ORIGINAL ARTICLE

Comparison of industrial by-product and natural limestone for their agronomic effectiveness, yield of food barley and acid soil properties in the central highlands of Ethiopia

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ABSTRACT

The application of lime is believed to enhance soil health status through improving soil pH, base saturation and reduces Al and Mn toxicities. Liming effects depend on the source, composition, purity and fineness of the lime. The objective of the study was to compare the effectiveness of hydrated lime ($Ca\ (OH)_2$), the industrial by-product and different natural liming materials produced at different regional bureau of Agriculture on neutralizing soil acidity and their concomitant effects on food barley yield. Lime characterization was undertaken at Holeta Agricultural Research centre (HARC) and field experiment was conducted at HARC field research station for two years. The treatments comprised of five different lime materials (Awash calcite and dolomite, Dejen lime, Senkele lime and $Ca\ (OH)_2$) and one control (without any lime type added) in randomized complete block design with three replications. The result indicated that neither the soil chemical properties nor the food barley yield showed significant difference between the hydrated lime and natural lime materials produced at different corners of the country, but nearly equal improvement of soil pH, exchangeable acidity, Al, P, Ca and Mg content. This implies that hydrated lime can serve as an alternative agricultural lime to ameliorate soil acidity. Hence, hydrated lime can be used as agricultural lime material after verifying the result at different locations having different soil acidity ranges with different testing crops.

Keywords: Agricultural lime, Lime quality, Neutralizing value, pH, Soil acidity.

INTRODUCTION

Soil acidity is the main soil related constraints to agricultural development in parts of developing countries like Ethiopia, which are relying on agriculture to feed their growing population. The potentials of using lime for soils sustainable management are among options to be explored in restoring soil health and fertility. In agriculture, the limes play a great importance in improving soil acidity and hence favour plant nutrition (Van Straaten, 2002, Kiiya *et al*., 2006, Crawford and US, 2008).

Several research reports indicated that soil acidity can be easily corrected by liming to increase crop yields of barley (Getachew *et al*., 2017; Temesgen *et al*., 2016); potato (Geremew *et al*., 2015) bread wheat (Mekonen *et al*., 2014; Geremew *et al*., 2020), soybean (Derib, 2019). Although not permanent, the direct effect of lime lasts longer than any other amendment (Fageria and Baligar, 2008), such as organic materials (Osundwa *et al*., 2013).

Application of lime to acidic soils reduced soil exchangeable acidity increased soil pH and available phosphorus (Temesgen *et al*.,2016, Geremew *et al*., 2020) raises base saturation, and Ca and Mg contents, (Fageria, and Baligar, 2008; Álvarez *et al*., 2009), decreases Al^{3+} in the soil solution as well as in the exchange complex (Delhaize *et al*., 2007; Álvarez *et al*., 2009), improves soil structure (Crawford and US, 2008; Osundwa *et al*., 2013), increases yield (Buri *et al*., 2005; Fageria and Baligar, 2008, Geremew *et al*., 2020), resulting in increased available P, and P up take and use efficiency (Osundwa *et al*., 2013; Geremew *et al*., 2020). Lime application enhances abundances and diversity of earthworms (Bishop, 2003); and improved OM decomposition and nutrient mineralization (Bradford *et al*., 2002).

In Ethiopia the current lime types in use are those natural limes produced by crashing industries, but those from different industrial by-products were not studied and put in use for the acidic soil reclamation. These liming materials can be used for agricultural purposes whose calcium and magnesium compounds are capable of neutralizing soil acidity, including limestone, burnt lime, hydrated lime, marl, industrial by product ($Ca(OH)_2$) and agricultural lime slurry. Industrial by product, is any industrial waste or by product containing calcium or calcium and magnesium in forms that will neutralize soil acidity. The neutralizing potential of industrial by-products and their impact on soil properties were studied in some countries. Some of them are pulp mill residues, cement kiln dust (CKD) and wood ash (WA), widely studied in the field regarding their effects on soil properties and crop yield (Demeyer *et al*., 2001; Gagnon and Ziadi, 2004). Chora Gas and Chemical Products Factory of Amaga Private Limited Company in Addis Ababa produces about 250 - 500 t $year^{-1}$ hydrated lime ($Ca(OH)_2$) as industrial by-product (personal communication with production manager).

Quality of liming material is very important characteristics in correcting soil acidity. The source of lime, chemical composition, its fineness and the purity of lime are extremely crucial for effective use of lime (Kemperl and Maček 2009). The efficiency of liming material is determined by its acid neutralising potential, fineness factors of the various particle size fractions, effective neutralizing value (ENV) and its effective calcium carbonate equivalence (CCE) (Foth and Ellis, 1996; Synder and Leep, 2007). The materials may differ in neutralizing power and nutrient or other elements associated with the liming agent. The main factors indicating lime quality used were purity and particle size distribution as indicated by (Scott *et al*., 1992). The chemical characteristic, assessed as percent CCE, and the physical characteristic, assessed as the size of the particles, are combined into one value that quantifies the effectiveness of the limestone. This value is known as the relative neutralizing value (RNV) which is calculated using the CCE and fineness value.

Currently, a variety of liming materials are available in Ethiopia. The materials differ in place of origin and parent material they were made from, and the quality of the grinding machine; hence, they may differ with neutralizing power, fineness, nutrients and/or other elements associated with the liming materials. All crushers planted by Ministry of Agriculture at different Regional National States produce an excellent fineness quality (Farina, 2011) but, no characterization was done about their elemental content and quality parameters. Similarly, knowledge on the effectiveness of various industrial by products liming materials in correcting soil acidity is lacking due to limited studies conducted in this area. In view of filling up this technical gap, this experiment was conducted to investigate the agronomic effectiveness of natural and industrial liming materials on acid reclaiming properties and yield of food barley grown on acid soils in central high lands of Ethiopia.

MATERIALS AND METHODS

Site description

The study was conducted at research field of Holeta Agricultural Research Centre (HARC), located about 30 km west of Addis Ababa on the way to Ambo. It is situated at 9^0 3.546′ N latitude and 38^o 30.36′ E longitude and altitude of 2281 meter above sea level (m a.s.l.) (Fig 1). During the year 2015-2016 the center received the main rainy seasons which occur from May to mid-September. The average, annual total rainfalls was about 669.1 mm with a peak in July and mean annual temperature fall between 8.0^o c and 25.6 ^{o}c (Fig 2).

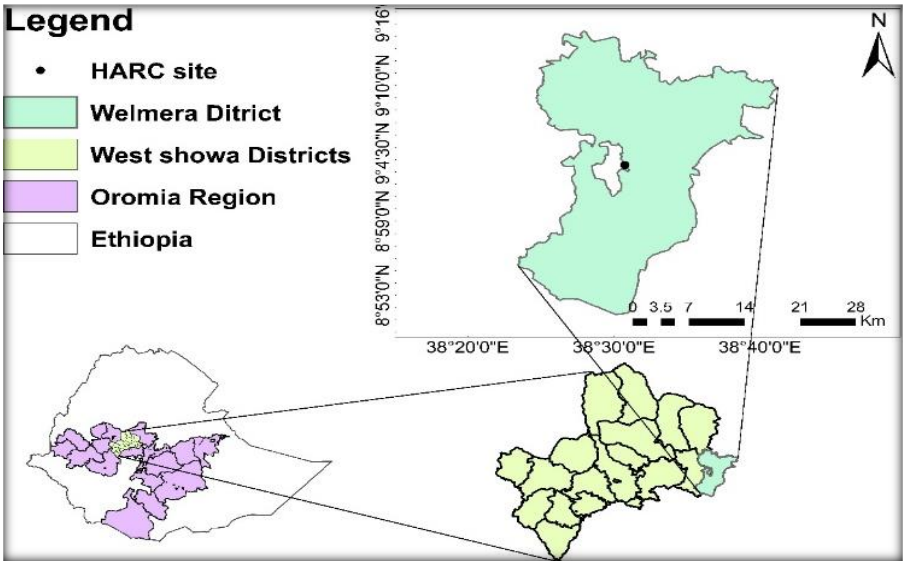

Figure 1. Map of the study area, HARC

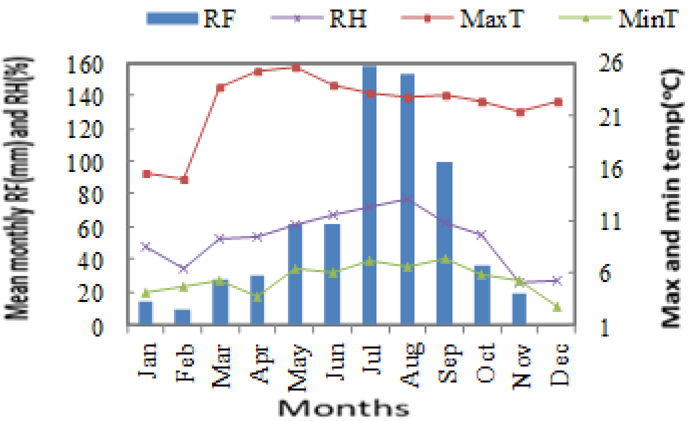

Figure 2. Monthly rainfall, Relative humidity and minimum and maximum temperature of crop growing seasons in Holeta Agricultural Research Centre (2015-2016).

Liming Material Quality Parameters

Lime materials collection

The hydrated lime ($Ca(OH)_2$) was collected from Chora Gas and Chemical Products Factory in Addis Ababa. The other lime materials were collected from different lime crushing industries, Senkele lime from Guder area (Oromia Regional National State), Dejen lime from Gojam (Amhara Regional National State). Both Awash calcite and Awash dolomite from Awash 7 kilo MEDROC company lime factory,

Determination of Calcium Carbonate Equivalence

To determine CCE, 1 g of lime and 50 mL of 0.5M HCl were mixed and boiled on steam bath for 5 minutes. The sample was cooled and 2-3 drops of phenolphthalein indicator was added and finally titrated with 0.25M NaOH as described by Effiong *et al*. (2009). Finally, percentage CCE was calculated as:

$$CCE(\%) = 2.5\left(\frac{VHCL-VNaOH}{2*Tv}\right)x\ 100 \quad (1)$$

Where: Tv - total volume of aliquot

Fineness

Fineness was determined by passing the lime materials through different mesh size sieve (10, 50 and 100 mesh) (Conyers *et al*., 1995). The fineness percentage was calculated as:

$$Pass\ 10\ mesh\ P1\ (\%) = \frac{Mp1}{Wts} x\ 100 \quad (2)$$

$$Pass\ 50\ mesh\ P2\ (\%) = \frac{Mp2}{Wts} x\ 100 \quad (3)$$

$$Pass\ 100\ mesh\ P3\ (\%) = \frac{Mp3}{Wts} x\ 100 \quad (4)$$

$$Fineness\ (\%) = \frac{P1+P2+P3}{3} \quad (5)$$

Where, Mp1-mass pass through 10 mesh, Mp2-mass pass through 50 mesh, Mp3-mass pass through 100 mesh

Determination of Relative Neutralizing Value

The RNV was determined from CCE and the fineness % using the formula;

$$RNV = \frac{CCE}{100} * Fineness\ \% \quad (6)$$

Determination of Calcium Carbonate

For determination of $CaCO_3$ 5 g of lime and 50 mL of 0.5 M HCl was mixed in 250 mL volumetric flask and stand for 1 hr. Then, boiled on hot plate for 5 minutes, cooled and filtered. The lime in the filter paper was washed by 25 ml distilled water and marked up to 100 ml volumetric flask. The filtrate was titrated with 0.1 M NaOH until pink colour was obtained as described by Jackson, (1970). Finally, percentage $CaCO_3$ was calculated as:

$$CaCO3(\%) = MNaOH\ \frac{(a-b)*50*mcf}{Wt\ (g)} \quad (7)$$

Where: a-blank, b-used for sample, mcf-moisture correction factor, M- morality NaOH, 50- equivalent weight of $CaCO_3$, Wt-weight

Determination of total Calcium and Magnesium

The lime materials were analysed for their chemical composition by wet acid digestion procedure allowed for the determination of calcium (Ca) and magnesium (Mg) oxide contents, and subsequently their acid neutralizing values, in terms of calcium carbonate equivalent as described by (FAO –UNDP, 1979).

For the determination of both calcium and magnesium 0.5 g of lime sample was weighed in digestion tube and 2 mL of distilled water was added then 5 ml HNO_3 and 2.5 ml perchloric acid was added in the sample tube. The sample was digested at 200 ^oC for 20 minutes. The digestion was continued until clear solution appeared by increasing the temp at 380 ^oC. The digested sample was cooled and filtered in 100 ml volumetric flask and marked up using distilled water. Calcium and magnesium in sample were determined by using Atomic absorption Spectroscopy after instrument was calibrated for each element.

Total Ca and Mg content were calculated as:

$$Total\ (Ca\ and\ Mg)(\%) = \frac{(R-B)*Tv*Df}{Wt*10{,}000} \quad (8)$$

Where: R-sample reading, B -blank reading, Df-dilution factor, Wt-weight of sample, TV-total volume of the extracted sample.

Determination of available Phosphorus in lime materials

For the determination of available phosphorus, 2 g of lime was weighed in 250 mL extraction bottle and 0.2 g of activated charcoal and 40 mL of 0.5 M of $CaHCO_3$ were added and shaken for 30 minutes on orbital shaker at 200-3000 revolution per minute. Then the sample was filtered with What-man filter paper and the aliquot was transferred to 50 mL volumetric flask and kept overnight. Then 2.5 mL of 2 N of H_2SO_4 was added, and then 8mL of reagent B was added for colour development and make up to the mark. The sample was read using spectrophotometer after calibrating by using the standard solution at 882 nm wavelength. The result was calculeted as follows:

$$P\ (ppm) = \frac{R*Vt*Vex}{Aliquot*Wt} \quad (9)$$

Where: R-Reading in µg (from spectrophotometer), Vt - total volume, Vex-volume of $CaHCO_3$ for extraction, Wt - weight of the sample, ppm - parts per million.

Experimental Design, Procedure and Treatments

The experiment was conducted for two years (2015 – 2016) at research field of HARC. The experiment was laid out in randomised complete block design (RCBD) with three replications. The treatments were five lime materials: Dejen lime, Awash Dolomite Ca Mg $(CO_3)_2$, Awash Calcite ($CaCO_3$), Senkele lime and hydrated lime (Ca $(OH)_2$) and control (without any lime type) at HARC. The plot area used was 3*4 m^2. Land preparation, planting, weeding and harvesting were undertaken according to the crop agronomic requirement. For all lime materials, the amount of lime to be applied was calculated on the basis of the exchangeable acidity for each site, bulk density and 15 cm plough depth. It was assumed that one mole of exchangeable acidity would be neutralized by an equivalent mole of $CaCO_3$ (adopted from Kamprath, 1984).

$$LR = \frac{Ac*0.15m*area\ (msq)*BD*1000}{2000} \quad (10)$$

Where: LR- Lime requirement (kg ha^{-1}), Ac-Exchangeable acidity ($cmol_{(+)}kg^{-1}$ soil) BD- Bulk density (kg m^{-3}), msq-meter square

Lime was broadcasted uniformly by hand and incorporated into the soil a month before planting. The recommended rate of NP was applied uniformly to all treatments. Urea (72 kg ha^{-1}) and DAP (150 kg ha^{-1}) were used as the source of N and P. The test crop was barley *(Hordeum vulgare L.)* (variety HB 1307). Data on crop yield and its components were collected following the crop's agronomic data collection procedures.

Soil sampling and analysis

Composite soil samples were collected before execution of the experiment and treatment based composite soil samples were collected after final harvest and analysed for their selected chemical properties (pH, total N, available P (Pav.), Organic carbon (OC), cation exchange capacity (CEC), exchangeable cations (Ca. Mg, K, Na), exchangeable acidity (Al^{+3} + H^+), Al and extractable Zn, Cu, Fe, and Mn. The soil samples collected after final harvest were air dried, sieved, stored with paper box and then analysed. The pH of the soil is determined with the potentiometric method

(1:2.5 Soil: Water) as described by Chopra and Kanwar (1976). Available phosphorus was measured using Bray II procedure (Bray and Kurtz, 1945). Soil OC was determined as described by Walkley-Black (1934) while TN was measured using the Kjeldahl method (Rainst *et al.*, 1999). Exchangeable acidity (Al^{+3} and H^{+1}) and exchangeable Al were determined by saturating the soil samples with 1 N KCl solution and the filtrate was titrated with 0.02 N NaOH and 0.02 N HCl, respectively, as described by Rowell (1994).

Data analysis

The data were subjected to analysis of variance (ANOVA) using Statistical Analysis Software (SAS, 2004). The difference among significant treatment means were tasted using least significant difference (LSD) at 5% level of significance. Before combined analyses test of homogeneity of error variance and normality was checked.

RESULTS AND DISCUSSION

Characterization of the lime materials

Physico-chemical properties of the different lime materials are indicated in Table 1. The reaction of Hydrated lime (Ca $(OH)_2$) and that of Senkele were very strongly alkaline, while Dejen lime, Awash calcite and Awash dolomite were strongly alkaline. Both Awash limes (calcite and dolomite) showed better P content followed by hydrated lime while the P content of Senkele lime was trace. All lime materials have nearly equal percent of $CaCO_3$. Hydrated lime ($Ca(OH)_2$) of Chora gas has a CCE higher than 100% while the lime materials have above 90% CCE (Table 1). This indicated that at least 90% of the material could dissolve and neutralize soil acidity, the higher the CCE the higher its speed of reaction to counteract the negative effects of soil acidity. This finding is in agreement with the report of (University of Kentucky College of Agriculture, 1960) which reported the minimum CCE to qualify as ground agricultural limestone is 80%. This means that at least 80% of the material could dissolve and neutralize soil acidity.

Dejen lime has better fineness percentage while hydrated lime ($Ca(OH)_2$) has the least fineness percentage (Table 1). This finding is in agreement with the report of (Conyers *et al.*, 1995) who reported that particle size analysis on limestone's undertaken using dry sieves do not extend reliably to < 50 micron or 0.05 mm. Both Awash calcite and hydrated lime have better Ca content than the other lime materials. Awash dolomite has better Mg content while hydrated lime has less Mg content. Senkele lime had less relative neutralizing value (Table 1) when compared with other lime materials. Similar finding was reported by Soil Survey Division Staff (1993).

Table 1. Physico chemical properties of the lime materials

Lime type	Parameters							
	pH	Pav (ppm)	% $CaCO_3$	% CCE	Fineness	% RNV	% Ca	% Mg
Dejen lime	8.7	3.12	11.90	96.70	92.41	89.36	37.58	0.75
Awash Dolomite	9.0	4.62	11.79	96.10	87.31	83.31	13.96	4.10
Awash-Calcite	8.5	4.34	11.82	95.54	89.56	85.57	40.29	0.57
Senkele lime	10.0	trace	11.68	91.88	86.91	79.57	22.22	0.29
Hydrated lime	12.5	1.59	12.20	>100	80.63	>80.63	44.90	0.12

Pav - available phosphorous, %CCE - percent calcium carbonate equivalence, %RNV - percent Neutralizing Value.

Soil Chemical properties before planting and after harvest

The nutrient content of initial soil samples taken from HARC was described before liming. Hence based on soil nutrient rating of Tekalign (1991), the soil was very strongly acidic, available P was very low (Jones, 2003). Total nitrogen content was high (Tekalign, 1991). Calcium content was medium according (FAO 2006) nutrient rating. Magnesium content was medium as nutrient rating (FAO, 2006). Similarly, potassium content was high (FAO, 2006). According to soil nutrient rating of Jones (2003) the micronutrient (Cu, Zn, Fe and Mn) content fall in the range of medium to high and this range was not changed even after lime application.

Table 2. Soil chemical properties before the start of the field experiment

pH	Ac	exAl	Pav	N	OC	CEC	Ca	Mg	K	Cu	Fe	Zn	Mn
4.43	1.1	0.54	6.23	0.15	1.36	19.57	6.4	1.17	1.21	3.01	44.16	0.6	47.5

Ac -exchangeable acidity, exAl- exchangeable Al, Pav- available phosphorous.

Soil pH, Exchangeable Acidity and Exchangeable Al

These parameters which were used as diagnostic tools for the prediction of Al toxicity, have been grouped together and their result after final crop harvest is shown in Fig 3.

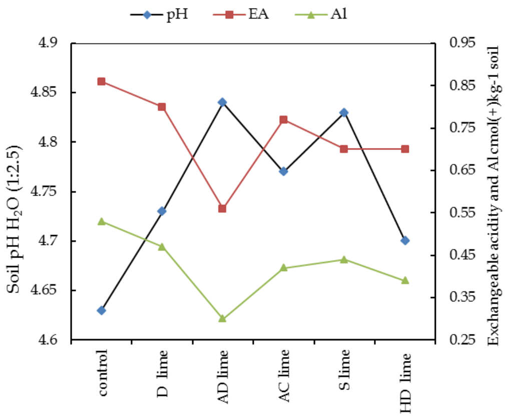

Figure 3. Soil pH, exchangeable acidity and Al content of the soils. Key: D- Dejen, AD- Awash dolomite, AC- Awash calcite, S- Senkele, HD– Hydrated.

Soil pH was initially extremely acidic (Table 2) and was improved to very strongly acidic after application of Awash dolomite and Senkele lime (Figure 3). Exchangeable acidity was 1.1 $cmol_{(+)}kg^{-1}$soil before lime application and improved to 0.56 $cmol_{(+)}kg^{-1}$soil after the application of Awash dolomite, similarly, it decreased Al content of the soil (Table 2 and Figure 3).

Available Phosphorus, Total Nitrogen and Organic carbon

Phosphorus content of the soil was improved with application of Awash calcite. Total N and organic carbon content of the soil did not show differences among treatments (Figure 4).

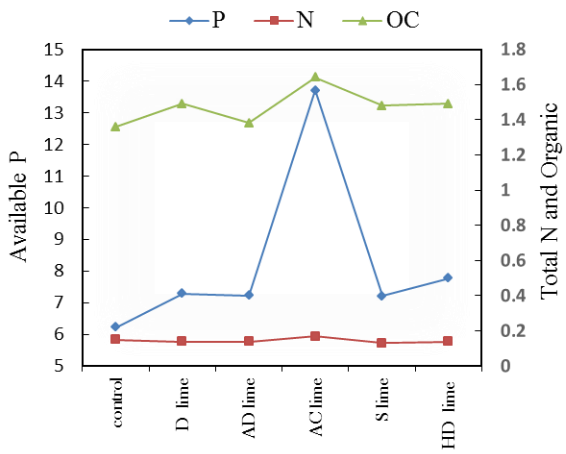

Figure 4. Soil available P, total N and organic C content of the soils. D - Dejen, AD - Awash dolomite, AC - Awash calcite, S - Senkele lime, HD – Hydrated.

Calcium, Magnesium, Potassium and Cation Exchange Capacity

All lime materials showed a very slight improvement of Ca content from the initial. The Mg content of the soil increased after the application of Awash dolomite (Table 2 and Figure 5). The present finding corroborates with Anetor and Akinrinde (2006) by asserting that lime increases soil pH, calcium and magnesium saturation of soil. Initial K content of the soil was 1.21 ($cmol_{(+)}kg$ soil) before lime application and improved to 1.67 ($cmol_{(+)}kg$ soil) after the application of Dejen lime. The CEC of the soil never showed observable difference for different lime sources (Figure 5)

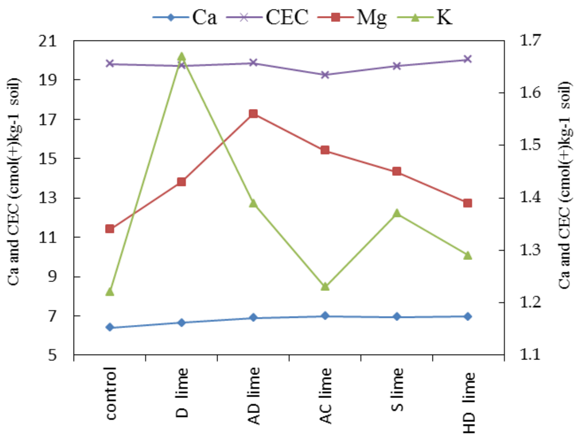

Figure 5. Calcium, Magnesium, Potassium and CEC content of the soil. Key: D - Dejen, AD - Awash dolomite, AC - Awash calcite, S - Senkele, HD – Hydrated.

Micro nutrients

Micro nutrient (Fe, Mn, Cu and Zn) after crop harvest is presented in Figure 6. The liming materials did not bring significant changes in soil micro nutrient content after crop harvest (Fig 6). The probable reason for this happening might be the amount of lime determined by exchangeable acidity lime rate determination method was not sufficient to bring change of micronutrient content.

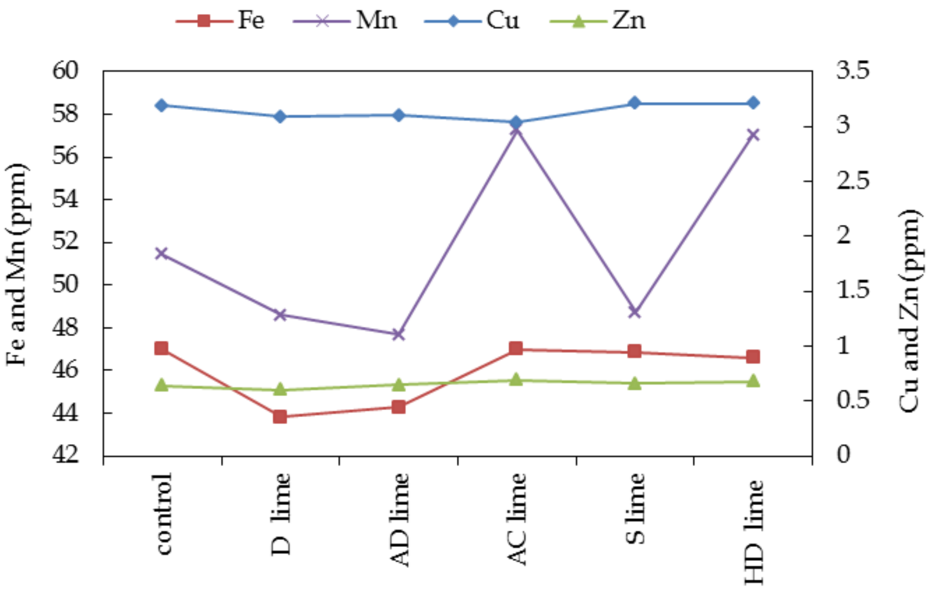

Figure 6. Micronutrient content of the soils; Key: D - Dejen, AD - Awash dolomite, AC - Awash calcite, S - Senkele, HD – Hydrated.

The effect of all lime materials on acidic soil properties such as pH, Ac and ex Al, Pav., TN and OC, Ca, Mg, K and CEC and micronutrients did not show significant variations. This might be because, all lime sources had nearly equal values of percent $CaCO_3$, CCE, fineness and RNV.

Hydrated lime ($Ca(OH)_2$), a by-product from Chora Gas and Chemical Products Factory, has performed well comparable to the lime materials produced both at Oromia and Amhara regional states and with that of Awash limes.

Effect on yield and yield components of food barley

The two years (2015 and 2016) combined analyses result showed no significant yield difference among lime materials, except when compared with the control treatment. Senkele lime gave (12.86%) more grain yield compared with the control treatment. Awash dolomite, hydrated lime and Awash calcite gave 11.41%, 10.97% and 10.55% grain yield compared with the control treatment respectively. This indicated that hydrated lime gave nearly equal grain yield with the two Awash lime types (Calcite and Dolomite). The two Awash limes gave an equivalent biomass. Similarly, Dejen, Senkele and hydrated lime gave nearly equal biomass. Hydrated lime gave 5.87% TSW compared with the control. Awash dolomite, Senkele, Dejen and Calcite gave 5.13%, 4.4%, 3.42% and 2.69% TSW compared to control respectively. This indicated that hydrated lime can almost equally ameliorate acid soil as conventional/natural limestone materials obtained from Awash area (Calcite and Dolomite), Senkele and Dejen lime (Table 3).

The probable reasons why change of soil chemical properties and yield difference was not significant among different lime materials is the mineralogical content of the lime materials might be nearly similar.

Table 3. Over year analysis result of food barley yield and yield component as affected by different lime materials (2015 and 2016)

Treatment	PLHT (cm)	Spkln (cm)	Spkpsp	BM (kg ha^{-1})	GY (kg ha^{-1})	HLW (%)	TSW (g)
Control	94.2^{b}	6.4^{a}	38.2^{b}	8360.7^{b}	4018.9^{b}	55.9^{c}	40.9^{b}
Dejen lime	100.3^{a}	6.6^{a}	43.7^{a}	11925.9^{a}	4347.8^{a}	59.4^{ab}	42.3^{ab}
Awash dolomite	101.7^{a}	6.7^{a}	38.6^{b}	12138.9^{a}	4477.6^{a}	60.4^{a}	43.0^{a}
Awash calcite	101.2^{a}	6.9^{a}	41.6^{ab}	12047.1^{a}	4442.8^{a}	59.1^{b}	42.0^{ab}
Senkele lime	102.0^{a}	6.7^{a}	41.3^{ab}	11926.8^{a}	4535.8^{a}	59.8^{ab}	42.7^{a}
Hydrated lime	99.3^{a}	6.6^{a}	41.6^{ab}	11694.5^{a}	4459.9^{a}	59.2^{ab}	43.3^{a}
Mean	99.81	6.66	40.84	11348.86	4380.44	58.98	42.36
CV (%)	3.12	6.97	8.12	13.66	5.70	1.72	2.93
LSD (0.05)	3.73	NS	3.97	1856.0	298.94	1.22	1.49

PLHT - plant height, Spkln - spike length, Spkpsp - spikelet per spike, BM -biomass, GY- grain yield, HLW- hectolitre weight, TSW -thousand seed weight.

CONCLUSION

The results of the study showed that the industrial by product hydrated lime has nearly equal percentage of $CaCO_3$ content with the natural liming materials (Dejen, Senkele, Awash calcite and Awash dolomite) produced in Ethiopia at different locations; hence neutralizes soil acidity nearly at equal capacity. Regarding the improvement of soil chemical properties hydrated lime improves the soil nearly at equal magnitude with other lime sources, but it has a bit better CEC than Awash calcite, which was highly recognized for its % Ca content. Hydrated lime gave nearly equal barley grain yield and yield components as of the two Awash lime types. Therefore, to identify the sincere effect of this industrial by product ($Ca(OH)_2$) it would be good if verification trial will be conducted by using Awash calcite the most predominant agricultural lime in the country as standard check at multi-locations of acid prone areas having different acidity levels with different test crops.

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