

## Elemental Analysis of Soil around Aykle in Chilga District North Gondar, Ethiopia using the Technique of Instrumental Neutron Activation Analysis (INAA)

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### ABSTRACT

The aim of this study was to determine the essential chemical composition of soils in Chilga district Northwest Ethiopia by the technique of non-destructive Instrumental Neutron activation analysis. The soil samples were collected, dried, pulverized and passed through sieve to get in a homogenous state. About 150mg of representative mass from each sample weighed, heat sealed, packed in polyethylene vial and was fed into the Nigeria research reactor (NRR-1) for irradiation by means of pneumatic transfer with the aid of rabbit capsules. After the activities of the samples were counted by HPGe detector gamma spectrometry and analyzed using gamma-ray spectrum analysis software WINSPAN 2004, the concentration of 33 elements were identified and quantified. Among the 33 elements Mg, Al, Ca, Ti, Na, K, Fe, Mn were found in the category of macronutrients; elements such V, Ba, Zn and Sr were present in micronutrients; elements like U, Co, As, Th and Cr were measured in trace concentration with others 16 nonessential elements measured at minor and trace levels. The results of this study showed that the median concentrations of Mg, Al, Fe, Ti, Mn, Zn, V, Co, As, and Cr in the soils of Chilga district were obtained above the world soil median values. In particular Al, Mn and Fe were found as toxics that hinder the normal growth of plants and crops.

**Key words:** INAA; Essential elements; macro-and micronutrients, worldwide soil median, HPGe detector Gamma spectrometry, NRR-1, Cluster analysis,

### INTRODUCTION

Soil is an essential component of the terrestrial ecosystem upon which man and all living things directly or indirectly depend on it as basic source of food [1]. Soil by its nature is a heterogeneous mixture of different organic and inorganic substances, micro-organisms, minerals, rock particles, water and gases [2, 3] and varies from place to place. Even though soil is the constituents of various inorganic and organic compounds, as studies suggest macro-nutrients (like K, Mg, P, S and N), and micro-nutrients (such as B, I, Mo, Co, Fe, Se, Cu, Mn and Zn) are the most essential components of soil for the healthy growth of plants and high productivity of various crops in agriculture fields [4, 5, 6].

Nowadays, however; soil pollution has become a worldwide problem. Soil can be polluted if the concentrations of heavy and trace elements (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Se, V, and Zn) resulting from natural and anthropogenic activities are in excess. For instance, atmospheric

particles emitted from forest fires, volcanic activity, flood-water transport, biogenic emissions and weathering process of parent rocks are the natural sources of soil pollution [7, 8, 9]. On similar fashion, soil can be adversely affected by anthropogenic activities such as unwise human interventions for agricultural purposes, adding of fertilizers to enhance soil fertility, burning of home based woods, coal ashes, polluted water sewerages, industrial processes and waste disposal; mining and drilling [7]. These excessive levels of elements which could be caused by natural and anthropogenic activities in soil can be introduced into the food chain via plants, cereal crops and ultimately into humans and animals that feed upon the plants and cereal crops. To put it simply, nutrients which are important for plants and crops can be toxic if their concentration amounts in soil are more than necessary.

On the other hand, soil can have essential mineral elements in scarcities, which are important for normal growth of plants and crop production. Such mineral scarcities could be arisen because of the unwise agricultural practices, erosion, natural wind blow and indiscriminate waste disposal, etc. In general, the availability, diversity, scarcity and toxicity of essential elements of soils need to be understood by employing different techniques of investigation to overcome and solve the specific agricultural and environment based problems.

The aim of present work was to assess the essential mineral composition and toxicity in soils of Chilga district, Northwest Ethiopia. Chilga district is an active geological area where its bed rocks consist of precious metals, heavy metals, coal, coal ashes and natural gases. Thus, elemental analysis of soils was carried to examine the essential elements distribution, availability, scarcity, toxicity, and the possible cause of soil acidity. The elemental analysis was done using the Instrumental Neutron Activation Analysis (INAA), which is a sensitive, nondestructive and versatile nuclear technique that is used for making qualitative and quantitative based elemental analysis.

## **MATERIALS AND METHOD**

### **Sample Collection and Preparation**

A total of six soil samples (0–5 cm depth) was obtained from six different sampling sites known as Serako, Nara Micheal, Nara awrdarda, Dilanba, Alemtsehay and Yihuseraba from around the town of Aykle in Chilga district. The name of sampling sites and their corresponding codes including GPS Coordinates are shown in figure 1. Chilga District is located at 60 km west of Gondar city in northwest Ethiopia lying at latitude of 12° 32'54.44" N and longitude of 37°05'11.22" E. The samples were made dried in open air for a few days; crushed by agate mortar and then passed through 100 micron mesh sieve to get a homogenized powdered form. After samples were pulverized, small representative sub-samples in the range of 150- 250 mg were weighed using a four-digit Melter model weighing balance and heat sealed in a cleaned polyethylene sheet for irradiation.

Similarly, for purpose of quality assurance and data validation of INAA, two standard reference materials (SRMs), namely: Soil-7 (IAEA) and Coal fly ash (NIST 1633b) whose mass equivalent to the mass of soil sample were weighed and heat sealed separately in a pre-cleaned polyethylene sheets. Finally, the samples and standard reference materials were packed together in a polyethylene vial for irradiation.

Table 1 Sample code, sampling site and GPS coordinate of the study area

Sample code	Sampling Site	GPS Coordinate
SSO1	Serako	Lat.12° 33'49.49'' N, Long.37°3'39.10'' E
SO2	Nara Michael	Lat.12° 32'29.42'' N, Long.37°6'1.54'' E
SSO3	Nara Awrdarda	Lat.12° 32'22.84'' N, Long.37°4'38.95'' E
SSO4	Dilanba	Lat.12° 33'51.21'' N, Long.37°4'41.56'' E
SSO5	Alemtsehay	Lat.12° 33'5.36'' N, Long.37°5'51.34'' E
SSO6	Yihuserako	Lat.12° 32'14.30'' N, Long.37°3'41.05'' E

### Irradiation and Counting

The samples and standard reference materials packed in a polyethylene vial were irradiated in the Nigerian Research Reactor (NIRR-1). The irradiation process was performed via a pneumatic transfer system assisted rabbit operating at pressure of 0.5 Mpa. There were two schemes of irradiation depending on activation products: short and long irradiation [8].

Table 2: Classification of radionuclides based on (n,γ) reaction, irradiation time ( $t_{irr}$ ), cooling time ( $t_{irr}$ ), counting time ( $t_c$ ), irradiation, counting scheme, and product radionuclide including half life time ( $\tau_{1/2}$ ) and energy (in keV).

$t_{irr}$	$t_d$	$t_c$	Counting scheme	Product radionuclide (with half time and energy) [Ref. 10]
1 min	3-15 min	10min	1 <sup>st</sup> short (1S)	<sup>27</sup> Mg (9.46 min, 1014.4keV), <sup>28</sup> Al (2.24 min, 1779.0 keV), <sup>49</sup> Ca (8.72 min, 3084.5 keV) & <sup>52</sup> V (3.75min, 1434.1keV)
	3-4 hrs	10 min	2 <sup>nd</sup> short (2s)	<sup>24</sup> Na (15.0 hrs, 2754.0 keV), <sup>42</sup> K (12.4 hrs, 1524.5 keV), Dy (2.23hrs,94.7) <sup>56</sup> Mn (2.58 hrs, 1810.7keV) & Sr(2.81,3884.4)
6hrs	3-4 days	30 min	1 <sup>st</sup> Long (1L)	<sup>140</sup> La (40.3 hrs, 1596), <sup>80</sup> Sm (46.3 hrs, 103.2 keV) & <sup>82</sup> Br (35.3 hrs, 776.5 keV), Ho(26.8hrs,80.6keV) & <sup>238</sup> U[ <sup>239</sup> Np](56.6h, 277.6keV)
	9-11 days	1hr	2 <sup>nd</sup> Long (2L)	<sup>Cr</sup> (27.7d, 230.1keV) <sup>Co</sup> (5.27yrs, 1332.), <sup>Sr</sup> (64.8d, 514.0keV), <sup>46</sup> Sc (83.8 days, 889.3 keV), <sup>59</sup> Fe (44.5 days, 1291.6 keV), <sup>65</sup> Zn (244 days, 1115.6), <sup>86</sup> Rb (18.7 days, 1076.6 keV), <sup>131</sup> Ba (11.8 days, 496.3 keV), <sup>152</sup> Eu (13.3 yrs, 1408.0 keV), <sup>Sb</sup> (4.27h, 564.2keV), <sup>147</sup> Nd (11 day, 91.1 keV), <sup>160</sup> Tb (72.3 days, 879.34 keV), <sup>Tm</sup> (129d, 84.3keV), <sup>Lu</sup> (6.71d, 208.4keV), <sup>Ta</sup> (115d, 1221.4keV), <sup>175</sup> Yb (4.19 days, 396.3 keV) & <sup>232</sup> U[ <sup>233</sup> Pa](27d,312.0, 277.6keV)

In short irradiation scheme, the samples were irradiated for 1 minute in the reactor's outer irradiation channel (B2) that generates a thermal flux of  $2.5 \times 10^{11} \text{ n.m}^{-2}.\text{s}^{-1}$ . The first round of counting for 10 minutes was performed using a 15cm height sample holder placed at the surface of the detector after a waiting time of 2-15 minutes for cooling time. The radiation counting at position is denoted by 1S (1<sup>st</sup> short counting). The second round of counting for the same sample was taken for 10 minutes after a cooling of time of 3 to 4 hours and the radiation counting is denoted by 2S (2<sup>nd</sup> short counting). The purpose of short irradiation scheme is to capture radionuclides with half-lives in the order of minutes.

In the case of long irradiation, about 6-8 samples in a polyethylene vial were irradiated for period of 6 hrs in the inner channel (B4) of the same facility that generates a thermal flux of  $5 \times 10^{11} \text{ n.m}^{-2}.\text{s}^{-1}$ . The first round of counting for 30 minutes was carried out after a waiting period of 3 to 4 days to capture radionuclides with half-lives in the order of hours or few days. This long term radiation counting is termed as 1 L (1<sup>st</sup> Long counting) and is carried out using a 2cm height sample holder above placed the surface of the detector. Finally, the second round of the counting for the same sample was done for 60 minutes after a cooling period of 9 to 11 days. This second long term radiation counting is termed as 2L and radionuclides with half-lives in the order of days and years were identified. In general the half-lives and energies of the identified product radionuclides in the soil sample are displayed in table 2.

### Gamma ray spectroscopy Analysis

The counting of the samples and standard reference material was performed using HPGe detector gamma spectroscopy and the gamma-ray spectrum analysis software WINSPAN 2004, software developed at CIAE, Beijing, China. However, before the start of counting the induced gamma-ray activity of the irradiated samples, the efficiency calibration and standardization of the HPGe detector, which was connected via the associated electronics to preamplifier, amplifier, a cortex 4096-multichannel analyzer and a PC desktop computer, was carried out using standard radioactive sources such as  $^{37}\text{Cs}$ ,  $^{22}\text{Na}$ ,  $^{60}\text{Co}$  and  $^{152}\text{Eu}$ . Such efficiency calibration was done using the 2cm and 15cm height sample holder placed at the surface of the detector. Similarly, the energy calibration was done at Full Width Half at Maximum (FWHM) = 1.3 keV at 1332 keV resolution using  $^{60}\text{Co}$ .

The method of analysis that was chosen in this study was relative method of neutron activation analysis. In relative method, uncertainties that could appear due to nuclear parameters such as cross sections, neutron flux, decaying scheme and detector efficiency would be eliminated. For this purpose the samples and standards were irradiated simultaneously and counted under the same geometry as a result of which nuclear parameters were cancelled. In relative method, the net peak areas for the gamma-rays of radionuclides in the samples were calculated and compared with those of Apple leaves (NIST 1515) and the concentration of each radionuclide in the sample could be determined using the equation (1).

$$C_{sam} = C_{std} \frac{A_{sam}}{A_{std}} \frac{M_{std}}{M_{sam}} \frac{(e^{-\lambda_d})_{std}}{(e^{-\lambda_d})_{sam}} \quad (1)$$

Where  $C_{sam}$  and  $C_{std}$  are the concentration elements in the unknown and standard samples,  $A_{sam}$  and  $A_{std}$  are activity rates of the elements in unknown and the standard samples,  $M_{sam}$  and  $M_{std}$

are the masses of the sample and standard,  $t_d$  is the decay time,  $(e^{-\lambda t})_{\text{sam}}$  and  $(e^{-\lambda t})_{\text{std}}$  are decay factors of the element in the sample and standard,  $\lambda = \frac{\ln}{T_{1/2}}$  the decay constant and  $T_{1/2}$  is nuclide half time.

## RESULTS AND DISCUSSION

In order to evaluate the accuracy and precision of the method of INAA two standard certified reference materials (SRMs) of geological origins known as IAEA-soil-7 and NIST 1633b Coal fly ash were irradiated and analyzed along with the soil samples. The measured concentrations of different elements in IAEA-Soil-7 and in coal fly ashes (NIST 1633b) in this work by relative method of INAA were in good agreement with the IAEA and NIST certified reference materials (Soil-7 and Coal fly ash) as shown in tables 3 and 4. In addition, the precision and trueness of the counting system was also calculated as percentage relative standard deviation (% RSD). It was obtained that most of the percentage values were observed to be less than 16.5 % indicating high order of accuracy and precision of our data with the exception of U and Yb which deviated a bit high from the certified values.

Table 3: Elemental Concentrations of Soil-7 (IAEA Soil-7 in ppm) for quality control purpose

Element	This work	Certified value	95% I.V	RSD (%\)
As	12.6±0.1	13.4	12.5-14.2	5.97
Co	8.5±0.3	8.9	8.9-10.1	4.49
Dy	3.7±0.4	3.9	2.5-5.3	5.13
Cr	63±2	60	49-74	-5.0
V	68±4	66	59-73	-3.03
Eu	1.3±0.1	1.0	0.9-1.3	-0.3
Hf	4.6±0.2	5.1	4.8-5.5	9.8
Mn	634±3	631	609-650	0.47
Rb	56±4	51	47-56	9.8
Sm	5.1±0.3	5.1	4.8-5.5	0
Sc	8.4±0.1	8.3	6.9-9.0	12.05
Ta	0.7±0.2	0.8	0.6-9.0	12.5
Tb	0.7±0.1	0.6	0.5-0.9	16.67
U	1.82±0.22	2.6	2.2-3.3	30
Th	8.35±0.18	8.2	6.5-8.7	-1.8

RSD (%) = percentage of relative standard deviation

In the present study, the concentrations of 33 elements were quantified using INAA in soil samples collected from Chilga Woreda as tabulated in table 5. The concentration amounts of the 33 elements were also compared with the worldwide top soil concentration as displayed in table 6. In short irradiation scheme, radionuclides with short half-lives such as Mg, Al, Ca, Ti, Na, K, Fe, Mn

and V were captured and identified whereas in long irradiation scheme radionuclides with intermediate and long half-lives such as Dy, As, Br, La, Sm, Sc, Ho, U, Cr, Lu, Co, Zn, Sr, Rb, Sb, Ba, Nd, Eu, Hf, Ta, Tb, Tm, Yb, and Th were identified as tabulated in table 1. Among the measured elements Mg, Al, Ca, Ti, Na, K, Fe and Mn were found as macro-nutrients in all soils as depicted in figure 1 and elements such as V, Sr, Ba and Zn were obtained as micro-nutrients as shown in figure 2 with Dy, As, Br, La, Sm, Ho, U, Sc, Cr, Co, Zn, Rb, Sb, Nd, Eu, Tb, Tm, Yb, Lu, Hf, Ta, and Tb measured at trace levels.

Table 4: Elemental Concentrations of coal ash fly (NIST-1633b in ppm) used for quality control purpose, mean  $\pm$ SD

Element	This work	Certified value
Mg (%)	0.482 $\pm$ 0.007	0.482 $\pm$ 0.008
Al (%)	15.05 $\pm$ 0.12	15.05 $\pm$ 0.27
K (%)	1.95 $\pm$ 0.02	1.95 $\pm$ 0.03
Ca (%)	1.51 $\pm$ 0.18	1.51 $\pm$ 0.06
Fe (%)	7.78 $\pm$ 0.05	7.78 $\pm$ 0.23
Na (%)	0.201 $\pm$ 0.001	0.201 $\pm$ 0.27
Ti (%)	0.791 $\pm$ 0.054	0.791 $\pm$ 0.140
As	136.2 $\pm$ 0.04	136.2 $\pm$ 2.6
V	295.7 $\pm$ 9.2	295.7 $\pm$ 3.6
Cr	198.2 $\pm$ 4.4	198.2 $\pm$ 4.7
Br	2.8 $\pm$ 0.2	(2.9)
Ba	709 $\pm$ 27	709 $\pm$ 55
La	94.0 $\pm$ 0.3	(94)
Ho	3.50 $\pm$ 0.24	(3.50)
Sr	1041 $\pm$ 80	1041 $\pm$ 14
Sm	20.00 $\pm$ 0.04	(20)
Nd	85 $\pm$ 3	(85)
Sb	6.00	(6.0)
Zn	210 $\pm$ 11	(210)
Th	25.7 $\pm$ 0.03	25.7 $\pm$ 1.3
Tm	2.1 $\pm$ 0.3	(2.1)

ppm = parts per million, Values in parentheses ( ) are information values

The concentration of magnesium in six of the samples ranged from 3792 $\pm$ 621 ppm to 11100 $\pm$  921 ppm with highest in soil of Dilanba area. Although the range of Mg was within the limit of world soil range [11] its median in Chilga soils were found above the worldwide soil median.



Table 5: Elemental concentrations (in ppm) obtained in soils

Element	Serako	N.Michael	N.Awrdarda	Dilanba	Alemtsehay	Yihuseraba
Mg	5592±951	3792±621	BDL	11100±921	7332±975	4529±811
Al	93040±744	97170±875	116100±696	88970±534	70070±631	83990±756
Ca	13980±1761	9707±1514	5990±1120	24990±2099	68430±3832	14670±1848
Ti	15470±727	20550±863	5160±857	13590±584	18760±7669	22290±758
K	8444±1777	5007±130	4685±159	4923±172	10200±592	11990±504
Fe	96720±484	117600±470	33690±337	90230±451	100600±12	90160±541
Na	2340±5	1164±4	1890±6	3422±7	14430±14	5873±504
V	329±9	425±8	223±6	2886±6	335±7	269±8
Mn	1544±5	2071±4	457±2	1745±4	1528±5	1549±
Dy	8.9 ±0.7	11±1	34±1	6.7±0.8	8±2	269±8
As	3.2±0.2	5.2±0.1	3.4±0.2	1.1±0.1	0.7±0.2	3.2±0.2
Br	10.2±0.3	29.7±0.4	1.9±0.2	13.9±0.4	BDL	10.0±0.5
La	27.2±0.2	38.6±0.2	117.9±0.2	14.8±0.1	26.7±0.2	47.03±0.23
Sm	7.48±0.02	10.35±0.03	27.9±0.1	5.57±0.02	9.00±0.03	11.51±0.03
Ho	1.2±0.2	1.9±0.2	10.9±0.2	1.3±0.2	1.1±0.3	1.71±0.0
U	0.8±0.2	2.35±0.2	5.8±0.3	BDL	BDL	BDL
Sc	33.0±0.1	36.1±0.1	21.6±0.1	31.4±0.1	22.9±0.1	19.0±0.1
Cr	202±4	13±4	72±3	248±4	BDL	68±3
Co	57±1	57.3±0.6	18±0.2	64.7±0.6	46±1	33.3±0.5
Zn	115±9	124±9	44±1	167±9	144±9	141±9
Sr	BDL	BDL	BDL	BDL	394±83	BDL
Rb	29±5	46±5	35±4	BDL	29±5	41±6
Sb	BDL	0.4±0.1	0.5±0.1	BDL	BDL	BDL
Ba	464±52	341±55	421±45	199±27	306±42	638±51
Nd	17±2	24±2	80±3	3.9±0.9	23±2	36.4±2.5
Eu	2.1±0.1	3.0±0.2	4.6±0.2	2.1±0.2	2.8±0.2	3.3±0.2
Tb	0.8±0.2	BDL	4.0±0.2	1.0±0.1	1.5±0.2	2.0±0.2
Tm	BDL	BDL	2.2±0.2	BDL	0.8±0.2	2.0±0.2
Yb	3.4±0.2	3.7±0.2	11.4±0.2	0.45±0.03	2.8±0.2	3.2±0.2
Lu	0.69±0.03	0.61±0.03	1.75±0.04	0.13±0.01	0.43±0.02	0.61±0.03
Hf	5.3±0.3	7.0±0.3	19.3±0.4	3.0±0.1	5.7±0.3	9.0±0.3
Ta	1.3±0.2	1.7±0.2	6.7±0.3	0.5±0.1	11.1±0.1	3.2±0.2
Th	4.7±0.2	6.3±0.2	15.5±0.2	1.1±0.1	2.1±0.2	6.2±0.2

ppm = parts per million, DL = Below Detection Limit

Table 6: Comparison of elemental concentration (in ppm) in terms of range, median and mean values between Chilga and worldwide soils

Element	Chilga soil			Worldwide soil [11]		
	Range	Median	Mean	Range	Median	Mean
Mg (%)	3792-11100	5590	5350	400-90000	5000	23000
Al (%)	70070-116100	91000	92000	10000-300000	71000	82000
K (%)	4685-11990	6725.5	7541.5	80-37000	14000	21000
Ca (%)	5990-68430	14100	22961	700-500000	15000	15000
Fe (%)	33690-117600	93475	88167	2000-550000	40000	41000
Na (%)	1164-14430	2881	4853	1500-25000	5000	23000
V	223-2886	332	745	3-800	90	160
Ti (%)	5160-22290	17100	15970	1500-25000	5000	5600
Mn	457-2071	1547	1737	20-10000	1000	950
As	0.7-5.2	3.2	2.8	0.1-40	6.0	1.5
Cr	13-248	72	121	705-1500	70	100
Br	1.9-29.7	10.20	13.14	2-270	0.37	NA
Ba	199-638	381.5	394.8	100-3000	500	500
La	14.8-117	32.9	45.3	1.9-29.7	NA	40.0
Ho	1.1-10.9	1.25	3.28	0.39-1.81	0.80	NA
Sc	0.8-5.8	2.03	2.64	0.4-6	2.00	NA
Sm	7.48-27.9	9.56	11.96	0.6-23	5.98	NA
Co	33.3-64.5	51.5	46.1	0.05-65	8.0	20.0
U	0.8-5.8	2.03	2.64	0.4-6	2.00	NA
Zn	44-167	135.2	122.5	1-900	90.0	75.0
Rb	29-46	35	36	1.5-1800	120	NA
Sb	0.4-0.5	0.225	0.225	1.00	7	NA
Nd	3.9-80	23.5	30.7	14.1-300	43.6	NA
Eu	2.1-4.6	2.9	2.9	0.1-2.6	1.28	NA
Tb	0.8-4.0	1.5	1.8	0.11-1.71	0.85	NA
Tm	0.8-2.2	2.0	1.7	0.34-1.2	0.62	NA
Yb	0.45-11.4	3.33	4.16	0.04-1.2	3.94	NA
Lu	0.13-1.75	0.61	0.70	0.1-0.95	0.46	NA
Hf	3-0-19.3	6.35	8.2	0.5-36	7	NA
Ta	0.5-11.1	2.45	4.08	NA	2	NA
Th	& 1.1-15.5	5.45	5.98	2-12	6	NA

NA = Not available



Magnesium is required by plants as secondary nutrient. As studies suggest taking Mg rich crops as a diet is also very important for human body because it plays a major role for the proper functioning of nerve system, muscle control and blood pressure. Similarly, the concentration of calcium was determined in the range between  $5990 \pm 120$  ppm to  $68430 \pm 3832$  ppm. In particular, the soils of Dilanba and Yihuseraba areas accumulated high content of Ca above the world soil median. The cause for high enrichment of Ca in these soils might be due to dead animals' bones decay, bush burning exercise by farmers and weathering of calcareous rocks [8]. Plants need Ca for the proper functioning of their cells and membranes and they take mainly from soil via their root uptake. Lack of adequate Ca content in both plants and animal bodies can cause physiological disorders.

Potassium like Mg and Ca was found in the present study in large concentration. The lowest and highest concentrations of K were found  $4685 \pm 159$  ppm and  $11990 \pm 504$  ppm in soils of Nara Awdarda and Dilanba respectively. This concentration range was found within the scope of the world top soil. According to Tisdale et al., 2004 [12], K concentration required by plant is in the range from 1000 to 40000 ppm. Potassium is the most essential elements for proper function of plants and humans bodies. It is required for osmotic and ionic regulation in cells, for carbohydrate, protein, fat metabolisms, enzyme activation and muscle function of human body [13]. Aluminum (Al) is most abundant element in the Earth's crust. However, as studies suggest Al has less biochemical roles in both plants and human bodies. An increased level of Al in soil can be a potential toxic plants' roots and also likely to reduce the existence of other important citation nutrients like K, Mg and Ca through competitive interaction [14]). In the present study, Al concentration was obtained in the range from  $70050 \pm 631$  to  $116100 \pm 696$  ppm. High content of Al was observed above the world median value in all soil samples with the exception of the soil of Alem Tsehay. Particularly, the soil of Nara Awdarda scored the highest concentration of Al which likely to produce highly acidic soil and hinder the growth of cereal crops that grow on it.

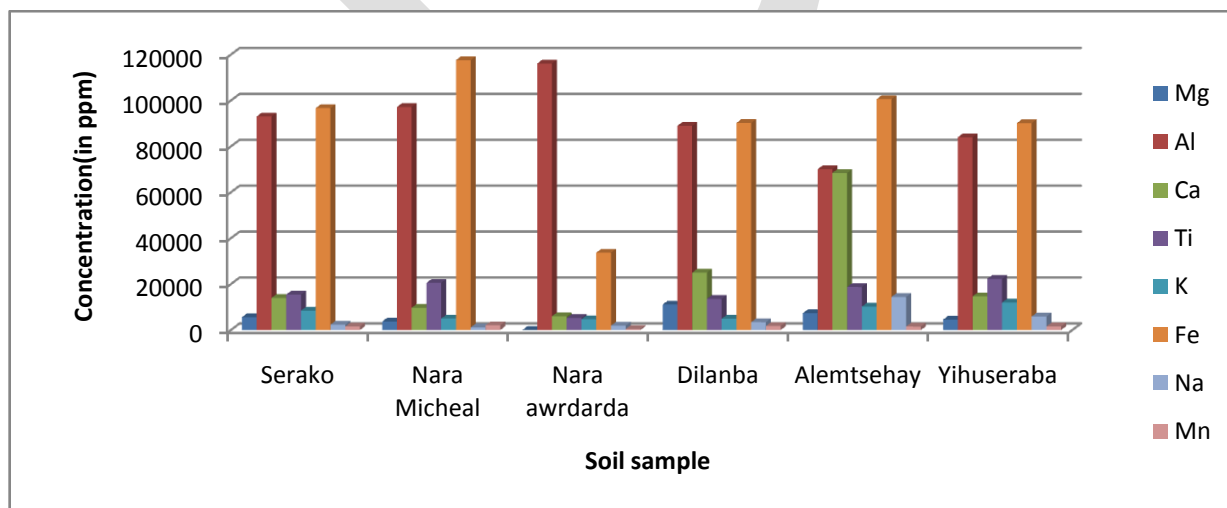


Figure 1 Macronutrients in six soil samples

Iron is the most essential mineral elements for both plants and animals. The concentration level of iron in this work was observed the highest in soil of Nara Michael in  $117600 \pm 470$  ppm and lowest in soil of in Nara Awdarda  $54930 \pm 75$  ppm. Elevated concentration of Fe above the world soil

median was found in all soils except the soil of Nara Awdarda. This implies that the soils of Chilga are rich in Fe content. However, studies suggest that excess intake of Fe can be toxic to plants and humans rather than its benefits. The other macro-nutrient obtained in the soils of the study areas was titanium. As studies indicate Titanium (Ti) has no known biological role in both plants and animals. The concentration of Ti obtained in this work ranged from  $5160 \pm 86$  ppm to  $22290 \pm 758$  ppm with highest concentration in soil of Yihuseraba.

Sodium is an essential element for the proper growth of plants and for the physiological metabolism of human body. Sodium is useful for osmotic pressure and acid-base equilibrium with Cl in human body. The excess or deficiency of Na intake in human body could likely be the sources of water retention, high blood pressure, stomach ulcer and cancer, confusion, weakness, seizures, coma and even death [15]. The concentration of Na in the present work was found in the range from  $1164 \pm 4$  ppm to  $14430 \pm 14$  ppm with the highest concentration in soil of Yihuseraba. All soil samples accumulated Na below the world soil median except the soil of Yihuseraba.

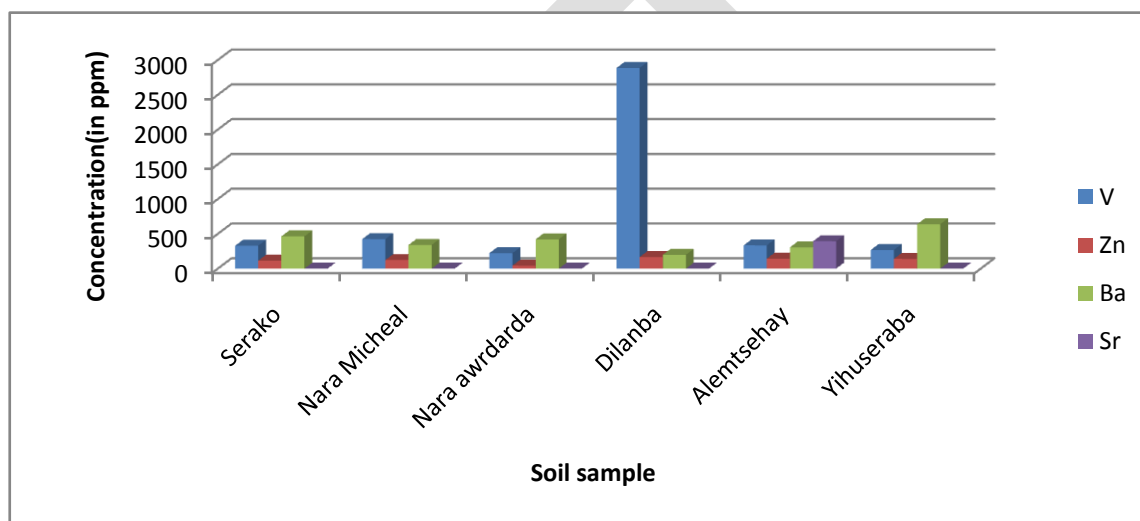


Figure 2 Micronutrients in six soil samples

In all samples, except the soil of Nara Awdarda, the concentration of manganese was recorded in the range from  $457 \pm 2$  ppm to  $2071 \pm 4$  ppm which is above the world soil median. This implies that the soils of Chilga were found rich in Mn contents. With regard to biological importance manganese is an essential micro-nutrient for plants and animals health. Plants take Mn via root uptake in the range of 20 to 500 ppm. Manganese is required by plant as enzyme activator for nitrogen assimilation and for the manufacture of chlorophyll in green plants. Similarly, the nutritional value of Mn is important for the metabolic process of human body to eliminate tiredness, fatigue and nervous irritability [16] but higher amount of Mn accumulation is not good for brain. As medical practitioners from Chilga clinics report the number of Epileptic patients has been increased through time due to unknown reasons. Since the excess intake of Mn through diet can contribute to brain disease further study should be undertaken.

Zinc, V, Ba and Sr were obtained in the category of minor concentrations as shown in figure 2. According to Brian (2008), zinc is an essential trace element found in varying concentrations in all soils, plants and animals [17]. It plays a vital role in such as wound healing, proper function of

nervous system, metabolic function, for growth and multiplication of cells and for treatments of malaria and diabetes Mellitus in human body [18]. In this study, the concentration range of Zn along all samples of soils was obtained in the range from  $44 \pm 1$  ppm to  $167 \pm 9$  ppm with highest in soil of Dilanba. Except the soil of Nara Awrdarda, all soils accumulated Zn above the world soil mean and median implying that the soils of the research areas are rich in Zn. The only soil that consists of strontium (Sr) at concentration level of  $394 \pm 83$  ppm above the world median was that one that obtained Alemtsehay area but in all other sample Sr was detected below detection limit. Like Zn, the concentration range of Vanadium ( $223 \pm 6$  ppm to  $425 \pm 8$  ppm) was found above the world mean value. Vanadium is required by micro-organism, cereal crops and small plants at very low concentration [19]. Taking V as nutritional diet is important for bone formation, and cellular replication. In addition, it works also the activities of insulin and decreases blood pressure.

On the other aspect U, Co, As, Th and Cr were measured in traces. These elements can be toxic if their amounts in both plants and animals are in excess. For instance U, Co and Th are radioactive elements which cause radiological hazards in human body when taken via ingestion due to the fact that they are the emitters of alpha and beta particles, and gamma rays. Uranium concentration in soil of Nara Micheal was found  $5.8 \pm 0.3$  ppm above the world median. Similarly except Co in soil of Nara Awrdarda, As and Co concentrations were obtained in all samples above the world soil median but their concentration ranges were found within worldwide soil range. Thorium like U is a natural radioactive element available at the surface of the Earth including soil. Th concentration in soils of Nara Micheal, Narawardarda and Yihuserba were obtained above the world soil median and its range in all samples range was also recorded above the worldwide soil limit.

Chromium concentration in soil varies from place to place depending on the natural sources of the areas and the extent of contamination from anthropogenic sources. The highest Cr concentration was found  $248 \pm 4$  ppm in soil of Dilanba and lowest  $13 \pm 4$  ppm at Nara Micheal. Elevated concentration of Cr above the world soil median was observed in soils of Dilanba and Serako areas. With regard to its nutritional value, Cr is known to be an essential element for the normal carbohydrate, protein and fat metabolisms in animals and humans if appropriate amount taken via the food chain. In addition, Cr has the function to reduce glucose tolerance and impaired insulin action [20]. Chromium can be toxic heavy metals if taken more than necessary. Rubidium (Rb) is another essential element for the production of hormones and various enzymes in human body [21]. In this study, Rb concentration was ranged from  $29 \pm 5$  ppm and  $46 \pm 5$  ppm which is below the world soil median. Europium, Dy, Br, La, Sc, Sb, Lu, Sm, Hf, Ho, Nd, Ta, Tb, Tm and Yb are the other nonessential elements obtained in this study in various proportions. As studies suggest the biological and nutritional benefits of these elements have not been known.

To assess the similarity among the concentrations of six soil samples a cluster analysis was also done using the cluster package contained in Minitab 16 on windows. The clustering was done in a two dimensional tree diagrams known as Dendrogram as shown in figure 3. Dendrogram is a multivariate diagram that helps to link together the similar concentrations of elements in the different samples. In figure 3, the highest clustering of soil samples was observed between soil of Serako and Yihu serba with the similarity level of 86.53 % followed by Serako and Dilanba with the similarity level 85.36%; Serako and Chelecbit in NaraWdarda with the similarity level of 78.30%; Serako and Alemtsehay with the similarity level of 51.69 % and the lowest clustering was seen between Serako and NaraWdarda with the similarity level of 35.83 %.

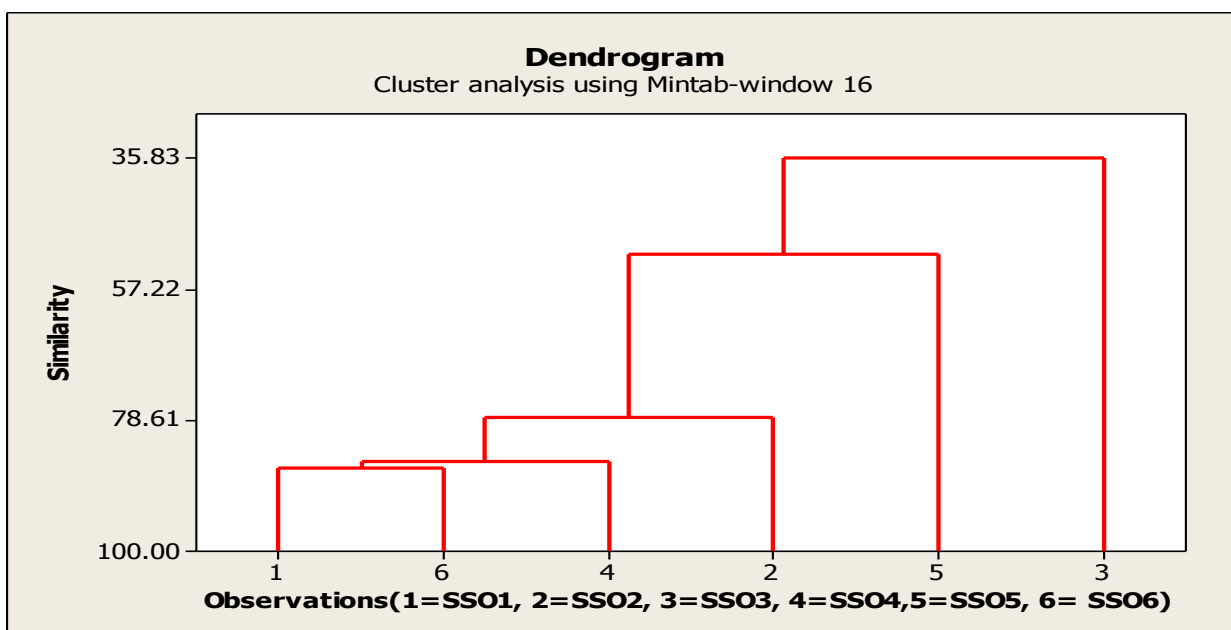


Figure 3: Cluster analysis of six soils from Chilga Districts

The cluster analysis showed that on one hand the soils of Serako and Yihuserba have almost similar elements with equivalent concentration contents and thus these soils have similar chemical properties. The same is true for Serako and Dilanba. On the other hand, the similarity between elements in soils of Serako and Lippa Adoensis were found so weak implying that the similar among the elements of the samples are different.

## CONCLUSION

The technique of INAA employed in the investigation of elemental composition soils of the Chilaga district in Northwest Ethiopia could determine a total of 33 elements. Among the 33 elements the concentrations of Mg, Al, Ca, Ti, Na, K, Fe, Mn were found at large concentrations (macro levels) in the range between  $457 \pm 2$  ppm to  $117600 \pm 470$  ppm with the highest concentration in soil of Nara awdarda. Compared with the world soil median, the concentrations of Mg, Al, Fe, Ti, Fe and Mn in all soil samples were found above world soil median whereas the concentrations of alkaline metals K and Ca was recorded below the corresponding world soil median values. Elements such as V, Ba, Zn and Sr were obtained in the range from 44 ppm to 2886 ppm relatively in small amounts (or micronutrient concentrations) but exceptionally the soil of Dilanba accumulates high content of V above the level of micronutrient. Although the concentration of Ba was measured below the world soil median except in soil of Yihuseraba, the concentrations of V and Zn nearly all samples of soil were found above the world soil median.

The data, in general, showed that the soils of Chilga district are substantially enriched in essential mineral compositions that are vital for the normal growth of plants and enhancement of crop production, however; the existences of excess amounts of Al, Mn and Fe in the soils are the most growth limiting factor for plants due to their high toxicities. Enhanced concentrations of acidic metals Al, Mn and Fe were found as compared to the alkaline metals Na, Mg and Ca, as a result of which the assumed soil acidity due to these metals was confirmed through this study.

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