{P} = \left(\frac{\text{Fe-P}}{\text{Fe}_{\text{ox}}} \right) \times 100.$$

Among the eight representative sampling sites, the soil samples collected from the Abalomeda and Kumbelie sites were analyzed for the mineralogical composition of the clay-sized fractions. The analysis was carried out on a semiqualitative basis by X-ray powder diffraction (XRD) method using a

long fine-focus Cu X-ray tube run at 45 kV and 35 mA power settings with Philips PW1830 generator, PW3020 goniometer equipped with curved graphite secondary monochromator, and X'Pert PW3710 MPD control unit.

2.4. Statistical Analysis. Pearson's simple correlation coefficient was executed using Statistical Analysis System (SAS) version 9.00 [37] to reveal the magnitudes and directions of the relationship between the different soil properties.

3. Results and Discussion

3.1. Soil Physical Properties and Mineralogy of the Clay Fraction. The textural class of all the soils was clay except Agawer I which was clay loam, indicating the similarity in parent material (Table 2). The mineralogy analysis of the clay-sized fraction of the two sampling sites (Abalomeda and Kumbelie) showed that they had similar mineral composition and relative proportion, implying similar source of parent materials and similar pedogenesis. In general, the mineral compositions of both samples were dominated by kaolinite and quartz. Smectite-group clay minerals and illite were present as minor components, and the Kumbelie soil contained minor potassic feldspar (microcline) and trace amounts of chlorite. High clay content meets one criterion of Vertisols (clay > 30%) but the predominantly kaolinitic mineralogy is not conducive to sufficient shrinking and swelling, so the soils were classified as Luvisols, assuming sufficient clay illuviation.

Organic carbon (OC) contents (Table 2) were similar to those reported for thirteen clay soils in Ethiopia with a mean value of 2.2% [38]. According to the rating by Tekalign [39], the soil OC contents were in moderate to high range. However, the total N contents of all the soils were in the high range (0.17 to 0.25%). The C:N ratios of 8.5 to 12.9 were usually slightly lower than the median of 12.9 that can be calculated from the results of Sillanpää [38] for soils of Ethiopia and C: N ratio in the A horizons of six soils of the Rift Valley (range 11.3–13.6) by Fritzsche et al. [40]. The result reflects the low inputs of organic material, such as straw, in

TABLE 3: Soil pH, buffer pH, and lime requirement (LR).

Sampling site	pH, H ₂ O	pH, KCl	Buffer pH	ΔpH, KCl	LR (Mg CaCO ₃ ha ⁻¹)	
					pH 5.5	pH 6.0
Ayermarefiya	5.0	4.0	5.7	1.0	6.1	8.2
Abalomeda	5.0	4.0	5.7	1.0	6.1	8.2
Kumbelie	4.9	3.8	5.6	1.1	7.0	9.2
Korekonch	4.7	3.8	5.5	1.0	8.0	10.2
Agawer 1	5.3	4.3	5.8	1.0	5.3	7.3
Agawer 2	5.4	4.1	5.9	1.3	4.5	6.5
Jura 1	5.4	4.3	5.9	1.1	4.5	6.5
Jura 2	5.5	4.2	6.0	1.3	—	5.6
Mean	5.2	4.1	5.8	1.1	5.9	7.7

ΔpH = change in pH; pH 5.5 and pH 6.0 = target pH (H₂O) values (5.5 and 6.0) to be achieved by the application of lime.

TABLE 4: Exchangeable cations and exchange properties.

Sampling site	Exchangeable cations and CEC (cmol _c kg ⁻¹)							PAIs (%)	PBS (%)
	Ca	Mg	K	Ac	Al	CEC _{soil}	CEC _{clay}		
Ayermarefiya	12.3	4.6	0.55	1.51	1.10	31.2	46.4	19.0	3.5
Abalomeda	14.6	5.0	0.20	1.58	1.39	35.4	54.6	21.5	3.9
Kumbelie	7.9	2.4	0.23	2.31	1.50	24.7	39.2	12.9	6.1
Korekonch	8.7	2.1	0.28	3.64	3.21	27.8	41.5	14.8	11.5
Agawer I	10.1	2.2	0.55	0.84	0.27	30.9	46.2	13.8	0.9
Agawer II	8.3	2.8	0.23	0.96	0.42	25.9	42.7	12.4	1.6
Jura I	9.5	2.6	0.20	0.63	0.20	28.1	39.3	13.0	0.7
Jura II	5.8	1.9	0.84	0.86	0.37	20.6	32.0	9.5	1.8
Mean	9.6	2.9	0.39	1.54	1.13	28.1	42.7	14.6	3.8

Ac = exchangeable acidity; CEC_{soil} and CEC_{clay} = cation exchange capacity of the soil and clay fraction, respectively; ECEC = effective cation exchange capacity; PAIs and PBS = percentage of Al saturation and base saturation, respectively.

these agricultural soils while N compounds are contained in the stable humus.

3.2. Soil pH, Buffer pH, and Lime Requirement (LR). According to the rating suggested by Jones [41], the pH (H₂O) of the soils (Table 3) was strongly acidic (50%) or very strongly acidic (50%). Hence, the soils of the sampling sites are chemically degraded as to hinder production of acid sensitive crops unless the magnitude of acidity is reduced. The change in pH [pH (H₂O) minus pH (KCl)] was greater than or equal to one across the soils sampling sites. Soil pH (KCl) indicates the potential acidity and presence of weatherable minerals when the difference (ΔpH) between pH (H₂O) and pH (KCl) is greater than unity [42]. On top of this, the positive value of ΔpH indicates the predominance of negatively charged clay colloids, which increases the CEC compared to the anion exchange capacity. This situation mainly occurs in tropical soils due to acidity and significant quantities of oxides, mainly those of Al and Fe [43]. Hence, our soils were rich in weatherable minerals as indicated by the presence of illite, smectite, and K-feldspar. The LR determined by the SMP single buffer method to raise the pH to target pH values of 5.5 and 6.0 is presented in Table 3. For example, the soil

sample collected from the Korekonch site required 8.0 and 10.2 Mg CaCO₃ ha⁻¹ to raise the pH from 4.7 to 5.5 and 6.0, respectively. Therefore, the soils of the study area need high amounts of lime to alleviate the acidity problem and increase the productivity of acid sensitive crops.

3.3. Exchangeable Cations and Exchange Properties. The CEC values (Table 4) were medium to high as per the rating established by Hazelton and Murphy [44]. In a global soil material of about 3700 soil samples, the 125 soil samples from Central and Western Ethiopia had nearly the highest CEC and clay content among the 30 countries that were sampled [45]. The present CEC values were lower than the mean of 48.2 cmol_c kg⁻¹ presented in that material [45] for soils of Ethiopia, the difference suggesting stronger dominance of kaolinite in our soils. However, the CEC values of the studied soils were high as compared to kaolinitic soils, supporting the presence of considerable amount of smectite which has contributed to the higher CEC values than is common in soils of pure kaolinitic mineralogy (10 cmol_c kg⁻¹) [42]. Exchangeable Ca was dominant in the exchange sites followed by Mg, K, and Na ions in that order. As per the ratings of FAO [46], the exchangeable Na in the soils of the sampling sites was

medium, indicating that the soils were not sodic, the leaching being sufficient to remove excess salts; the exchangeable Ca and Mg were medium except at the Ayermarefiya and Abalomeda sites which had high values while the exchangeable K was low except at the Ayermarefiya, Agawer I, and Jura II sites which had high values. According to Barber [47], the critical level of exchangeable K for optimum crop production is $0.38 \text{ cmol}_c \text{ kg}^{-1}$. On this basis, only three of our sampling sites had optimum levels of exchangeable K. The result was in agreement with the findings of Alemayehu [48] who reported K deficiency in Nitosols in Wolega state farm. In terms of K, the results were in contrast to the common belief that Ethiopian soils are rich in K. For example, in the thirteen Ethiopian clay soils of Sillanpää [38] the average K content was $0.88 \text{ cmol}_c \text{ kg}^{-1}$, with only two soils being below the critical level. There is obviously a large variation in K supply among the clay soils of Ethiopia. This conclusion is supported by many results from different parts of the tropics in which soil type and mineralogy, intensity of weathering, climatic factors, intensive cultivation, and use of acid forming inorganic fertilizers affect the distribution of K in soil and enhance its depletion [49, 50]. For example, a study on exchangeable K in some cropped acid soils of India indicated that among the 400 samples tested more than 92% had very low to low K content [51].

The percentage base saturation (PBS) of our soils (Table 4) varied from 40 to 56% and qualified as moderate [44], indicating that the weathering is not yet at an extreme state to result in a high Al saturation. In general, the CEC_{soil} , CEC_{clay} , ECEC, and PBS of the soils followed the same trend in all soils. It was also shown in an earlier study [52] on the fertility status of some Ethiopian soils that Ca and Mg ions dominate the exchange sites of most soils. Exchangeable Al had a strong and negative correlation with pH ($r = 0.90$, $P \leq 0.01$) and strong positive correlation with LR ($r = 0.92$, $P \leq 0.01$). Therefore, both the pH and exchangeable Al determined the amount of liming material required for the proper management of acid soils of the sampling sites.

3.4. Total Phosphorus. The total P contents of our soils varied from 685 to 1432 mg kg^{-1} , mean at 994 mg kg^{-1} (Table 5), and ranged from medium to very high as per the rating suggested by Murphy [53]. The total P contents of Ethiopian soils have ranged from 200 to 800 mg kg^{-1} [54], 185 to 1981 mg kg^{-1} [55], 300 to 1900 mg kg^{-1} [30], 226 to 1570 mg kg^{-1} [56], and 553 to 976 mg kg^{-1} [57]. Indeed, these results seem not to be low but as a matter of fact they are in the same range as in heavily fertilized soils of Europe. For example, in a material of 135 agricultural soils from 12 European countries, the total P averaged at 683 mg kg^{-1} [58], which is lower than measured in seven out of eight soils of the present study. Moreover, in another study, in nine noncalcareous soils, called "*European soils overfertilized with P*" the total P content averaged at 1111 mg kg^{-1} , the maximum no higher than 1920 mg kg^{-1} [59]. Our results also indicated that the total P content of the studied soils was much above 200 mg kg^{-1} which was the value indicated by Olsen and Engelstad [60] as the maximum total P value for highly weathered tropical soils.

TABLE 5: Total phosphorus content of the soils.

Sampling site	Total P (mg kg^{-1})
Ayermarefiya	968
Abalomeda	960
Kumbelie	685
Korekonch	890
Agawer I	1121
Agawer II	985
Jura I	913
Jura II	1432
Mean	994

Also, compared to some other African countries, the soils of our study area showed higher total P contents. In soils of Niger, the total P contents were between 29 and 349 mg kg^{-1} with a mean value of 109 mg kg^{-1} [61] and in Nigeria it varied from 79 to 1410 mg kg^{-1} [62]. Total P contents of nine top soils from the Savanna regions of Ghana ranged from 60 to 173 mg kg^{-1} [63], while Acquaye and Oteng [64] obtained 104 to 270 mg kg^{-1} for 48 top soils developed over principal parent materials in different ecological zone of Ghana. Therefore, it can be concluded that the total P contents of Ethiopian soils are not as poor as in many other tropical soils studied.

3.5. Inorganic Phosphorus Fractions. The abundance of the various inorganic P fractions (Table 6) was commonly as follows: $\text{Fe-P} > \text{reds-Fe-P} \gg \text{occl-Al-Fe-P} > \text{Al-P} > \text{Ca-P}$ in seven soils except in the Jura I sites which followed the same trend but $\text{Ca-P} > \text{Al-P}$. The most easily soluble P contents (extracted with $1\text{M NH}_4\text{Cl}$) were extremely low (less than 1 mg kg^{-1}) and, hence, not presented in Table 6.

Previous studies on different Ethiopian surface soils showed that the active inorganic P fractions occurred in the order $\text{Ca-P} > \text{Fe-P} > \text{Al-P}$ [5]. On the other hand, Piccolo and Gobena [65], working on seven Ethiopian soils (three vertisols, two Nitosols, one Cambisol, and one Fluvisol), found that the relative abundance of the inorganic P forms was $\text{Fe-P} > \text{Al-P} > \text{Ca-P} > \text{reds-Fe-P}$. Mamo and Haque [55] studied the P status of 32 surface soil samples and reported that the relative abundance of the inorganic P forms was generally $\text{Ca-P} > \text{reds-Fe-P} > \text{Fe-P} > \text{Al-P}$. Wakene and Heluf [66], working on Nitosol under different land use system such as research, farmers, and virgin fields, found that the abundance of the fractions was $\text{Fe-P} > \text{Al-P} > \text{Ca-P}$ in the research field which received high P fertilizer doses but the order in the other land use systems was $\text{Fe-P} > \text{Ca-P} > \text{Al-P}$. In all studies, the abundance of different forms of Fe-bound P was high and Al-bound P was low, which agrees with our results.

It can be pointed out that on average as much as 88% of inorganic P recovered in the fractions was associated with Fe. The percentage of Fe-P even among the total active inorganic P fractions varied from 70 to 85%, with a mean value of 79%; Al-P varied from 7 to 16% with mean value of 12%. The low content of Ca-P (6–18%) is in line with the acidity and advanced pedogenesis of the soils, indicating that nearly

TABLE 6: Inorganic P fractions and percentage distribution of active P forms.

Sampling site	Al-P	Fe-P	Ca-P	reds-Fe-P	occl-Al-Fe-P	Sum fract.	Sum active P
				(mg kg ⁻¹)			
Ayermarefiya	21	161	16	124	61	383	197
Abalomeda	17	153	16	140	66	391	185
Kumbelie	25	156	13	68	30	292	194
Korekonch	33	210	15	140	71	469	258
Agawer I	20	152	26	180	65	442	197
Agawer II	15	195	20	230	74	534	230
Jura I	38	224	58	182	70	572	319
Jura II	88	426	40	308	113	975	554
Mean	32	210	25	171	67	507	267

Al-P, Fe-P, and Ca-P = Al, Fe, and Ca bound P, respectively; reds-Fe-P = reductant soluble Fe bound P; occl-Al-Fe-P = occluded Al and Fe bound P.

TABLE 7: Olsen P, oxalate extractable Al, Fe, and P, and citrate dithionite bicarbonate extractable Al and Fe.

Sampling site	Olsen P (mg kg ⁻¹)	Al _{ox}	Fe _{ox}	P _{ox} (mmol kg ⁻¹)	PSC	Al _{ox} -P ^a	Fe _{ox} -P ^b	P _{ox} ^c	Al _d	Fe _d (mmol kg ⁻¹)	Fe _{ox} /Fe _d
Ayermarefiya	3.1	137	63	6.1	200	0.49	8.3	3.1	159	562	0.11
Abalomeda	2.3	164	78	5.3	242	0.33	6.3	2.2	192	650	0.12
Kumbelie	7.0	137	83	7.6	220	0.58	6.1	3.5	95	359	0.23
Korekonch	6.2	156	80	10.3	236	0.68	8.5	4.4	165	415	0.19
Agawer I	2.0	177	70	5.4	246	0.36	7.0	2.2	179	629	0.11
Agawer II	3.8	137	89	4.5	226	0.36	7.1	2.0	148	639	0.14
Jura I	6.2	165	67	9.9	232	0.74	7.8	4.3	138	463	0.14
Jura II	24.3	176	97	17.5	274	1.61	14.2	6.4	101	380	0.26
Mean	6.9	156	78	8.3	234	0.64	8.5	3.5	147	512	0.16

Al_{ox}, Fe_{ox}, and P_{ox} = oxalate extractable Al, Fe, and P, respectively; PSC = P sorption capacity; DPS = degree of P saturation; a and b = degree of P saturation of the Al-P and Fe-P with respect to Al_{ox} and Fe_{ox}; Al_d and Fe_d = dithionite citrate bicarbonate extractable Al and Fe, respectively; c = degree of P saturation of P_{ox} with respect to P sorption capacity.

all native apatite has weathered away, contrary to the less weathered soils of 15 noncalcareous soils of five European countries, where the Ca-P had a median of 122 mg kg⁻¹, or 33% of the sum of Al-P, Fe-P, and Ca-P [36]. In the European soil material, the sum of Al-P, Fe-P, and Ca-P averaged at 475 mg kg⁻¹ while in our soils this sum of active P fractions was 44% smaller. The very high contents of Fe-P among the active inorganic P fractions compared to the other fractions is due to the high content of Fe-oxides, low pH, and advanced stage of weathering (Tables 2, 3, and 7). Rather low content of Al-P reflects the fact that Al-P fraction, which controls the plant available P in acidic soils in the first place, has been severely depleted in the study area. The degree of P associated with Al, Fe, and Ca was directly related to the intensity of weathering in that when Al and Fe fraction dominated in the soil system, the soil is highly weathered and vice versa [65].

3.6. Olsen P, Oxalate Extractable P, Al and Fe, and Dithionite Citrate Bicarbonate Extractable Al and Fe. Besides the quantity of P in soil, the amount of sorption components essentially controls the level of easily soluble P and plant availability of soil P reserves. The poorly crystalline oxides of Al (Al_{ox}) and Fe (Fe_{ox}) are considered the active components in acidic

soils to retain P. The Al_{ox} contents of our soils varied in a narrow range, averaging at 156 mmol kg⁻¹ (Table 7) being two times higher than Fe_{ox}. However, P in the oxide-bound pools was not related to the quantity of the corresponding poorly crystalline oxides; the correlation coefficient (*r*) between Al_{ox} and Al-P was only 0.51 and that between Fe_{ox} and Fe-P was 0.54 (Table 8), both being statistically nonsignificant. A similar low correlation has been reported by Hartikainen et al. [36]. Compared to Fe_{ox}, 6.5 times more Fe was extracted with a reducing agent. The ratio of Fe_{ox}/Fe_d has been taken as an indicator of crystallinity of Fe oxides in the soils [67]. The mean value of the Fe_{ox}/Fe_d for the studied soils was 0.16, indicating that most Fe oxides were crystalline. Our soils differ strongly from the nine “overfertilized soils of Europe” [68] where the average ratio of Fe_{ox}/Fe_d was 0.44, indicating much lower degree of Fe oxide crystallinity. Even though the Fe_{ox} was higher in our Ethiopian soils, the difference arises mainly from the fact that the Fe_d content in the Ethiopian soils was as much as fivefold compared to the European soils, reflecting the difference in soil age and degree of pedogenic development. Piccolo and Gobena [65] working on seven Ethiopian soils found that the Fe_d varied between 10 and 525 mmol kg⁻¹ with a median value of 125 mmol kg⁻¹. Mamo

TABLE 8: The linear correlation coefficients between the selected soil chemical properties.

	Silt	Clay	pH	LR	Ex. Ca	Ex. Mg	Ex. Al	CECs	OC	Olsen P	Total P	Al-P	Fe-P	Ca-P	Al _{ox}	Fe _{ox}	P _{ox}	DPS	Al _d
Clay	-0.74*																		
pH	0.29	-0.26																	
LR	-0.22	0.17	-0.98**																
Ex. Ca	-0.30	0.53	-0.35	0.29															
Ex. Mg	-0.36	0.57	-0.29	0.16	0.90***														
Ex. Al	-0.13	0.23	-0.92**	0.92*	0.09	0.03													
CECs	-0.21	0.43	-0.35	-0.34	0.97**	0.76*	0.11												
OC	0.43	-0.59	0.08	0.05	0.15	-0.17	-0.22	0.34											
Olsen P	0.21	-0.14	0.40	-0.45	-0.70	-0.48	-0.16	-0.79*	-0.44										
Total P	0.55	-0.22	0.67	-0.70	-0.29	-0.21	-0.51	-0.32	0.44	0.67									
Al-P	0.14	-0.03	0.42	0.47	-0.64	-0.48	-0.18	-0.72*	-0.39	0.98**	0.71*								
Fe-P	0.24	-0.06	0.53	-0.57	-0.66	-0.47	-0.25	-0.73*	-0.45	0.96**	0.77*	0.97**							
Ca-P	-0.28	0.22	0.71*	-0.68	-0.31	-0.36	-0.60	-0.30	-0.12	0.41	0.39	0.53	0.52						
Al _{ox}	0.33	-0.04	0.44	-0.39	-0.06	-0.29	-0.31	-0.03	0.31	0.38	0.66	0.50	0.45	0.55					
Fe _{ox}	0.56	-0.39	0.24	-0.26	-0.64	-0.43	0.04	-0.70	-0.39	0.68	0.39	0.54	0.64	-0.07	0.07				
P _{ox}	0.04	0.05	0.27	-0.31	-0.65	-0.52	-0.01	-0.70	-0.44	0.94**	0.58	0.98**	0.93**	0.51	0.47	0.50			
DPS	-0.11	0.14	0.17	-0.21	-0.63	-0.50	-0.07	-0.69	-0.49	0.89**	-0.45	0.93**	0.86**	0.51	0.37	0.40	0.98**		
Al _d	0.13	0.29	-0.21	0.24	0.78*	0.53	0.12	0.88**	0.40	-0.69	-0.06	-0.60	-0.55	-0.26	0.18	-0.51	-0.60		
Fe _d	0.18	0.04	0.08	-0.06	0.72*	0.59	-0.27	0.77*	0.43	-0.76*	-0.10	-0.75*	-0.64	-0.28	-0.09	-0.42	-0.84**	-0.89**	0.82*

* and ** = significant at 0.05 and 0.01 probability levels, respectively; LR = lime requirement; Ex. Ca = exchangeable Ca; Ex. Mg = exchangeable Mg; Ex. Al = exchangeable Al; CECs = cation exchange capacity of soil; OC = organic carbon; TP = total P; Al-P = Al bound P; Fe-P = iron bound P; Ca-P = calcium bound P; Al_{ox}, Fe_{ox} and P_{ox} = oxalate extractable Al, Fe, and P, respectively; DPS = degree of P saturation; Al_d and Fe_d = citrate dithionite bicarbonate extractable Al and Fe, respectively.

and Haque [6] also reported that the Fe_d contents of 32 Ethiopian soils ranged from 12.5 to 1168 mmol kg⁻¹. Our soils thus seem to represent nearly the average amounts of Fe_d in soils of Ethiopia.

The P sorption capacity (PSC), calculated on the basis of Al_{ox} and Fe_{ox} (Table 7), was practically double in our Ethiopian soils than in the two European noncalcareous soil materials [36, 68] where the median PSCs were 118 and 110 mmol kg⁻¹, respectively. The difference is strongly attributable to the high Al_{ox} content of the Ethiopian soils, a property that is often neglected. While the amount of oxalate extractable P, assumed to be mostly retained by Al_{ox} and Fe_{ox} , had the median of 11.7 mmol kg⁻¹ in the European soils [36], it was only 6.8 mmol kg⁻¹ in the Ethiopian soils. High PSC and low P_{ox} in Ethiopian soils resulted in the median DPS of 3.3% as opposed to 10.5% in the European soils. In the present material, the DPS calculated on the basis of the Al-P and Fe-P of the Chang and Jackson fractionation resulted in the same DPS with the correlation coefficient of 0.90 with that based on the oxalate extraction. This outcome suggests that the same P fractions are extracted by the oxalate extraction and the Chang and Jackson procedure.

The DPS calculated on the basis of the P fractionation data separately for Al_{ox} and Fe_{ox} sharply points out that the DPS for Fe_{ox} -P (range 6.1 to 14.2%) was much larger than the DPS for Al_{ox} -P which was extremely low (range 0.3 to 1.6%). As a matter of fact, the DPS calculated for Fe_{ox} in our soils did not differ from the median of 7.1% that was presented by Hartikainen et al. [36] for 15 European noncalcareous soils while the DPS for Al_{ox} in that material was five times higher than in the Ethiopian soils.

As per the rating established by Cottenie [69], the Olsen P contents (Table 7) of most of the studied soils represented the very low (<5 mg kg⁻¹) to low (5–9 mg kg⁻¹) available P status except the Jura II sampling site with a high (18–25 mg kg⁻¹) P status. The higher Olsen P content of the Jura II soil may be due to the accumulation of fertile and fertilized top soil from agricultural upland areas to this sampling site. According to the critical values for the Olsen P (8.5 mg kg⁻¹) established by Mamo and Haque [55] for some Ethiopian soils, the available P contents were below the critical level in almost all the sampling sites. The low contents of available P observed in our soils were in agreement with many earlier studies [7, 53, 54, 70, 71]. The Olsen P concentrations here were nearly the same as in 13 Ethiopian soils of Sillanpää [38] while a larger material of 125 soils by the same author [45] had the average of 14.4 mg kg⁻¹ and represented the medium availability class, indicating a substantial variability within Ethiopia. Thus, almost all our soils were P deficient despite the medium to high contents of total P and the DPS of Fe_{ox} comparable to soils of Europe where the averages of Olsen P are usually much higher. For example, the mean values obtained in different laboratories for 135 soils of 12 countries range at 15–30 mg kg⁻¹ [58], 67 mg kg⁻¹ in 9 “overfertilized soils” [59], and 83 mg kg⁻¹ in 35 normal agricultural soils of Belgium [45]. In the present material, the available Olsen P was strongly and positively correlated with the Al-P ($r = 0.98$,

$P \leq 0.01$), Fe-P ($r = 0.96, P \leq 0.01$), P_{ox} ($r = 0.94, P \leq 0.01$), and DPS ($r = 0.89, P \leq 0.01$) (Table 8).

However, Olsen-P had a negative correlation with Fe_d ($r = -0.76, P \leq 0.05$), suggesting that the large reserves of soil Fe, even if in crystalline forms, may have an adverse effect on soil P availability. In a similar manner, Fe_d had a negative correlation with both the P_{ox} ($r = -0.84, P \leq 0.01$) and the DPS ($r = -0.89, P \leq 0.01$), indicating that the higher the Fe_d content in soil, the lower the DPS. These results propose that the oxalate extraction of Fe and Al, which may be a good method to explain P availability in less weathered soils, underestimates the actual P sorption capacity of highly weathered soils where the Fe oxides are predominantly in crystalline forms and not extracted with the oxalate solution. The low Olsen P is in contradiction with the rather high DPS of Fe_{ox} in the Ethiopian soils. Instead, the DPS of the Al_{ox} seem to better explain the P status of soil measured in soil testing.

4. Conclusion

The soils of the study area are clayey in texture and rich in kaolinite and have strong to very strong acidity and high lime requirements. The relatively high CEC values of the soil suggest that there are still weatherable minerals, including 2:1 clay minerals in the soil. The rather high content of exchangeable Ca and Mg and the relatively low content of exchangeable Al are also worth mentioning. Although the soils had a higher content of total P, the Olsen extractable P was low to very low. This reflects the very small reserves of Al-P and very low P saturation of Al oxides (0.3 to 1.6%) which was the best explanation for the low available P status. Aluminum oxides were abundant in these soils but their P concentrations were low, owing to continued nutrient mining with very small P inputs into the soils. Instead, P saturation of Fe oxides (6.1 to 14.2%) was much higher, but low concentration of Olsen P proves that Fe-P is not contributing much to plant available P. The high content of Al and Fe (hydro)oxides is also responsible for the strong fixation of the native P and the applied P.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

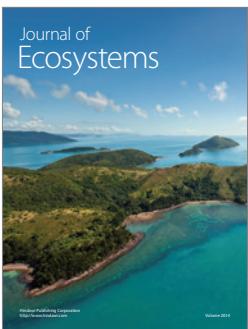
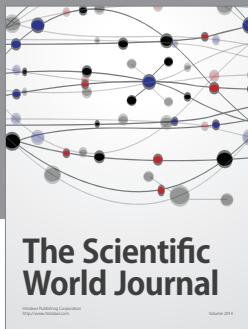
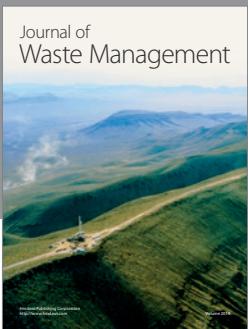
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