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Selected Heavy Metals Concentration in Soils Collected from some Nurseries, Kindergadens and Primary Schools of Eastern Hararghe, Ethiopia.

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ABSTRACT

Soil samples were collected from 15 Nurseries, Kindergardens and Primary schools located in the easterly part of Harerghe, Ethiopia. The samples were prepared and analyzed to determine the concentration level of some heavy metals (Cd, Cr, Cu, Pb, Hg and Zn) using 0. 05M EDTA extraction. The metal concentration was determined by AAS. The results of this study revealed that heavy metal distribution is different among the schools selected. Among schools selected from Dire Dawa, Harar, Haramaya and Awoday towns, concentration range of heavy metals such as lead, chromium, copper and zinc was found to be 7.65-92.9,13.3-60.8,1.54-9.28 and 13.8-33.1 ppm, respectively. The concentrations of these heavy metals were compared with the standard developed by European Regulation. The present finding has shown that the concentration of Pb was maximum (92.9ppm) in the Life Line Nursery, Kindergarden and Primary school where as Cr found to be maximized (60.8ppm) in its concentration at Model No 2 Nursery, Kindergarden and Primary school (Dire Dawa). Besides this Cu (9.28 ppm) and Zn (31.1 ppm) where maximum concentration at Dandi Boru (Haramaya) and Baby Land Nurseries, Kindergardens and Primary school (Harar), respectively. In contrary to above, Hg and Cd (except in Sabyan Nurseries, Kindergardens and Primary school) were not detected.

Key word: heavy metals, soils, copper, lead, chromium, mercury, zinc, cadmium, correlation.

INTRODUCTION

Heavy metals in soils exist in different chemical forms or types of binding. The term "heavy metal" has been used as a general term for those metals and semi-metals with potential human or environmental toxicity. This definition includes a broad section of the periodic table under the rubric of interest (Sonmez and Pierzynski, 2005).

Heavy metal toxicity is an uncommon diagnosis. Heavy metals are dangerous because they tend to bioaccumulate. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc, but excessive levels can be detrimental to the organism. In medical usage, the definition is considerably looser, and "heavy metal poisoning" can include excessive amounts of manganese, aluminum, or beryllium as well as the other heavy metals.

There are 35 metals of concern, with 23 of them called the heavy metals. Toxicity can result from any of these metals. The environment in recent time is increasingly being modified through the various activities of man in the environment. Whereas pollution problem in Ethiopia is somewhat rapidly increasing with industrial activities as the leading causes, the problem of pollution and general degradation arising from the waste dispose, different industries sector deserves special attention, especially in the urban.

Urban soils are strongly influenced by anthropogenic activities (Ljung *et al*., 2006a). Over time the soils in the inner city have accumulated large amounts of these metals and polycyclic aromatic hydrocarbon (PAH) which were added to their geological background concentration level. It is a mixture of wastes of building materials, urban fire residues, house and industrial waste and natural soil (Haugland *et al.*, 2005). Several investigations have been carried out with special regard to health hazards for children by heavy metals in soils or dust (Dorsch Consult, 1995; Haugland *et al*., 2005; Hemond and Solo-Gabriele, 2004; Ljung *et al*.,2006a; Mielke *et al*., 1999, 2005; Moya *et al.*, 2004; Tong and Lam, 1998) and sources for pollution in urban soils were tried to identified by (Bretzel and Calderisi , 2006; Ljung *et al*., 2006a,b; Tijhuis, 2003;Tong and Lam , 1998). Contaminated soils near or in kindergarden and primary schools with heavy metals influence learning achievement of the students. This is responsible for the diminished skills and behaviors that interfere with learning (Meikles *et al.*, 2005). Another survey in New Orleans showed an intimate correlation between bloods Pb levels from children under six years and the lead content in the topsoil layer (Mielke *et al.*, 1999). The heavy metals Cd, Zn, Pb, Cu and Hg are assumed to have anthropogenic sources. Cr, Ni and As are rather natural (Ljung *et al.*, 2006a; Tijhuis, 2003). For many daycare institutions, remediation was necessary due to elevated, some of these metals, concentration levels (Ottesen *et al*., 2003).

In the environmental studies, the heavy metals pollution has deteriorating effects on children growth, development and survival since these polluted soils may transfer the heavy metals pollution to children through ingestion (Ljung *et al.*, 2006b).

A survey of the literature shows that there is some information on the levels of heavy metals in water and sediments of Ethiopian River and Agricultural land. Fisseha (2002) reported that there is a large accumulation of heavy metals in soil irrigated with waste water and leafy vegetables grown in Addis Ababa, Ethiopia which has a toxicological implication. However, there was no literature reported on about the concentration and distribution of heavy metals in the soils of the school environment of Dire Dawa, Haramaya, Awoday and Harar towns in Ethiopia. Thus, there was the need to carry out an extensive assessment of heavy metals in the soils of Nurseries, Kindergartens and Primary Schools in Ethiopia, Africa. Therefore, the objective of this paper was to investigate the concentration level of some selected heavy metals (Pb, Zn, Cr, Hg, Cu and Cd) in soils collected from Nurseries, Kindergartens and Primary Schools of Dire Dawa, Haramaya, Awoday and Harar towns in Ethiopia (Africa).

MATERIALS AND METHODS

The study area comprised fifteen Nurseries, Kindergartens and Primary Schools of the four towns of Eastern Harerghe, Ethiopia (**Figure 1**) namely: Awoday, Dire Dawa, Haramaya and Harar towns. These Schools were selected based on their susceptibility to contaminant from nearby environments. The basic criteria apart from nearby contaminant sources such as municipal waste, industrial effluents, heavy traffic density, etc. were the direct exposure of the soil to the students. All the selected schools have got a compound completely unasphalted or uncemented. The selection was made after the preliminary survey made in the schools.

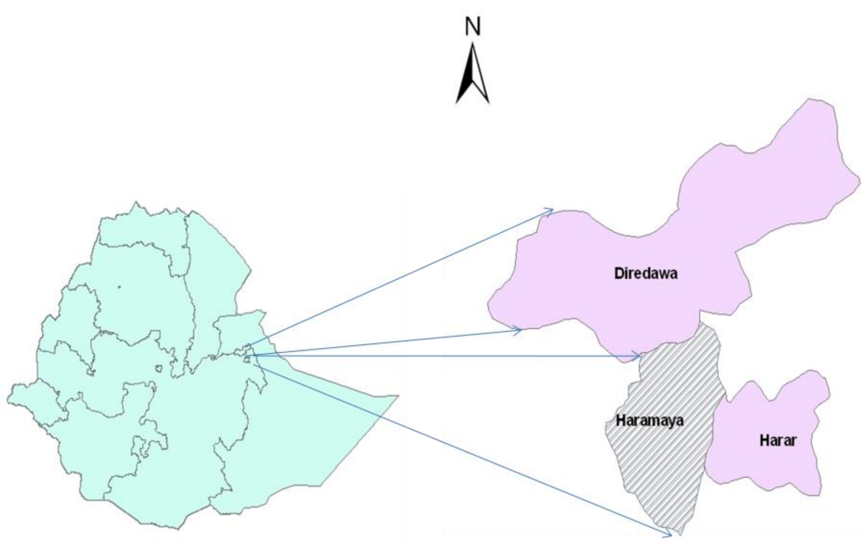

Figure 1. Map of Ethiopia indicating the sampling site

Experimental

A potentiometric digital pH meter (Jenway 3320) was used to determine the pH of the sample stirrer (Hanna instruments, model H1200,UK). FAA spectrometer (Buck Model Scientific 210VGP) was used to determine the absorbance of each of the heavy metals being investigated using an air-acetylene flame. Hydride generator (GFAAS) (NOV MODEL 400) was employed for the determination of mercury. Digital analytical balance (Explorer, Ohaus, Model E11140, Switzerland) with ± 0.0001 g precision was used for all weight measurements of sample and chemicals. All reagents used were of analytical grade.

Soil samples were collected at a depth of 0-15 cm from different location of each school. These were air dried, grounded and sieved through a 2 mm-sieve. P^H was measured in a 1:2.5 soil to water ratio suspension using glass electrode RS232 (15).Particle size analysis was made using the hydrometer method after the dispersion of the soil with sodium hexametaphosphate, (16). Organic carbon was determined using the Walkley-Black oxidation technique (17). Calcium carbonate measurements were made by the acid neutralization method after soils were treated with standard HCl.

Determination of Heavy Metals

For determination of heavy metals (Cd, Cu, Zn, Cr, Pb and Hg); 50 ml of 0.05 Mol l^{-1} EDTA solution and 10 g soil was added into 250 ml Erlenmeyer flask and shook in an end-over-end shaker for 1 hour at 250 rpm at 20 ± 2 ^{0}C(18,19). The extracts were separated from the solid residue by filtration using Whatman No. 40 filter paper. The filtrate was collected in glass bottles and stored at 4 °C until metal analysis. Blanks were measured in parallel for each batch of analysis using the extracting reagents described above without the sample. AAS was carried out by aspirating the extracts directly.

Air–acetylene flame and a deuterium lamp for continuous background correction were used. Measurements were performed at 324.3 nm for Cu, 213.9 nm for Zn, 228.9 nm, for Cd (20), 253.7 nm for Hg and 357.9 nm for Cr. Three replicates were performed for each sample.

Calibration curves were used to determine the concentration of Cu, Cr, Hg, Pb, Zn and Cd in the experimental solutions. In plotting the calibration curves, blank solution was prepared for the method. For the standard working solutions of Cd, 10 ml of the standard Cd stock solution was diluted to one liter with deionized water and the solution was mixed thoroughly. Then 0.0, 5.0, 10.0, 20.0, and 30.0 ml aliquots of this standard working solution was pipetted into 50 ml calibrated flasks and fill up to the mark with 0.05 M EDTA. The concentrations of these solutions were 0.0, 1.0, 2.0, 4.0, and 6.0 ppm, respectively. For the standard working solutions of Pb, 50 ml of the standard Pb stock solution was diluted to 500 ml with deionized water and the solution was mixed thoroughly. Then 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml aliquots of this standard working solution was pipetted into 100 ml calibrated flasks and fill up to the mark with 0.05 M EDTA. The concentrations of these solutions were 0.0, 5.0, 10.0, 15.0, 20.0, and 25 ppm, respectively.

For the standard working solutions of copper, 25 ml of the standard copper stock solution was diluted to 500 ml with deionized water and the solution was mixed thoroughly. Then 1.0, 2.0, 4.0, 8.0 12.0 and 16.0 ml aliquots of this standard working solution was pipetted into 100 ml calibrated flasks and fill up to the mark with 0.05 M EDTA. The concentrations of these solutions were 0.5, 1.0, 2.0, 4.0, 6.0 and 8.0 ppm, respectively.

For the standard working solutions of Zn, 12.5 ml of the standard zinc stock solution was diluted to 500 ml with deionized water and the solution was mixed thoroughly. Then 4.0, 8.0, 16.0, 24.0 and 28.0 ml aliquots of this standard working solution was pipetted into 100 ml calibrated flasks and fill up to the mark with 0.05 M EDTA. The concentrations of these solutions were 1.0, 2.0, 4.0, 6.0 and 7.0 ppm respectively.

For the standard working solutions of Cr, 5 ml of the standard stock solution was diluted to 500 ml with de ionized water and the solution was mixed thoroughly. Then 0, 12.5, 25, 37.5 and 50.0 ml aliquots of this standard working solution was pipetted into 50 ml calibrated flasks and fill up to the mark with 0.05 M EDTA. The concentrations of these solutions were 0.0, 2.5, 5.0, 7.5, and 10.0 ppm, respectively.

For the standard working solutions of Hg, 50 ml of the standard Hg stock solution was diluted to 500 ml with de ionized water and the solution was mixed thoroughly. Then 0.28,0.6,1.12,2.24 and 4.48 ml aliquots of this standard working solution was pipetted into 50 ml calibrated flasks and fill up to the mark with 0.05 M EDTA. The concentrations of these solutions were 0.56, 1.2, 2.24, 4.48 and 8.96 ppb respectively. After 7 minutes the absorbance of each solution was measured using Buck Model GPV 210 AA spectrophotometer and AAS NOV 400 for Hg (hydride forming) at independent wave length against a reagent blank for each metals (Cd, Cr, Cu, Hg, Pb, and Zn). Then 1 drop of reagent ($LaCl_3$), if necessary, was added especially in the determination of zinc due to the interference of phosphates. The absorbance of the solution was measured at their wave length and a calibration curve (absorbance versus concentration) was plotted for each methods.

Recovery Test

To check the efficiency of the method used in the chemical analysis recovery study was conducted. 0.674, 13.7, 2.06, 11.6 and 9.18 ppm of Cd, Cr ,Cu, Pb and Zn, respectively, which contains a total of 1.8607 ml from the stock solution of each metal solution were spiked at once into a 250 ml Erlennmerey flask containing known amount of soil sample. Each recovery test for the sample taken was performed in triplicate.

Method Detection Limit

For the present study, replicate analyses for nine blank samples were performed for Cd, Cr, Cu, Pb, and Zn and the pooled standard deviation of the nine reagents blank was calculated. The detection limits were obtained by multiplying the pooled standard deviation of the reagent blank by three.

Data Analysis

To compare the concentration level of Hg, Zn, Cr, Cd, Cu and Pb from the investigated soil samples, one-way analysis of variance was carried out using SPSS 12. The correlation coefficient between heavy metals and soil parameters were assessed by using Pearson correlation analysis to assess relationships among soil parameters that might show linkages with the concentration level of these metals. The difference was investigated using one way ANOVA analysis. The position of soil sample locations was recorded as a coordinate system using GPS.

RESULTS AND DISCUSSION

The present investigation consisted of a laboratory study to determine the concentration level of six heavy metals v*iz.*Cd, Cr, Cu, Hg, Pb and Zn by using EDTA and analyzed by using AAS.The instrument was calibrated using standard working series of solutions for each metal.

For the present study, replicate analyses of nine blank samples were performed and the pooled standard deviation of the nine reagents blank was calculated. In this study, method detection limit for cadmium is lower than that of the instrument. The wavelengths at which analysis was done, the correlation coefficients of the calibration curve for each of the metals and a method detection limit of each metal is shown in Table 1.

Table 1. Instrument calibration and detection limit

Metal	Wavelength (nm)	Correlation coefficient	Instrument detection limit (mg l^{-1})	MDL* soil samples (mg kg^{-1})	flame
Cd	228.8	R^2=0.99	0.01	0.00	Lean, blue
Cr	341.5	R2=0.993	0.04	1.5	Rich, yellow
Cu	213.9	R^2=0.999	0.005	0.06	Lean, blue

Hg	253.7	R^2=0.999	5	-	Lean, blue
Pb	217.0	R^2=0.99	0.04	0.75	Lean, blue
Zn	324.8	R^2=0.987	0.005	0.051	Lean, blue

*MDL= Calculated method detection limit

Evaluation of analytical method

The recovery test using the proposed method was performed for soil samples using non-spiked and spiked samples, and each sample was determined in triplicate (Table 2). The result of percentage recoveries for the studied heavy metals in the soils were between 90.1 to 104 %. Similar test was not conducted for Hg as the reading was done at Environmental protection authority in Ethiopia. The recovery test for the samples determined was within the acceptable range indicating the reliability and accuracy of the proposed method for heavy metals analysis in soils.

Table 2. Percent recovery test of the metals in replicating

Metal	Con.in sample (ppm)	Amount added (ppm)	Conc. In spiked sample (ppm)	Recovery (%)
Cd	0.674	0.674	1.33	97.5±6.84
Cr	30.4	13.7	43.0	92.3±3.5
Cu	2.58	2.06	4.44	90.1±2.6
Hg**	nd	-	-	-
Pb	29.1	11.6	40.2	104±8.14
Zn	30.6	9.18	39.3	95 ± 6.5

nd= not detected ** = done at EPA

Physico-chemical properties of studied soils

The soils have shown physicochemical properties that influence soil heavy metals content not much significantly. Preliminary visual inspection showed that the soils were dark gray in color indicating a low amount of humus. Textural analysis showed the predominance of 77 to 97.2 % sand fraction, followed by 2.4-23.0 % silt and finally between 0 and 3 % clay **(table 3**). The highest sand content may be because of flooding and covering the layers of the school environment with it, depositing a deep layer of sand on topsoil to a depth of about 20-30 centimeters.

Soil pH influences ion- pair formation, solubility of organic matter, as well as surface charge of Fe, Mn and Al –oxides, organic matter and clay edges (21). The soils examined in this area were found with a pH (soil: water) range of 7.46 to 8.43. According to Murphy (1962)(22), these soil pH is categorized under mildly to moderately alkaline and contains free percentage carbonate varying from 0.7 to 12.45. The average carbonate content of soil taken from 15 locations was 6.22 % with the lowest and highest amounted 0.7 % and 12.45 % from Medresatuselam and Yenege Tesfa Nurseries, Kindergardens and Primary schools, respectively. The lower and higher in the carbonate content is relatively contradicting the data obtained in relation to the pH values.

Table 3. Selected physiochemical properties of tested soils

Soil types	%Sand	%Clay	%Silt	%OC	pH	%$CaCO_3$
BN3 [d]	86	1	13	0.068	8.14	1.65
MDL2 [d]	91	1	8	0.162	8.33	5.3
SYN [d]	81	1	18	0.088	7.81	12.35
DBL [d]	83	2	15	0.128	7.94	12.25
BGL [d]	92	0	8	0.126	8	5.2
YTF [d]	77	0	23	0.073	7.75	12.45
BTL [d]	83	3	14	0.058	8.31	12.4
GGD [d]	82	0	18	0.143	8.43	5
ABI [d]	92	-	10	0.18	7.46	4.4
ABY [d]	97	-	5	0.143	7.57	6.55
DDB[ha]	81	0	19	0.102	7.84	2.05
BBL[h]	86	2	12	0.07	8.06	3.4
NSR[h]	92	2	6	0.141	8.09	2.35
LFL[h]	93	-	8	0.172	7.89	3.2

MTS[a]	97.2	0.4	2.4	0.076	7.6	0.7

d=Dire Dawa, ha=Haramaya, h=Harar ,and a=Awoday town,BN3= Beza No 3,MDL2=Model No 2, SYN= Sabiyan, DBL= Dire Betel, BGL= Bisrat Gebreal, YTF=Yenegetesfa, BTL=Betel,GGD=Gendegerada,ABI=AbuneIndrias,ABY=AbayYohannes,DDB=Dandiboru, BBL=Baby Land,NSR=Nigus Shira,LFL=Life line,MTS=Medresatu Selam

Organic content of soil samples collected from selected schools ranges from 0.058 to 0.18 % with an average of 0.116 %. The lowest and the highest amounted of OC is found in Dire Dawa soils of Betel (0.058) and Abune Indrias (0.18) Nurseries, Kindergartens and Primary schools. The average OC content of soils taken from 15 locations was very low (0.116 %). The relatively low levels of silt, clay, and OC indicate the high permeability, hence leachability of heavy metals in the soil and suggest that it might be amenable to remediation by soil washing (23, 24). The characterization result also revealed very low, heavy metal concentrations.

Concentration Level of Heavy Metals

A correct evaluation of the risk associated with heavy metal accumulation in soil requires a comparison between the metal concentrations estimated and reference values reported in the literature or those established by regulatory bodies. In the present study heavy metals like Cd, Cr, Cu, Hg, Pb, and Zn were investigated in the soil of fifteen schools of selected towns of Eastern Hararghe in Ethiopia (Table 4).

Cadmium was not detected in all soil samples investigated except at Sabyan nursery, kindergarten and primary School. Similarly, Hg was not detected in ppm in all the soils sample investigated. The average concentrations of heavy metals, Cd, Cr, Cu, Hg, Pb and Zn for replicate measurements of each of the soil samples is depicted in Table 4.

Cadmium

In this study cadmium content of the soil samples has not been reported in almost all of the study area except for soil sample from Sabyan School (Table 4). Cd extracted by the method was the minimum following mercury (0.0118 ppb) when compared to the other elements. The detected soil sample concentration was 0.67 mg kg^{-1} from Sabyan Nursery, Kindergarden and Primary school.

This concentration of cadmium is also below the human risk criteria set for child resident (2 ppm) (25). In line with the above limits the concentration resulted in this experiment is about 29 % of the soil toxic limit. In contrast, normal cadmium ranges of 0.07 and 1.1 mg kg^{-1} (26). The present finding indicates that of the total sample taken, one of them has shown a slight increment in the concentration of cadmium compared with the above reported value. Despite the different set of critical values for Cd, in general, the concentration of Cd (0.67 mg kg^{-1}) is not far from the limit value.

Chromium

F-test indicated a significant difference ($p \leq 0.05$) among schools with respect to the concentration of chromium (Table 5). The maximum concentration of chromium (60.8 ppm) was recorded at Model No 2 followed by Medresatu Selam (59.3 ppm) and Nigushira (59.2 ppm) nurseries, kindergardens and primary school. This may be due to the same source of contaminants which might have resulted from painting residues and flooding of different areas. In contrast to this result,

less chromium concentration was recorded at Yenege Tesfa (13.3 ppm) and Gendegerada (25.8 ppm) (Table 5). Although most of schools have shown significant differences ($p \leq 0.05$), Dire Betel and Abay Yohannes, Beza No 3 and Abayohanis , Dire Betel and Beza No 3 nurseries, kindergartens and primary schools resulted in non- significant difference in the concentration of Cr. This finding showed a value below the standard developed by European Council Directive 86/278/EEC Sewage Sludge Metal level Standards and Wild (1996) (27). The level of chromium is therefore found to be smaller and thus has no toxic effect.

Copper

Analysis of variance showed a significant statistical difference ($p \leq 0.05$) among some schools in the values of copper. The highest copper concentration was recorded at Dandi Boru (9.28 ppm), Dire Betel (8.68 ppm) and Babyland (6.98 ppm) (Table 5). In contrary to this result, less copper concentration was recorded at Betel (1.54 ppm), Beza No 3 (1.88 ppm) and Gendgerad (2.04 ppm) (**Table 5).** F test has also shown a non significant difference in copper concentration among some schools studied.

The Cu extracted from the soils investigated ranged from 1.54 to 9.28 mg kg-1. All are below the limit set by European regulations (150- 300 mg kg-1) (27). Regulatory bodies in the U.S DoI also reported a threshold limit of copper in the soil be 74 ppm. Even with this as a reference, the Cu in the soils studied is quite less. The concentration of Cu in the investigated soils, therefore, has no adverse effect on children's health.

Lead

The concentration of lead was significantly ($p \leq 0.05$) different among the schools. Maximum Pb concentration was recorded at Life Line (92.9 ppm) followed by Bisrat Gebriel (89.2 ppm) and Babyland (80.0 ppm). This may be due to nearby sources of contaminants from garages and traffic density.

In contrary to this result, less lead concentration was recorded at Betel (7.65 ppm), Gendegerada (8.67 ppm) and Yenege Tesfa (8.75 ppm). Analysis of variance has also shown non- significant difference in lead concentration among some schools studied. In this study, some of the samples results have shown that concentration of lead parallel with the metal level standard developed by Environmental Protection Agencies of Slovenia (85 mg kg^{-1}) and Germany (100 mg kg^{-1}) . Although the currently acceptable soil Pb guideline for residential housing is 300 mg kg^{-1} (28), in Norway the soil Pb guideline for children's play areas is 100 mg kg^{-1}, and in California the draft soil Pb guideline is 80 mg kg^{-1} (29), the present study revealed that the concentration of Pb in some schools is found to be near and even greater than the different set of critical values. Such relatively high lead content in the soils warrants a closer watch by the concerned bodies to at least curb further accumulation of the metal.

Table 4. Concentration (mg kg^{-1}) of heavy metals in soil (0-15 cm) samples

Sample no	Cd (mg kg-1)	Cr (mg/ kg)	Cu (mg/kg)	Hg(µgkg-1)	Pb (mg/ kg)	Zn (mgkg^{-1})
BN3 [d]	Nd	41.2±1.04	1.88±00.12	0.0118	35.0±3.31	21.2± .56
MDL2 [d]	Nd	60.8±1.44	3.64±0.21	nd	69.6±1.90	27.9±0.74
SYN [d]	0.67*±0.01	55.2±0.29	2.71±0.11	nd	30.4±1.44	30.6±0.5
DBL [d]	Nd	34.3±2.06	8.68±0.21	0.0064	34.2±1.91	25.4±0.8
BGL [d]	nd	37.5±1.25	2.78±0.14	nd	89.2±6.4	31.6±0.2
YTF [d]	nd	13.3±1.44	2.82±0.06	nd	8.75±0.0	29.6±0.71
BTL [d]	nd	34.2±1.9	1.54±0.03	nd	7.65±0.37	17.4±0.00
GGD [d]	nd	25.8±1.4	2.04±0.15	nd	8.67±0.72	13.8±0.29
ABI [d]	nd	58.3±1.44	2.68±0.08	nd	13.3±0.83	25.2±0.64
ABY [d]	nd	35.3±1.4	2.41±0.05	0.0029	16.7±0.72	31.4±0.64
DDB[ha]	nd	55±2.5	9.28±0.25	nd	15.3±1.44	29.8±0.61
BBL[h]	nd	44.2±2.8	6.98±0.67	nd	80±1.25	33.1±0.35
NSR[h]	nd	59.2±2.8	2.53±0.02	nd	10±0.0	15.4±0.51
LFL[h]	nd	51.7±1.44	3.98±0.09	nd	92.9±8.02	30.4±0.00
MTS[a]	nd	59.3±4.25	7.91±0.26	0.0093	11.6±0.08	19.4±0.24

nd= Not detected

Table 5. Concentration of some heavy metals on the study areas (in ppm)

Name of school	Mean value of Cr oncentration	Mean value of Zn concentration	Mean value of Pb concentration	Mean value of Cu concentration
Abay Yohannes	35.3	31.4	16.7	2.41
Abune Endrias	58.34	25.2	13.3	2.68
Babyland	44.2	33.1	80.0	6.98
Betel	34.2	17.4	7.65	1.54
Beza No 3	41.2	21.2	35.0	1.88
Bisrat Gebreal	37.5	31.6	89.2	2.78
Dandi Boru	55.0	29.81	15.3	9.28
Dire Betel	34.3	25.4	34.2	8.68
Gendegerada	25.8	13.8	8.67	2.04
Life Line	51.7	30.4	92.9	3.98
Medresatuselam	59.3	19.4	11.6	7.91
Model No 2	60.8	27.9	69.6	3.64
Nigushira	59.2	15.4	10.0	2.53
Sabyan	55.2	30.6	30.4	2.71
Yenege Tesfa	13.3	29.6	8.75	2.82
$LSD_{5\%}$	1.77	0.784	4.74	0.33
SE	1.25	0.29	1.71	0.13

SE=error mean square LSD=least significance difference

Mercury

In this study the result reported is in ppb for some of the study area (0.0118, 0.0064, 0.0029 and 0.0093 ppb from Beza No. 3, Dire Betel, Dandi Boru and Medresatuselam Nursery, Kindergarden and Primary school, respectively (**Table 4)** and the others are even not detected in this unit (ppb).

The result reported in ppb shows the highest concentration for Beza No 3 (0.0118 ppb) which might be due to some pollution from textile factory. For the element Hg the AAS result has not been reported in ppm because its concentrations were below the detection limits. This indicated that there is less sources of pollution and minimum health adverse effect of the element mercury, in the sites investigated.

Zinc

The concentration of zinc was significantly ($p \leq 0.05$) different among the schools (**Table 5**). The highest concentration of zinc was recorded at Babyland (33.1 ppm) followed by Bisrate Gebreal (31.6 ppm) and Abay Yohannes (31.4 ppm), however, less concentration was recorded at Gendegerada (13.8 ppm), Nigushira(15.4 ppm) and Bete l(17.4 ppm) (**Table 5**). Most of the schools, zinc concentration has shown significant difference; however, Model No 2 and Abune Endrias, Yenege Tesfa and Dandi Boru, Dandi Boru and Life Line, Sabyan and Life Line, Sabyan and Bisrat Gebreal, Bisrat Gebreal and Abay Yohannes were not significantly different from each other. This showed these heavy metals in the above schools had similar pollution level and pollution sources. The lower value recorded might be resulted from lower sources of contaminants of this metal.

Alloway *et al*. (1990) reported the soil concentration of zinc ranging from 70 to 400 mg kg^{-1} and taken as critical, above which toxicity is considered likely (30). In view of these directives the concentration of zinc from soil sample extracts was below the toxic range (Table 1). This finding indicated that the concentration of zinc will not have a serious health effect on children.

Correlation among different parameters

The correlation between heavy metals and soil physical chemical properties is shown in **Table 6.** Soil pH, heavy metals and organic carbon have shown no correlation. Similar results have been reported earlier (31,32,33).

Table 6. Correlation coefficients (r) of physico-chemical parameters and metals

Variable	Cr	Cu	Pb	Zn
pH	-0.186	-0.245	-0.198	-0.423
%OC	0.307	-0.147	0.226	0.056
%Silt	-0.538*	0.075	-0.272	0.075
%Sand	0.508	0.046	0.254	0.009
%clay	0.045	0.034	-0.049	-0.317
%CaCO3	-0.533	-0.203	-0.201	-0.136

OC=organic carbon, pH=power of hydrogen, CaCO3= calcium carbonate, Pb=lead, Cu=coppe, Cr=chromium, Zn=Zinc, r= correlation coefficient * =significant ($p<0.05$) ** =highly significant ($P<0.001$)

This finding is also consistent with the particle size distribution of the soils (**Table 3**). Fine grained soils fractions exhibit higher tendency for heavy metal adsorption than coarse-grained since it contains soil particles with large surface areas such as clay minerals, iron and manganese Oxy-hydroxides, humic-acids (31). The soils investigated have very little amount of fine grained soils and hence humic acids which might be responsible for the observed poor correlation.

CONCLUSION AND RECOMMENDATIONS

Conclusions

Results obtained from this study showed that some Nurseries, Kindergardens and Primary schools in Eastern Hararghe, Ethiopia have low levels of heavy metals content in soils. The examined soils can be considered unpolluted (except, Pb from life line) since their total and bioavailable concentrations were generally low. Data analyses suggested that the moderate enrichment factor exhibited by some of the soils was indicative of possible sources of heavy metals that may come from external sources such as building paint residues, Garage, Road vehicular emission, furniture scrub materials, and building material. Children under six years old in Life line school could possibly be at risk due to soil lead exposure because soil ingestion and hand-mouth contact is an important pathway of exposure. The reduction of soil lead metal concentration in this school outdoor playground could be worth considering.

Recommendation

In general, in order to reduce children exposure to heavy metals poisoning caused by contaminated soils and dust, more attention should be directed towards the general cleanliness of the schools environment, such as good housekeeping practice, following safe way wastes disposal procedures from urban and children should be encouraged to wash their hand frequently to reduce ingestion of contaminated dusts.

Further to establish the detailed distribution of metal contamination, further investigation should be conducted to provide information on the depth of contamination below 15cm which requires more extensive sampling of the soil profile..

Also, there is a need for soil remediation in regards to the concentration level of lead in some schools such as Life Line Nursery, Kindergarten and Primary school.

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