Assessment of the Status of Selected Heavy Metals Contamination of Soils Nearby Nekemte Town, Ethiopia

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Abstract: Heavy metals are highly reactive and often toxic at high concentrations; they may enter soils and groundwater, bio-accumulate in food webs and adversely affect biota. The study was initiated during 2016 and designed in random sampling technique. A total of nine representative soil samples (0-25cm depth) from three sites (Hadiya River, Laga Mariam and Sorga Lake) were collected from sampling nearby Nekemte Town, *Ethiopia*. Soil pH of the study areas were ranged from 4.4 to 5.1 and rated as very strongly acidic soils. The concentration of Fe, Mn, Cr and Cu were varied from 0.83 to 1.12 mg/kg and contamination in soils were evaluated by concentration factor mean value results ranged from not detected to 26×10^{-3} and contamination level of Laga Mariam greater than Hadiya River, Hadiya River is greater than Sorga Lake. Similarly the enrichment factor mean value ranged from not detected to 0.83, by contamination level Hadiya River, Sorga Lake and Laga Mariam, respectively. Index of geo-accumulation mean value ranged from not detected to -1.46 at study areas and in contamination level Sorga Lake, Hadiya River, Laga Mariam, respectively. Degrees of contamination mean value of Cu, Cr, Mn and Fe varied from 0.02 to 0.03 at Laga Mariam; 0.01 constant at Sorga Lake; 0.01 to 0.02 at Hadiya River within samples. The results of the present study indicated that, low contamination with Cu, Mn and Fe in all sampling sites but the concentration of Cr was not detected in limit concentration in mg/kg and also average value of pollution load index indicated that unpolluted and lower than international quality guidelines recommended by WHO/USEPA.

Key words: Contamination · Concentration · Heavy Metals · Soil pollution · Laga Mariam

INTRODUCTION

Heavy metals are defined as elements in the periodic table having high atomic number, atomic weight, specific gravity greater than 5 and atomic densities of more than 5 g/cm³ generally excluding alkali metals and alkaline earth metals [1]. The environmental problems associated with heavy metals are that they as elements are undestroyable and most of them have toxic effects on living organism when exceeding their limited concentration. Furthermore, some heavy metals are being subjected to bioaccumulation, geo-accumulation and may pose a risk to human health when transferred to the food chain, soils for metals released into the environment from a wide variety of anthropogenic source. Heavy metals are harmful because of their non biodegradable nature, long biological half-lives and their potential to accumulate in human being [2].

Soil as a vital natural resource which performs key environmental, economic and social functions is non-renewable within human time scales. Soil is a long-term sink for the group of potentially toxic elements often referred to as heavy metals, including copper (Cu), chromium (Cr) and at high concentrations of iron (Fe) and manganese (Mn). Whilst these elements display a range of properties in soils, including differences in mobility and bioavailability, leaching losses and plant uptake are usually relatively small compared to the total quantities entering the soil from different agricultural sources. The behavior of some heavy metals in soils does not only depend on the level of contamination as expressed by total concentration, but also on the forms and origin of the metals and the properties of the soils themselves [3].

Nowadays heavy metals are ubiquitous because of their excessive use in industrial applications so waste water contains substantial amounts of their toxic heavy

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metals ion, which create problems [4]. The problem of urban soil contamination by heavy metals emerged due to rapid industrialization and urbanization. The wastewater from town drop forward to the study site rivers and the presence of intensive human activities in urban areas have worsened the problem of heavy metal contamination in urban soils. The high concentrations of heavy metals in urban soils have posed adverse effects on human health because metals can be easily transferred into human bodies from suspended dust or by direct contact. This, heavy metals contamination of the urban environment can have long-term and far-reaching environmental and health implications. Soil serves as both a sink and a source for heavy metal contaminants in the terrestrial environment [5]. However, information on the significance and extent of soil contamination with heavy metals from different sources are required so that appropriate actions can be effectively targeted to reduce inputs to soil environment. Human activities have resulted in a continuous increase in the levels of toxic heavy metals in the environment and anthropogenic activities such as agriculture and urban life increase the concentration of these elements in soils and waters [6]. So far no scientific research works on the evaluation of the status of some selected heavy metals concentration with in soil nearby Nekemte town have been studied. Therefore, to fill the gap this present study was initiated with the general objective of the assessing of the status

of selected heavy metals concentration in soil nearby Nekemte town compared with WHO/USEPA guidelines concentration.

MATERIALS AND METHODS

Description of the Studyarea: The study was conducted in Nekemte area, east Wollega zone, Oromia National Region State, in Western Ethiopia. The district is situated at a road distance of 310 km from the capital, Addis Ababa, 08° 59° and 09°06` north latitude and 37° 09° and 37° 51` east longitude. Sampling sites of the present study were soils nearby Laga Mariam, Sorga Lake (Haro Sorga) and Hadiya River showed in Figure 1. In the present research work, a total of nine representative soil samples in three study sites from nearby these rivers were collected for the evaluation of the status of selected heavy metal concentration for thrice (March, April, May) in 2016. The location map of the present study site is given in Figure 2 shown.

Instruments and Chemicals: A ZEEnit700P model Flame Atomic Absorption Spectrophotometer (FAAS) (analic JENA, Germany), instrument was used, four lamp positions and automatic lamp selection, was used for the determination of the concentration of Cu, Cr, Fe and Mn in soil samples. The chemicals used were 37% HCl (Riedel-de Haen, Germany) and calibration standards
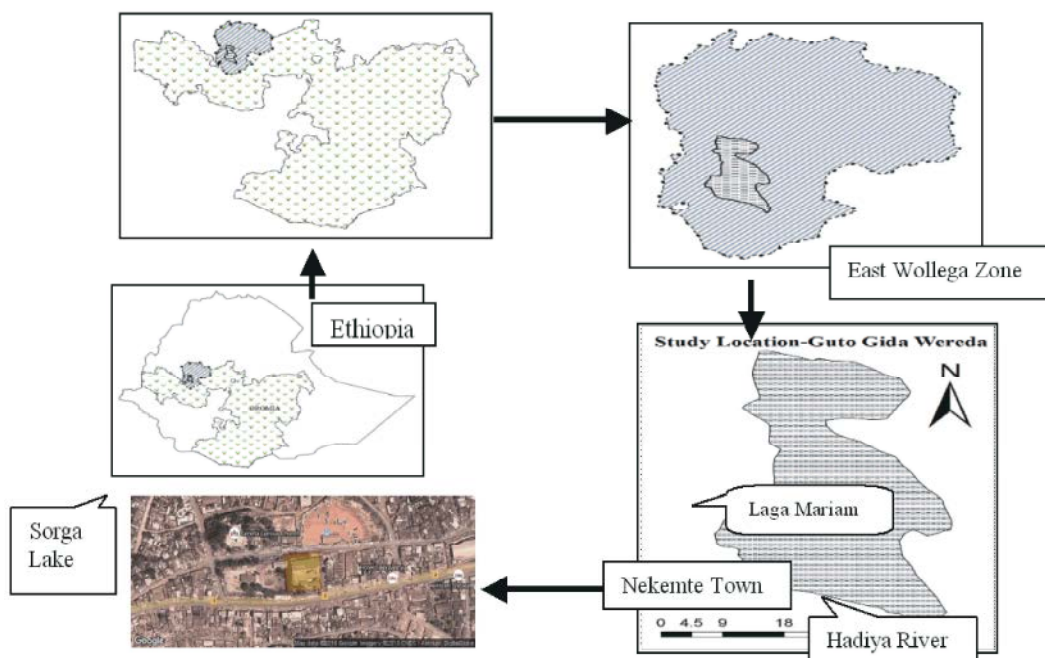

Fig. 1: Sampling area map of Laga Mariam, Sorga Lake and Hadiya River.

Fig. 2: Location Map of the Study Area

(SPECTROSCAN, Industrial Analytical (pyt) Ltd, South Africa) for determination of the concentrations of Cr, Cu, Mn and Fe ions in soils.

Sample Collection and Preparation: soil samples were collected in replications during March to May, 2016. Representative from surface soil samples were collected with a stainless steel auger at 0-25 cm depths and composited from 12 sub location areas for each sampling sites (Laga Mariam, Sorga Lake and Hadiya River) in three different plastic bags. About 1 kg of each composite soil sample was taken from three study sites and subsamples were taken at random sampling sites within the study area. All samples were well mixed and one-fourth of each sample was air-dried. The dried soil samples were ground and sieved through a sieve with 2 mm mesh size and analyzed using standard laboratory procedure [7].

Preparation of Standard Solutions for Calibration: Stock standard solutions containing 1000 mg/L of Cu, Mn, Fe and Cr (SPECTROSCAN, Industrial Analytical (pty) Ltd, South Africa) were used for preparing working standards (0, 0.25, 0.50, 1.0, 1.5, 2, 3 and 4 mg/L). Using a micro pipette, exactly 1.00 mL of the 1000 mg/L stock standard was poured into a labeled 100 mL volumetric flask; 20 mL concentrated hydrochloric acid was added to the flask and diluted to the mark with distilled water. The 0, 2.5, 5.0, 10.0, 15, 20, 30 and 40 mL of 10 mg/L working standard was added in clean 100 mL volumetric flasks for preparing 0, 0.25, 0.50, 1.00, 1.50, 2.00, 3.00 and 4.00 mg/L working standards, respectively. 1.96 gm solid DTPA was

dissolved in 950 mL distilled water in 1 liter volumetric flask with adjusted the pH of 7.30 and HCl (1:1) to prepare 0.005 M DTPA extracting solution. Analyses of the soil samples were performed after determining the detection limits. The detection limits for analytical methods for soil samples were obtained from three times the pooled standard deviation, that is, mean±3 s of six determinations of the reagent blanks.

Analysis of Soil Samples: The soil pH was measured potentiometrically with a digital pH meter in the supernatant suspension of 1:2.5 soils to water ratio. To estimate heavy metals concentration in the soil samples of the present study sites, 25 g dried soil sample was mixed with 50 mL of DTPA extracting solution at pH 7.3 and kept on a reciprocal shaker at 120 rpm for 2 h. Ten ml of sample extracts, the blank extract and the working standard solutions of Fe, Mn, Cu and Cr were added in to test tube with 1 mL of 0.1% lanthanum solution (lanthanum was added to prevent condensed phase interference) and homogenize. The mixture was shaken and poured back to the beaker and settled for 30 min. The aliquot of 10 mL for each sample was centrifuged at 5000 rpm for 5 min and supernatants were collected for heavy metal determination [7]. Finally, supernatant sample was taken by 9×150 mm test tubes and analyzed for heavy metals using FAAS.

Evaluation of Contamination of Heavy Metals: For the assessment and quantification of the level of contamination of heavy metal ions in the soil samples, the following quantitative contamination indices were

adopted to illustrate the concentration trends and to allow easy comparison among the measured parameters as follow [8].

Contamination Factor (CF): The level of contamination of sediment by metals were expressed in terms of CF calculated as shown in equations (1)

$$CF = C_m / B_m \qquad (1)$$

where, C_m = concentration of the element in the sample, B_m = Background value of the metal equals to the world surface rock average given by [9]. Contamination factor has four categories which include; less than 1 low contaminations factor; 1 to 3 moderate contaminations, 3 to 6 values indicate considerable contamination factor; greater than 6 values very high contamination factor [10].

Degree of Contamination (C $_{deg}$): Expressed as the sum of all the contamination factors in the sample and indicated as showed below in equation (2)

$$C_{deg} = \Sigma(C_m / B_m) \qquad (2)$$

where C_m = measured concentration in soil; B_m = background concentration (value) of metal, m within the pristine area of the catchment. Four categories have been defined for the degree of contamination which includes: less or equal to 8 values indicate low degree of contamination; 8 to 16 values show moderate contamination; 16 to 32 shows considerable contamination; greater than 32 predict very high degree of contamination [10].

Enrichment Factor (EF): Is a useful indicator reflecting the status and degree of environmental contamination. The EF calculations compare each value with a given background level, either from the local site, using older deposits formed under similar conditions, but without anthropogenic impact, or from a regional or global average composition[11]. The EF was calculated using the method proposed by [12] and shown below in equation (3)

$$EF = [Me/Fe]_{sample} \Big/ [Me/Fe]_{background} \qquad (3)$$

where (Me/Fe) sample = the Me(metal) to Fe (iron) ratio in the sample of interest; (Me/Fe) background = the natural background value of metal to Fe ratio. The enrichment factor of an element in the study samples is based on the

standardization of a measured element against a reference element. A reference element is often the one characterized by low occurrence variability. It is used to differentiate heavy metals originating from human activities and natural sources. As we do not have metal background values for our study area, we used the values from surface world rocks [10]. Iron was chosen as the element of normalization because natural sources (1.5%) vastly dominate its input [13]. Enrichment factor categories are less than 2 deficiency to minimal enrichment, 2 to 5 moderate, 5 to 20 significant, 20 to 40 very high and greater than 40 extremely high enrichment [14].

Index of Geo-accumulation (I $_{geo}$): This is widely used in the assessment of contamination by comparing the level of heavy metal obtained to a background levels originally used with bottom sediments [15] which can also be adopted to soil contamination [16, 17]. It is calculated by using equation (4) shown below.

$$I_{geo} = \log 2\,[(C_m)/(1.5 * B_m)] \qquad (4)$$

where C_m Sample = the measured concentration of element in the soil sample and B_m Background = the geochemical background value (world surface rock average) given by [9]. The factor 1.5 is introduced to include possible variation of the background values due to lithogenic effect. Muller [15] proposed seven classes of the geo-accumulation index are less than zero indicates unpolluted, 0 to 1 values shows unpolluted to moderately polluted, 1 to 2 values moderately polluted, 2 to 3 indicates moderately to strongly polluted, 3 to 4 value shows strongly polluted, 4 to 5 indicates strongly to extremely polluted and greater than 6 shows extremely polluted condition.

Pollution Load Index of Soil: PLI, for a particular (Laga Mariam, Sorga Lake and Hadiya river) site, has been evaluated following the method proposed by Sinex and Helz. The determination of pollution load index expressed as shown below equation (5).

$$PLI = [CF_1 * CF_2 * CF_3 \dots CF_n]^{1/n} \qquad (5)$$

where, n = the number of metals; CF = contamination factor

The PLI provides simple but comparative means for assessing a site quality, where a value of PLI less than one denotes no overall pollution; PLI equivalent to one

136

presents that only baseline levels of pollutants are presented and PLI greater than one would indicate deterioration of site quality [12].

Data Analysis and Interpretation: The data obtained from each of soil samples were analyzed statistically to assess the changes in various parameters of the study as described [18]. The mean value of data comparison design was applied on the data to assess the significance of different sources of variation and the differences among the means were compared by using Statistical software Package (Microsoft excel package).

RESULTS AND DISCUSSION

Instrumental working of heavy metals analysis in soil samples were standardized for calibration and result of each element expressed on this bases. Instrument working condition and detection limits are presented in Table 1 below.

Soil pH is one of the most common and important measurements in standard soil analyses. Soil pH of the study areas (Laga Mariam, Sorga Lake and Hadiya River) were measured by using digital pH meter and value ranged from 4.4 - 5.1 where the lowest soil pH was recorded at Laga Mariam and the high pH value was recorded at Sorga Lake soil. However, according to the rating classification described by Jones [19] the soil pH

recorded at the sampling sites were rated as strongly acidic soils. This values of pH suggested that Laga Mariam has lower pH value but Sorga Lake higher. The lower pH indicated due to depletion and leaching of basic cations from the topsoil surface to the nearby rivers and also due to its highest microbial oxidation that produces organic acids, which provide hydrogen ions to the soil solution, lowers its soil pH value. At low soil pH, many oxides of iron get into soil solution and through stepwise hydrolysis and release hydrogen ions resulting into further soil acidification [20]. The variation of the concentration of heavy metals in nine different samples in three average value of soil collected from nearby Laga Mariam, Sorga Lake and Hadiya River are shown in Table 2.

The concentration of Cu in soil samples collected from nearby Laga Mariam, Sorga Lake and Hadiya River were varied between 0.70 and 0.98 mg/kg at Laga Mariam, 0.29 and 0.37 mg/kg at Sorga Lake, 0.19 and 0.48 mg/kg at Hadiya River and the mean values were 0.83, 0.33 and 0.34 mg/kg, respectively. It was less than the world surface rock average and WHO as a geochemical background level in all sampling sites. However, higher concentration of Cu was found during the rain than before and after rain at Laga Mariam and Hadiya River showed higher concentration of Cu (1.08 and 0.76 mg/kg respectively) and lowest concentration was found after rain at both 0.70 and 0.19 mg/kg respectively. At Sorga Lake high

Table 1: Instrument working condition and detection limits

Element	Cr	Cu	Fe	Mn
Lamp current (mA)	4	2	3	3
Fuel	C_2H_2	C_2H_2	C_2H_2	C_2H_2
Support	Air	Air	Air	Air
Wave length (nm)	357.9	324.7	248.3	275.9
Slit width (nm)	0.2	1.2	0.2	0.2
Instrument detection limit	0.01	0.007	0.006	0.002
Soil (mg/kg)	1.0	1.0	1.0	1.0
r^2	0.9999	0.9728	0.9789	0.9873
Linear equation	Y = 0.085x + 0.001	Y = 0.296x − 0.033	Y = 0.264x + 0.068	Y = 0.218x + 0.004
MDL(Soil)	ND	0.315	0.653	0.278

r^2 = coefficient of determination; MDL = Method Detection Limit; ND = Not Detected

Table 2: Concentration of heavy metals (Mean±SD) in soil samples (mg/kg)

Metal	Laga Mariam	Sorga Lake	Hadiya river	Chemical background		
	Mean±SD	Mean±SD	Mean±SD	World surface rock average	WHO	USEPA
Cu	0.83±0.142	0.33±0.039	0.34±0.145	32	25	16
Cr	BDL	BDL	BDL	71	25	25
Mn	0.76±0.137	0.46±0.079	0.65±0.073	750	-	30
Fe	1.12±0.354	0.83±0.172	1.05±0.150	35900	-	30

BDL = Below Detection Limit; WHO = World Health Organization

USEPA = Unite State Environmental Protection Agency

Table 3: Statistical summary of the contamination indexes of heavy metals in the experimental soils

		AF/CF (X10^{-3})			I-$_{GEO}$			EF			
	Metal	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Background
Laga Mariam	Cu	22	31	26	-1.54	-1.39	-1.46	933.8	725.0	828.3	32
	Cr	ND	ND	ND	ND	ND	ND	ND	ND	ND	71
	Mn	0.80	1.20	1.01	-2.95	-2.79	-2.87	35.76	28.33	32.10	750
	Fe	0.20	0.40	0.30	-4.51	-4.25	-.4.38	1.00	1.00	1.00	35900
Sorga Lake	Cu	9.10	11.50	10.18	-1.92	-1.81	-1.87	494.5	411.9	441.1	32
	Cr	ND	ND	ND	ND	ND	ND	ND	ND	ND	71
	Mn	0.51	0.72	0.63	-3.17	-3.02	-3.09	27.95	25.81	26.57	750
	Fe	0.20	0.30	0.23	-4.62	-4.42	-4.53	1.00	1.00	1.00	35900
Hadiya	Cu	6.08	15.12	10.65	-2.09	-1.69	-1.85	230.1	444.4	364.8	32
	Cr	ND	ND	ND	ND	ND	ND	ND	ND	ND	71
	Mn	0.76	0.94	0.86	-3.00	-2.90	-2.94	28.48	27.57	29.38	750
	Fe	0.03	0.04	0.03	-4.44	-4.34	-4.41	1.00	1.00	1.00	35900

ND = Not Detected; CF = contamination factor; I$_{geo}$ = geo-accumulation index;

EF = enrichment factor

concentration found after rain 0.37 mg/kg due to discharge less of waste water entre to Lake. The mean value of Cu concentration did not exceed the WHO and USEPA sediment quality guidelines. According to WHO and USEPA all sampling sites were unpolluted by Cu.

The chromium concentration in the representative soil samples collected from nearby Laga Mariam, Sorga Lake and Hadiya River were recorded below the detection limit of the instrument. It has low concentration than standard concentration of Cr quantified by using FAAS. There were very low sources of Cr that cannot cause pollution of soils of the present study sites. Though chromium is an essential trace nutrient and a vital component for glucose factor but, Cr toxicity (especially in its hexavalent form) damages the liver, lungs and causes organ internal bleeding.

The manganese level in soil samples were varied between 0.63 to 0.90 mg/kg at Laga Mariam, 0.39 to 0.54 mg/kg at Sorga Lake and 0.0.57 to 0.71 mg/kg at Hadiya River. The mean values of Mn at Laga Mariam, Sorga Lake and Hadiya River were found 0.76, 0.46 and 0.65 mg/kg respectively. The concentration of Mn in soil at Laga Mariam site was the highest with value of 0.76 mg/kg and the lowest concentration found at Sorga Lake with a value of 0.46 mg/kg. The mean value of Mn was less than world surface rock average as geochemical background level, Table 3. The level of Mn obtained in the soil from all sampling sites was lower than the USEPA recommended limit but for WHO, there was no limit amount prescribed.

The concentration of Fe in soil samples collected from the three representative sites were varied from 0.84 to 1.52 mg/kg at Laga Mariam, 0.66 to 1.00 mg/kg at Sorga Lake and 0.95 to 1.22 mg/kg at Hadiya River and mean

values were 1.12, 0.83 and 1.05 mg/kg. Iron concentration was less than of the World Rivers average [9]. According to BIS [21] the acceptable limit of iron is 0.3 mg/kg. Generally, during the beginning of rain 1.12 mg/kg, higher concentrations of Fe in the soil samples were observed when compared with the other and the low concentration 0.83 mg/kg at Sorga Lake site may be due to high discharge of waste, irrigation water from town. The mean values of Fe lower than the USEPA and WHO sediment quality guidelines. In comparison with sediment quality guideline, the mean value did not exceed the limits and this result revealed that soils collected from nearby Laga Mariam, Sorga Lake and Hadiya River sites were not polluted by Fe.

Evaluation of heavy metal contaminations in the experimental soils: The heavy metal contaminations and the statistical summary of the contamination factor, enrichment factor and index of geo-accumulation were presented in Table 3. The world surface rock averages were used as background values for the soil samples in order to give a comparative idea about the concentration and degree of heavy metal contamination of the soil samples collected from nearby Laga Mariam, Sorga Lake and Hadiya River with worldwide standard [22].

Contamination Factor (CF) or Anthropogenic Factor (AF): The CF for each element was computed and the result presented as in Table 3. The average contamination factors of Cu, Cr, Mn and Fe in soil samples collected from nearby Laga Mariam, Sorga Lake and Hadiya River were ranged from ND to 26 X 10^{-33} at Laga mariam, ND to 0.63 X 10^{-3} at Sorga Lake and ND to 10.65 X 10^{-3} at Hadiya

River, which indicate moderate contamination factor in Cu but in Mn and Fe shown low contamination factor and Cr not detected in three sampling site [23, 24]. The source of the enrichment factor in Laga Mariam, Sorga Lake and Hadiya River was high discharging of wastage from Town and from various agricultural practices in the area (irrigation, use of fertilizers, organic manure and human activities can cause soil contaminated by heavy metals) as well as emission of Cu from tyre and brake abrasions of tractors [16, 24, 25]. The CF values for Mn, Cu and Fe in Laga Mariam, Sorga Lake and Hadiya soils varied from 0-1. At all sampling sites, the CF values were lessthan 1. According to Hakanson [10], Laga Mariam, Sorga lake and Hadiya soils were low contaminated by Mn and Fe.

The CF values for Cr in soils collected from nearby Laga Mariam, Sorga Lake and Hadiya River were not detected by using FAAS instrument due to occurrence of Cr below the standard concentration used in analysis of Cr indicates very low concentration. At all sampling sites, the CF values of Cr negligible, this suggests that soils were not contaminated by Cr and there was very low source of Cr that cannot cause pollution.

Geo-accumulation Index (Igeo): Results obtained from geo-accumulation index (Igeo) of the soil of present study revealed that value of the geo-accumulation for Cu in soil samples collected from the three sites ranged from -1.54 to -1.39 and mean value was -1.46 at Laga Mariam; -1.92 to -1.81 and mean value was -1.87 at Sorga Lake and lastly at Hadiya River ranged from -2.09 to -1.69 and mean value was -1.85. The I_{geo} amounts for Cu at all sampling sites were negative. These negative values indicate that the soils around the study area were unpolluted by Cu and result of Cu Less than world surface rock average [23, 24]. According to Muller's [15] classification, soils from nearby Laga Mariam, Sorga Lake and Hadiya River were found to be unpolluted by Cu where as at Laga Mariam, its value is -1.46 from remaining site was somewhat pollute.

The I_{geo} results for Cr in soils collected from nearby Laga Mariam, Sorga Lake and Hadiya River were not detected at all sampling site. Cr, has value less than detection concentration indicating practically unpolluted [22, 23]. According to Muller's [15] classification, soil from all sites nearby Laga Mariam, Sorga Lake and Hadiya River were unpolluted by Cr metal.

The I_{geo} of Mn in soil collected from nearby Laga Mariam, Sorga Lake and Hadiya River varied from -2.95 to -2.79 in Laga Mariam, -3.17 to -3.02 in Sorga Lake and -3.00 to -2.90 in Hadiya River and mean values were -2.87, -3.09

and -2.94 respectively. The I_{geo} values for Mn at all sampling sites were negative. The negative result mean that Mn less than the world surface rock average as a background level. The values of Mn in I_{geo} at all site when compared together, in small extent Laga Mariam more polluted by Mn. According to Muller's [15] classification, soils found around Laga Mariam, Sorga Lake and Hadiya River were less than zero in results indicated that unpolluted by Mn.

The I_{geo} values for Fe in soil samples collected from nearby Laga Mariam, Sorga Lake and Hadiya River ranged from -4.51 to -4.25 at Laga Mariam, -4.62 to -4.42 at Sorga Lake and -4.44 to -4.34 at Hadiya River and the mean values were -4.38, -4.53 and -4.41 respectively. The results of I_{geo} for Fe at all sampling sites were negative. Negativity value imply that amount of Fe in study area was less than the world surface rock average as a background level. When the values of I_{geo} for each site compared together somewhat Fe can cause pollution of soil at Laga Mariam. According to Muller's [15] classification, soils collected from nearby Laga Mariam, Sorga Lake and Hadiya River were less than zero, indicates the present study areas unpolluted by Fe. The overall total geo-accumulation index (I_{tot}) of the entire study area for different metals were found to be negative and shown in Table 3. This suggests that concentration mean of most heavy metals in soil collected from nearby Laga Mariam, Sorga Lake and Hadiya River are less than world surface rock average. However, the estimated index of geo-accumulation revealed I_{geo} less than zero for all sampling area. These results indicate that there is no contamination of heavy metals in soil with respect to Cu, Cr, Mn and Fe metals.

Enrichment Factor (EF): The enrichment factors in the heavy metals of the soil samples were presented in Table 3. The values of the heavy metals fall within the range of high enrichment. The EF values obtained for Mn and Cu are similar to those [14] obtained for the same metals in their study area. The mean values of EF Cu and Mn were larger and indicated that there might be common anthropogenic sources of Cu and Mn from Town wastage drop out to around the study areas. The EF values for Cu in soil samples collected from nearby Laga Mariam, Sorga Lake and Hadiya River were vary from 933.70 to 725.00 at Laga Mariam, 494.40 to 411.89 at Sorga Lake and 230 to 444.44 at Hadiya River. The average value of EF in Laga Mariam, Sorga Lake and Hadiya River for Cu were as follows: -828.28, 441.08 and 364.76, respectively. All sampling sites have EF values greater than 40, suggesting that soils were classified as extremely significant enrichment for Cu.

Table 4: Degree of contamination and its interpretations

Sample site	Sample ID	Cdeg	Interpretation of Cdeg
Laga Mariam	S1	0.03	LDC
	S2	0.03	LDC
	S3	0.02	LDC
Sorga Lake	S1	0.01	LDC
	S2	0.01	LDC
	S3	0.01	LDC
Hadiya River	S1	0.02	LDC
	S2	0.01	LDC
	S3	0.01	LDC

LDC = Low degree of contamination; S_1 = Sample round 1; S_2 = Sample round 2; S_3 = Sample round 3.

Table 5: Pearson`s correlation coefficient of heavy metals in soil samples

	Laga Mariam			Sorga Lake			Hadiya River		
Metal	Cu	Mn	Fe	Cu	Mn	Fe	Cu	Mn	Fe
Cu	1			1			1		
Mn	0.99	1		0.99	1		0.71	1	
Fe	0.99	0.98	1	0.99	0.99	1	-0.09	0.64	1

The enrichment factor values for Mn in soil samples collected from nearby Laga Mariam, Sorga Lake and Hadiya River ranged from 35.76 to 28.33 at Laga Mariam, 27.95 to 25.78 at Sorga Lake and 28.47 to 27.57 at Hadiya River with average values 32.60, 26.57 and 29.38, respectively (Table 3). The EF values for Mn at majority of sampling sites were less than 40. At these sites (Laga Mariam, Sorga Lake and Hadiya River), the results of soils were classified as very high enrichment for Mn.

The EF values for Cr in soil samples collected from nearby Laga Mariam, Sorga Lake and Hadiya River were not detected at limit concentration. Iron was chosen as the element of normalization because natural sources (1.5%) vastly dominate its input [13].

Degree of Contamination (C_{deg}): The degree of contamination computed for each soil of the different (three) location together study sites with the interpretation presented in Table 4.

Degree of contamination and its interpretations expressed with bases of world surface rock standard [8]. 99% of the samples give low degree of contamination while 1% gives moderate degree of contamination due to environmental condition. The degree of contamination in the soil samples is low; but there should be thorough keeping of the level of these heavy metals in the soil to prevent relative health hazards to human and the livestock in the area.

Pollution Load Index (PLI) of experimental Soil: To effectively compare whether the sampling sites suffer contamination or not, the pollution load index (PLI), was used. The PLI values of the analyzed samples ranged from 0.53 to 0.92 with a mean value of 0.70. The PLI for heavy metals in soil samples collected from nearby Nekemte Town River were 0.92 for Laga Mariam, 0.53 for Sorga Lake and 0.64 for Hadiya River. The results of the analyses are reflected the computation of the pollution load indices of the various elements in each sample. At all sampling sites, the PLI valueswere less than one. According to Sinex and Helz [12], all sampling sites suggest perfection (or no overall pollution). Relatively high PLI value at Laga Mariam sampling site suggests input from anthropogenic sources exist around.

Statistical Analysis: Table 5 presents the correlation matrix of the heavy metals showing their level of association from specific sources. The correlation coefficient of heavy metals ratio: Mn/Fe (0.98); Cu/Fe (0.99) and Cu/Mn (0.99) in Laga Mariam; Mn/Fe (0.99); Cu/Fe (0.99) and Cu/Mn (0.99) in Sorga Lake have strong correlation with each other depicting same source. In other words, strong correlations signify that each paired metals have common contamination sources [14]. The Mn/Fe (0.64), Cu/Fe (-0.09) and Cu/Mn (0.71) in Hadiya River correlation of those heavy metal was very low. However, weak correlation (range=0.02-0.22) was
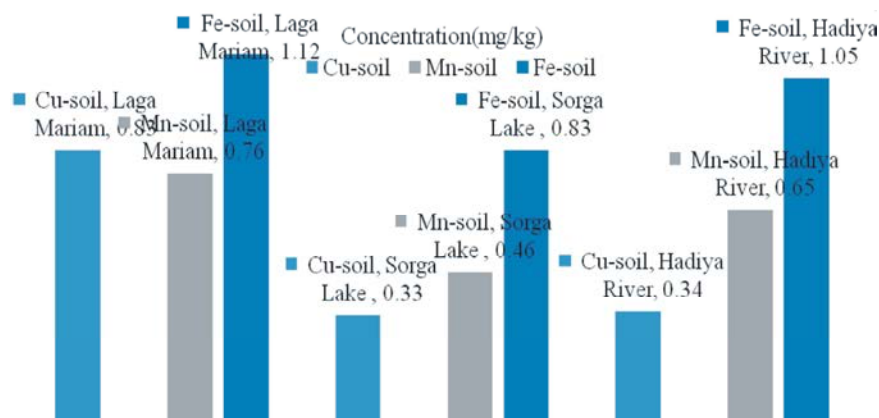
Fig. 3: Correlation of Fe, Mn and Cu concentrations in soil nearby study area.

found between Cu/Fe and the other heavy metals which shows that they have very weak degree of association. In general, the correlation coefficients between soils collected from different sites with similar metal showed that Laga Mariam greater than Hadiya River greater than Sorga Lake in concentrations of Cu, Mn and Fe in soil samples and presented in Figure 3. High Fe concentrations in both soil samples were found around Nekemte Town, this might be due to high abundance percentage of iron exist in earth crust.

CONCLUSION

To evaluate the status of heavy metal (Cu, Cr, Fe and Mn) concentrations in soil of the present study sites were estimated in nine representative sampling sites. The status of concentrations of heavy metals: in increasing order Cu, Mn, Fe respectively in all sites for soils but, not detected under prescribed concentration for Cr in soil sample. The enrichment factor values suggest that in these sampling sites were very high enriched for Cu and extremely high for Mn when evaluated with reference element Fe. Data obtained from the contamination factor indicated that, all soil sampling sites were responsible for very low contamination Cu, Cr, Mn and Fe. The geo-accumulation index values showed that all soil samples collected from the three study sites were unpolluted. In general, total geo-accumulation index indices for the selected heavy metals were negative and implied that mean concentrations of heavy metals in soil samples collected from the present study sites were lower than world surface rock average. Pollution load index results indicated that all sampling sites were perfection or no overall pollution. The correlation analysis of mean concentrations showed soil samples strong correlations

among Fe and Mn, suggesting that these metals have common sources. The status of concentrations of Cu, Cr, Mn and Fe in soils nearby Laga Mariam, Sorga Lake and Hadiya River are apparently less than the permissible limits set by WHO/USEPA for soil.

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