Assessment of Heavy Metal Pollution in Soil and Barley Crop Grown Around Mugher Cement Factory, Ethiopia

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Abstract

Different researches showed that cement manufacturing is one of the significant sources of heavy metal pollution in soil through precipitation and fallout. In this study, heavy metals pollution in soil and barley crop grown around Mugher cement factory were investigated. A total of 36 soil samples at different distance from the factory (0-500m, 500-1500m and 4000m) and 22 barley sample were collected and analyzed at Holetta Agricultural Chemistry Laboratory. The parameters analyzed in soil sample includes: Available heavy metals, total heavy metals and major physico-chemical properties. Dry ashing method was used to determine the level of heavy metals in barley sample. Analysis for the concentration of heavy metals were conducted using Atomic Absorption Spectrometer. One-way ANOVA were used to compare the mean values between experimental treatments with SPSS statistical software. The Geo-accumulation Index and transfer factor of each heavy metal were computed and interpreted. The Igeo values are below zero indicates that the soil quality is practically unpolluted. The results in soil physico-chemical properties showed that neutral to moderately alkaline soil pH, clay to clay loam soil texture, medium to high category of phosphorus, nitrogen, and potassium. The cement dust therefore effluence to enhance the pH level to the alkaline, as a result the contents of major soil physico-chemical properties declines near to the factory. The values of heavy metals transfer factors from soil to barley crop are below one indicates that the crop have not influenced by heavy metals that uptaked from cement dust polluted fields. The levels of heavy metals determined in the analyzed barley samples also found to be below the permissible limit set by FAO/WHO; hence, the concentration of these heavy metals in the barley crop analyzed, may not presently pose a health hazard and can as well serve as sources of essential trace metals to the population.

Keywords: Heavy metals, Atomic Absorption Spectrometer, pollution indices, transfer factor

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1. Introduction

Environmental pollution related to urbanization and industrialization is inevitable unless proper measures are taken. Air pollution is one of the serious problems in recent times as a result of rapid increase in number of vehicles, cement factories, steel and coal industries and petrochemical industries coupled with deforestation of natural forest. In comparison to the effect of gaseous pollutants on the air quality, little attention is given to the effect of particulate pollutants on soil and vegetation properties [1, 2].

Heavy metals enter the surroundings by natural means and through human activities. It is projected that the anthropogenic emission into the atmosphere is one-to-three orders of magnitude higher than natural fluxes [3]. The emission of anthropogenic heavy metal compounds causes considerable changes in biogeochemical cycles of some elements. Increasing industrialization and urbanization had anthropogenic contribution of heavy metals in biosphere and had largest availability in soil and to a relatively smaller proportion in atmosphere as particulate or vapors [4]. They are different sources of heavy metals in agricultural fields: all sources of heavy metals can be divided into five categories as follows [5]:- 1, geochemical sources: in geological terms, heavy metals are included in the group of elements referred to as (trace metals) which together constitute less than 1% of the rocks in the earth crust; the macro elements (O, Si, Al, Fe, Ca, Na, K, Mg, Ti, H, p and S) comprise 99% of the earth crust. The natural enrichment of metals in the soils may still give rise to harmful effect to living organisms. 2, agriculture material: agriculture constitutes one of the most important non-point sources of metals pollutants; the main sources are (impurities in fertilizers, pesticides, disscants, wood preservative, wastes from intensive pig and poultry productions, composts and manures, sewage sludge. 3, metallurgical industries. 4, waste disposal. 5, other sources in manufacture and disposal (include: batteries, pigments and paints, catalysts, polymer stabilizers, additive in fuels and lubricants).

Metal-bearing solids at contaminated sites can originate from a wide variety of anthropogenic sources in the form of metal mine tailings, disposal of high metal wastes in improperly protected landfills, leaded gasoline and lead-based paints, land application of fertilizer (trace amounts of heavy metals as impurities), animal manures, biosolids (sewage sludge), compost, pesticides, waste water (such as: sanitary sewage, chemical waste water, industrial mining waste water and urban mining mixed sewage). coal combustion residues, petrochemicals, and atmospheric deposition (airborne sources of metals include stack or duct emissions of air, gas, or vapor streams, and fugitive emissions such as dust from storage areas or waste piles) [6].

Soil is of major importance for life since it represents a source of both water and nutrients for plants and soil-living microorganisms and animals. Quantitatively, micronutrients are negligible constituents of soils, but the concentrations and availability of these nutrients are still of great importance for plant development and for obtaining high yields in crop production. Soil micronutrients are derived from minerals in the geological parent material, where the composition of the bedrock, the texture and the degree of weathering of the mineral soil have a large influence on the amount of micronutrients stored and released.

The heavy metals essentially become contaminants in the soil environments because (i) their rates of generation via man-made cycles are more rapid relative to natural ones, (ii) they become transferred from mines to random environmental locations where higher potentials of direct exposure occur, (iii) the concentrations of the metals in discarded products are relatively high compared to those in the receiving environment, and (iv) the chemical form (species) in which a metal is found in the receiving environmental system may render it more bio-available [7].

The concentration of heavy metals in soil is influenced by various physicochemical characteristics of soil such as pH, particle size distribution, organic matter, cation exchange capacity, and moisture content of the soil [8]. The method of binding heavy metals, and hence their bioavailability, depends on several soil properties, which include [9]: Organic matter content, granulometric composition, occurrence and form of cations, pH value, content of macro and micronutrients, oxidation-reduction potential, activity of microorganisms, bioavailability for plants. Soils having granulometric composition characteristic for clay, silt and dust, and those with a high content of organic matter, have a high sorption capacity and a strong ability to bind metallic elements [10]. Soil pH is a major determinant of metal mobility in the soil, as pH decreases the solubility of the metal cation increases due to desorption from soil minerals such as carbonates, metal oxides and hydroxides [11]. The increase of hydrogen ion concentration affects the mobilization intensity of heavy metals. In highly acidic soils, the mobility of metallic elements is much higher than in soils with neutral and alkaline reaction [12].

The cement industry is an energy intensive and significant contributor to climate change. The major environment health and safety issues associated with cement production are emissions to air and energy use. Cement manufacturing requires huge amount of non renewable resources like raw material and fossil fuels. It is estimated that 5-6% of all carbon dioxide greenhouse gases generated by human activities originates from cement production [13]. Raw material and Energy consumption result in emissions to air which include dust and gases. The exhaust gases from a cement kiln contains are nitrogen oxides (NOx), carbon dioxide, water, oxygen and small quantities of dust, chlorides, fluorides, sulfur dioxide, carbon monoxide , and still smaller quantities of organic compounds and heavy metals [14]. Toxic metals and organic compounds are released when industrial waste is burnt in cement kiln. Other sources of dust emissions include the clinker cooler, crushers, grinders, and materials-handling equipment.

Air pollutants such as heavy metals, generated in the process of crushing limestone, bagging, and transportation of cement are carried by wind and deposited on soil, plants and water bodies [15].The dust deposition from cement factory influenced by wind velocity, particle size, and stack fumes. Among the metals especially recognized in environmental studies on emission from cement plants to have toxic effect on soil are arsenic, cadmium, lead, mercury, thallium, aluminum, beryllium, chromium, copper, manganese, nickel and zinc [16]. Arpita and Mitko (2011)[17] reported that top soils near a cement factory are enriched in Pb, Zn, Cr, Cd, V, Pb and Hg which are released into the air from the cement kilns. The results of elementary chemical analysis, expressed in weight percent of oxides, conducted by (Young-Chull and Jae-Min, 2004) [18] showed that the raw material dust of the first grinding process primarily consisted of CaO (41.77%), SiO_2 (11.72%), Al_2O_3 (3.45%), and Fe_2O_3 (1.47%). (Samuel and Aynalem, 2012) also reported that two soil depths (0-5 cm & 5- 15 cm) are similarly categorized as moderately to heavily contaminated on the level of heavy metals.

Due to the increasing trends of heavy metals contamination in the environment and their negative impact on plants and other organisms, it is important to mitigate the toxicity of heavy metals from the environment which has become a burning issue. Determining the physicochemical properties of soil and their trace metal content is therefore important to monitor environmental pollution related to cement industries. Therefore, the study was undertaken with a general objective of investigating the level of heavy metals in soil and barley crop around Mugher cement factory, central Ethiopia. The specific objectives of the study were:

- To investigate the available and total concentration of heavy metals (Fe, Mn, Cu, Zn, Cd, As, Cr and Pb) in soil
- To determine the level of heavy metals (Fe, Mn, Cu, Zn, Cd, As, Cr and Pb) in barley crop
- To evaluate major physico-chemical properties of soil (pH, EC, Moisture, Bulk density, Total nitrogen, P, K, Oc, S and Cation Exchange Capacity)

2. Materials and Methods
Equipment and reagents
The instruments and apparatus that used in this study were: Atomic Absorption spectrophotometer (Agilent, 200

Series AAS), Spectro photometer (Janway 6300), pH meter (HI 9017 microprocesser HANNA), conductivity meter (Janway 4310), Muffle furnace, analytical balance, pistel and mortar and crop grinding machine .
All reagent chemical used were analytical grades; distilled water was used for dilution and preparation of reagents. Traceable to NIST stock solutions, 1000 ppm, were used to prepare a serious of heavy metal standards.

Description of sampling site
The study area is Mugher, around Mugher cement factory, which is located 90 km North West of Addis Ababa, Ethiopia. It lays at an elevation of 2,450 m above sea level. The average wind speed at a height of 10 m above ground level was 1.0 km/h between October- November and 0.72 Km/h between April- May [19]. The mother plant of the factory has three production lines with production capacity of 5000 tons of clinker per day. The farmers around in this area commonly harvests cereal crops such as Wheat, Barley, Teff and Sorghum once in a year from October to November.

Sample collections and preparation
Soil sample collection and preparation
The soil samples were collected at the time of harvesting cereal crop at 20 cm depth. Random sampling techniques were followed to collect soil samples from experimental fields of: 0-500 m, 500-1500 m and ≈4000 m from the factories regards to the cement dust concentration gradients and the availability of selected crop. With auger, about 1 kg a total of 36 soil samples, were taken from the experimental fields. Every sample was coded properly, the sample bags marked with codes using permanent marker. All the sample information regarding sampling locations, source, date of collection and allotted codes were recorded in the observation register and brought to Holetta Agricultural Research laboratory for preparation and analysis. The collected soil samples were transferred to plastic trays and break up the large clods to speed up drying. The sample then air-dried, crushed with mortar and pestle and passed through a 10-mesh (2-mm opening) stainless steel sieve and preserved for laboratory analysis [20,21].

Barley crop sample collections and preparation
Before sowing at the time of harvesting, about 100g a total of 22 barley crop samples, were collected from the spots of soil samples taken. Paper bags were used to store the collected sample and brought to Holetta Agricultural Research laboratory for preparation and analysis. The collected crop samples were threshed, placed in clean acid washed porcelain crucibles and oven dried at 70 ^{o}C for 24 hour in drying oven. The dried samples were then grounded in to a fine powder and kept in desiccators before analysis begun [22].

Sample digestions and extractions
Dry ashing, barley samples
1.0 g of grounded barley samples were weighed in crucible, placed in muffle furnace and ash to 550 ^{o}C for 2 hours. The ash dissolved with 1 mL concentrated hydrochloric acid, filtered in 100 mL volumetric flask and marked with distilled water [22]. Dilution applied when the sample reading was not in acceptable working standard range.

Extraction of soil samples, available heavy metals using NH_4HCO_3 -DTPA
Reagent preparation of extraction reagent,
0.005 M diethylene triamine pentaacetic acid (DTPA) solution was prepared by adding 9.85 g DTPA to 4500 mL water in a 5000 mL volumetric flask. It was shaked constantly for 5 h to dissolve the DTPA, and brought to 5000 mL with distilled water. This solution is stable with regard to pH. To 900 ml of the 0.005 M DTPA solution, 79.06 g ammonium bicarbonate (NH_4HCO_3) gradually added and stirred gently with a rod to facilitate dissolution and prevent effervescence when bicarbonate is added. The solution was diluted to 1000 mL with the 0.005 M DTPA solution, mixed gently with a rod and the pH adjusted to 7.6 with drop wise additions of 2M hydrochloric acid (HCl) and slow agitation with a rod.

Extraction Procedure
10 g soil sample were weighed in a 125 mL conical flask and 20 mL extraction reagent (0.005 M diethylene triamine pentaacetic acid solution) was added and shake on reciprocal shaker for 15 min at 180 cycles/min with flasks kept open. The extracts were filtered immediately through Whatman 42 filter paper [23].

HNO_3-$HClO_4$ soil total heavy metals digestion
Following the procedure recommended by the AOAC (1990), one gram of sample was placed in a 250 ml digestion tube and 10 ml of concentrated HNO_3 was added. The mixture was boiled gently for 45 min to oxidize all easily oxidizable matter. After cooling, 5 ml of 70% $HClO_4$ was added and the mixture was boiled gently until dense white fumes appeared. After cooling, 20 ml of distilled water was added and the mixture was boiled further to release any fumes. The solution was cooled, further filtered through Whatman No. 42 filter paper and <0.45 μm Millipore filter paper and transferred quantitatively to a 25 ml volumetric flask by adding distilled water.

Preparation of working standard solution, calibration and instrument condition
Working standard solutions of copper (Cu), iron (Fe), zinc (Zn), manganese (Mn), chromium (Cr), arsenic (As), lead (Pb) and cadmium (Cd) were prepared from the stock standard solutions (1000 ppm). The instrument was

calibrated with five series of calibration standard solutions and measurements of elements were done by using the atomic absorption spectrophotometer (AAS) (Model: Agilent, 200 Series AA).

Table 1. Instrument operating conditions and detection limit of AAS

Heavy metals	Wavelength (nm)	Slit width (nm)	Flame type	Required detection limit (mg/l)	Instrument detection limit (mg/l)
Fe	372.0	0.2	Air-acetylene	0.50	0.0060
Mn	403.1	0.2	Air-acetylene	0.20	0.0020
Zn	213.9	1.0	Air-acetylene	0.10	0.0010
Cu	324.8	0.5	Air-acetylene	0.50	0.0030
Pb	283.3	0.5	Air-acetylene	1.00	0.0010
Cr	429.0	0.5	Air-acetylene	0.25	0.0060
Cd	228.8	0.5	Air-acetylene	0.20	0.0020
As	197.2	1.0	N_2O- acetylene	1.00	0.3000

Data quality control

Appropriate quality assurance procedures and precautions were carried out to ensure reliability of the results. De-ionized water was used to the reagent preparation and sample dilution throughout the study. The analytical balances, drying oven, muffle furnace and glass wares used in the laboratory were calibrated and certified by the calibration body.

For each physico-chemical parameters of soil samples: triplicate analyses were conducted together with the internal laboratory (Holetta Agricultural Research) control sample to verify the precision and accuracy of the results. The internal quality control sample is the sample used as a control by the laboratory in each soil physico-chemical parameters. It has known method validation summary: - precision (reproducibility and repeatability), measurement uncertainty and known Mean±SD values. Outliers between triplicates measurement of sample analysis were checked by verifying the % RSD (percent relative standard deviation).

During analysis with Atomic Absorption Spectrometer; freshly prepared working standard serious, method blanks and internal control samples were used. Instrumental sensitivity was checked during calibration with absorbance reading of prepared working standard. The instrument adjusted:-Each sample, reagent bank and standard results obtained by averaged three points (<5 % between duplicates) of a single measurements; the correlation coefficient values of working standards is >0.9998. Re-calibration and re-slop were done in the intervals of 20 sample measures (referred by the instrument default value, i.e. 50). Duplicates and spikes used during each batch of analysis and the summery of the result are indicated in Tables 5 & 6.

Data analysis

Statistical analyses were carried out using SPSS software, version 20. One way ANOVA, descriptive statics, was used for comparing the mean concentration physico-chemical properties of soil and level of heavy metals in barley with in experimental treatments (distances from the factory). Significance difference among treatments (0-500 m, 500-1500 m and 4000 m from the factory) indicated for each parameter at $p< 0.05$ and the results were reported as mean ± standard deviation.

3. Results

Effect of cement dust pollution on the level of soil heavy metals content

Table 2: Extractable heavy metals (AB-DTPA) and Total heavy metals (HNO_3-$HClO_4$)

Type of HMs	Treatments	Fe	Mn	Zn	Cu	Cr	Pb
		--- (ppm) ---					
Extractable (AB-DTPA)	0-500m	194.33±9.87c	1.25±0.16c	9.37±0.84c	0.90±0.18c	1.40±0.17a	0.73±0.09a
	500-1500m	335.33±20.79b	8.12±1.13b	22.44±4.27b	2.19±0.22b	0.19±0.00b	0.48±0.04b
	≈4000m	683.67±10.41a	11.26±0.99a	42.05±2.13a	2.68±0.02a	0.22±0.03b	0.20±0.03c
Total heavy metals (HNO_3-$HClO_4$)	0-500m	58.61±4.53a	1255.92±37.62a	105.66±8.11b	76.28±4.29a	15.55±2.63a	11.63±1.48a
	500-1500m	36.33±5.13b	734.32±57.06c	127.54±7.99a	57.06±2.69b	10.28±1.53b	5.81±0.57b
	≈4000m	29.89±1.20c	1101.18±33.10b	70.58±2.11c	52.02±0.89b	8.23±0.90ca	4.61±0.00c
Permissible limit (ECC 1986)		___	____	150-300	50-140	100	50-300

Mugher site, around Mugher cement factory. The mean±SD value, experimental treatments (0-500m, 500-1500m and ≈4000m). Except to Fe in total heavy metals that expressed in percent (%); Cu, Mn, Zn, Pb and Cr level are expressed in ppm (mg/kg). ECC, limits described by European community commission for the level of total heavy metals. The significance difference indicated as 'a', 'b' and 'c'.

Effect of cement dust pollution on major soils physico-chemical properties
Table 3: pH, EC, BD and Texture

Parameters		Experimental treatments (distance from the factory)		
		0-500m	500-1500m	≈4000m
pH		8.09±0.14a	6.93±0.21b	5.86±0.10c
EC (µS/cm)		133.08±18.29a	98.33±41.65ab	68.00±17.20b
BD (g/cm^3)		1.280±0.08ab	1.305±0.07a	1.188±0.04b
Moisture (%)		10.47±2.76a	9.20±2.24a	9.13±1.10a
Texture	(%) clay	46.25±16.89a	33.13±7.47a	50.00±6.07a
	(%) silt	20.00±2.04a	26.88±7.18a	25.00±0.70a
	(%) sand	33.75±15.07a	40.00±5.40a	25.00±2.00a
CEC (cmol$_c$ kg^{-1})		40.30±8.71a	39.69±2.31ab	31.50±1.00b
Corg. (g/kg)		9.07±3.74c	18.66±4.03b	35.52±0.00a
Ntot. (g/kg)		0.64±0.32c	1.46±0.28b	2.74±0.11a
S-SO$^{-2}_4$ (mg kg^{-1})		4.08±0.99c	5.86±1.81b	6.83±0.09a
P(mg kg^{-1})		25.25±17.36b	51.15±14.17a	57.21±3.24a
k(cmol kg^{-1})		0.69±0.10a	0.68±0.04a	0.76±0.00a

µ±SD of pH, Electric conductivity, Bulk density, Texture, Cat-ion Exchange Capacity,
 Organic carbon, Total nitrogen, S-SO$^{-2}_4$, Phosphorus and Potassium

THE LEVEL OF HEAVY METALS IN BARLEY
Table 4: The average concentration of Heavy Metals in barley sample

Parameters	Experimental treatments (distance from the factory)			FAO/WHO limit
Heavy metals (ppm)	0-500m	500-1500m	≈4000m	
Fe	199.09±5.88c	289.90±11.53a	256.40±3.00b	425.5
Mn	34.74±2.06a	18.66±0.14b	20.78±1.80b	500
Zn	26.16±2.19a	20.68±2.09b	20.01±0.98b	99.4
Cu	3.83±0.29b	4.28±0.19a	3.09±0.08c	73.3
Cr	0.77±0.08a	0.83±0.05a	0.65±0.01b	2.3
Pb	0.12±0.01a	0.12±0.02a	0.09±0.01a	0.3

The level of heavy metals express in ppm (mg kg−1) dry weight. The significant differences at
 p< 0.05 are indicated by 'a', 'b' and 'c'.

QUALITY CONTROLS

Table 5: Quality control values of soil chemical properties

No.	pH	EC (μS/cm)	CEC (cmol/kg)	O_C (%)	TN (%)	P (mg/kg)	K (cmol/kg)	S (mg/kg)
				Duplicates				
1	5.93	76.4	32.40	1.838	0.196	7.411	0.58	8.39
	6.02	74.2	31.30	1.861	0.189	7.690	0.60	8.10
2	7.32	90.4	35.40	2.506	0.213	9.978	0.62	10.48
	7.47	93.1	33.90	2.540	0.220	9.706	0.61	9.99
3	7.97	131.2	31.48	1.297	0.099	24.360	0.66	5.81
	8.01	134.2	33.00	1.251	0.102	25.190	0.63	5.81
4	7.94	171.6	24.90	1.074	0.099	34.560	1.00	5.81
	7.89	175.3	24.38	1.112	0.103	35.780	0.96	5.67
5	7.90	97.0	37.44	1.532	0.121	41.595	0.62	5.86
	7.82	99.2	36.10	1.582	0.124	42.614	0.59	5.72
6	7.14	105.0	36.12	2.828	0.219	40.243	0.78	8.38
	7.23	108.0	35.11	2.871	0.211	40.991	0.76	8.38
7	7.01	77.4	37.46	1.793	0.168	59.672	0.68	3.77
	7.14	74.6	36.99	1.712	0.164	61.841	0.67	3.63
8	7.02	123.0	34.28	3.521	0.275	122.430	0.84	1.89
	7.14	117.2	35.32	3.574	0.271	118.012	0.81	1.80
RPD (range)	**0.50-2.03**	**2.13-4.83**	**1.26-4.71**	**1.24-3.48**	**1.24-3.64**	**1.84-3.70**	**1.48-4.65**	**0.00-4.87**
				Spikes				
1				1.847	0.168	11.189	0.58	
				1.896*	0.161*	11.714*	0.59*	
2				1.423	0.102	32.938	0.76	
				1.397*	0.099*	31.847*	0.74*	
3				1.010	0.087	13.883	0.65	
				1.021*	0.084*	13.954*	0.62*	
4				3.552	0.274	57.21	0.76	
				3.641*	0.284*	54.76*	0.77*	
% recovery				**97.42-101.86**	**96.48-104.35**	**95.52-104.47**	**98.31-104.84**	

'*' refers spikes values

The result showed in Table 5 showed the quality control values of soil sample analysis. Duplicates and spikes were used in each batch of chemical analysis. Relative percent deviation and recovery values are reported for duplicates and spikes respectively. In general, Relative percent deviation (RPD) ranges between 0.00 to 4.87 and % recovery from 95.52 to 104.84 from duplicates and spikes respectively.

Table 6: quality control values for heavy metals in soil and barley samples

No.	Duplicates(for soil samples)					
	mg/kg					
	Fe	Mn	Zn	Cu	Cr	Pb
1	421	37.25	10.90	4.01	0.182	0.512
	416	35.92	10.40	3.87	0.179	0.492
2	368	16.70	10.36	3.90	2.892	1.204
	374	15.93	10.12	3.75	2.761	1.224
3	359	9.23	25.80	2.08	2.304	0.525
	342	8.97	24.90	2.10	2.208	0.500
4	188	1.22	10.80	1.23	1.981	1.431
	197	1.26	10.30	1.19	2.011	1.501
RPD (range)	1.19-4.85	2.86-4.72	2.34-4.74	0.96-3.92	1.50-4.63	1.64-4.65
	Duplicates(for barley samples)					
	mg/kg					
	Fe	Mn	Zn	Cu	Pb	Cr
5	185.045	38.060	21.637	3.998	0.803	0.080
	180.240	39.146	22.107	3.988	0.804	0.081
6	273.050	18.583	19.228	4.400	0.772	0.108
	279.104	18.412	19.023	4.541	0.781	0.11
7	245.740	46.334	22.083	5.598	1.201	0.204
	254.81	45.395	21.997	5.675	1.222	0.209
8	281.694	18.079	18.156	4.099	0.820	0.123
	290.031	18.103	18.391	4.162	0.831	0.125
RPD (range)	2.19-3.62	0.13-0.28	0.39-2.15	0.24-3.15	0.16-1.70	1.24-2.31

Note: RPD , relative percent deviation between duplicates samples.

The result indicated in Table 6 showed that the quality control values of heavy metals in soil and barley. The RPD in soils ranges from 0.96 to 4.85 and from 0.13 to 3.62 in barley sample. The quality control results (Table 5 and Table 6) between duplicates and spikes in over all have shown that <5%, implies that it has in acceptable range [24].

4. DISCUSSION
Extractable heavy metals
Ammonium bicarbonate-diethylenetriaminepentaacetic acid extracting solution was used to extract available forms of heavy metals from the soil sample. It is widely accepted that determining the total content of heavy metals in a soil is neither sufficient to understand their relative mobility and ecological availability as contaminants nor particularly useful as a tool to estimate potential risks. At $p < 0.05$, the descriptive statics shows that there is significance difference among experimental treatments (0-500 m, 500-1500 m and ≈ 4000 m away from the factories). Except to chromium and lead one way ANOVA revealed that higher and significantly different level of extractable heavy metals obtained go away from the factory. It is well known that metals solubility in soils mainly depends on soil pH, organic C, CEC, and clay contents [25, 26]. Therefore the variation of the extractable heavy metals dominantly related with the pH variation of the study area that have showed in Table 5 (moderately acidic> neutral> moderately alkaline) comes from liming effects by the cement dust. Limits described by MacLean [27] on Cr, Pb and Cd level extracted with AB-DTPA are 8µg/g, 13µg/g and 0.31µg/g respectively. This shows that extractable chromium, lead and cadmium level in the study area are below the critical permissible levels.

Total heavy metals
The di-acid wet oxidation carried out by employing oxidizing acids, HNO_3-$HClO_4$. The control field (≈4000 m from the factory) significantly different and lower in contents than cement polluted areas of the experimental fields (0-500 m and 500-1500 m). The levels of Fe consistently decline towards go away from the factory. Young-Chull [28] pointed out that the results of elementary chemical analysis on the raw material dust of the

first grinding process consisted of 1.47% Fe_2O_3.This is therefore enhances the level of iron in the study area with respect to the control field ($\approx$4000m from the factory). The following table shows the pattern of heavy metals pollutions of cement dust polluted areas with respect to the control site.

Table 7: Geo-accumulation Index

Barley experimental Plot		
Heavy metals	$Igeo= log_2 [^Cn /1.5B_n]$	
	0-500m /$\approx$4000m	500-1500m /$\approx$4000m
Fe	-0.19	-0.40
Mn	-0.42	-0.65
Zn	-0.30	-0.22
Cu	-0.31	-0.47
Cr	-0.20	-0.38
Pb	-0.07	-0.38

Mugher site, around Mugher cement factory. The pollution indices, the pattern of metal contamination in the area. The value calculated for each heavy metal is with respect to the control (the value obtained $\approx$4000m) i.e. treatment1(0-500m)/control & treatment2(500-1500m)/control.

Table 7 shows the pattern of heavy metals pollutions of cement dust polluted areas with respect to unpolluted. Igeo is calculated through the following equation as applied by [29-31]. $Igeo = log_2 10[\frac{Cn}{1.5Bn}]$, where Cn represents the measured total concentration of metals in the soil (mg/kg); and Bn represents the geochemical background values of the metals (mg/kg). For the analysis of the geochemical background values of heavy metals (Bn), uncontaminated surface soils were used where both anthropogenic and industrial activities are minimal and can represent geological background with reference to heavy metals. The constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithological variations in the soils [32]. The constant 1.5 also helps to analyze natural fluctuation between the content of a given substance in environment and very small anthropogenic influences.

Table 8: Igeo classes with respect to soil quality

Class	Value	Soil quality
0	Igeo< 0	Practically unpolluted
1	0 < Igeo < 1	unpolluted to moderately polluted
2	1 < Igeo < 2	Moderately polluted
3	2 < Igeo < 3	Moderately to strongly polluted
4	3 < Igeo < 4	strongly polluted
5	4< Igeo < 5	strongly to very strongly polluted
6	5 < Igeo < 6	Strongly polluted

Table 8 refers that the seven ranges of contamination values have been determined to assess the degree of trace metals' pollution [33]. According to Galkus and Boszke [33, 34], the value indicated Igeo< 0 that the soil quality is practically unpolluted.

Therefore the pollution index and the permissible limit on soil quality have proved that the soil in the study area is unpolluted with heavy metals.

pH, EC, BD and Texture

The mean±SD of pH, EC, BD and Texture are summarized in Table 3. Soil pH is a crucial soil indicator defined as the negative log of the hydrogen ion activity. The pH range normally found in soils varies from 3 to 9. The significance of pH lies in its influence on availability of soil nutrients, solubility of toxic nutrient elements in the soil, physical breakdown of root cells, and CEC in soils whose colloids (clay/humus) are pH-dependent and biological activity. Most crops grow best when the soil pH is between 6.0 and 8.2. From the table, pH value are significantly differ in all treatments in the order of treatment one (0-500m, moderately alkaline)> treatment two (500-1500 m, neutral)> treatment three ($\approx$4000 m, slightly acidic).

Particle size distribution (soil texture) is an important parameter in soil classification and has implications for soil water, aeration, and nutrient availability to plants. Laboratory procedure [35] normally estimate percentage of sand (0.05 – 2.0 mm), silt (0.002 – 0.05 mm), and clay (<0.002 mm) fractions in soils. Soil texture triangle shows that the samples in the study area are clay to clay loam soil.

Soil bulk density (BD) is ratio of the mass (oven-dry weight) of the soil to the bulk volume which includes the volume of both solids and pore space at specified soil water content (usually the moisture content at sampling). Soil moisture influences crop growth not only by affecting nutrient availability, but also nutrient transformations and soil biological behavior.

Soil salinity refers to the concentration of soluble inorganic salts in the soil. It reflects the extent to which

the soil is suitable for growing crops. Values of 0 to 200 µS/cm are safe for all crops; yields of very sensitive crops are affected between 200 to 400 µS/cm; many crops are affected between 400 and 800 µS/cm; while only tolerant crops grow reasonably well above that level. I.e. Barley (Hordeum vulgare) upper tolerable limit is 1800 µS/cm [36]. In the Table 3 the results have shown that the soil salinity (electric conductivity) is safe and suitable to grow barley as well as for all cereals crops.

Total nitrogen, Organic carbon, phosphorus and Sulfur
Total nitrogen analysis measures N in all organic and inorganic forms. The organic fraction constitutes the majority of total N in soils (usually >95 %). It is composed mostly of plant and microbial remains, in variable composition. The inorganic phase of soil N is composed of ammonium (NH_4), nitrate (NO_3), and-very little though-nitrite (NO_2) forms. Environmental (temperature and moisture) and agronomic management (fertilization, cropping, etc.) factors influence its dynamic relationship with the organic fractions and also within the inorganic forms [36]. Only 1 to 4 percent of this total N becomes plant-available (converts via microbial activity from organic form to inorganic form) during a growing season [37]. Soil organic matter (OM) has a major influence on soil aggregation, nutrient reserve and its availability, moisture retention, and biological activity. As soil test interpretation guide [37], soil OM increases so does CEC, soil total N content, and other soil properties such as water-holding capacity and microbiological activity increases parallel. The contents of total nitrogen and organic carbon of treatment 1(0-500 m) is significantly differ and lower than the respective treatments. Soil test interpretation guide [37] refers that the organic carbon and total nitrogen in soil are collarets each other, Table 3 also support the correlation.

The level of phosphorus in treatment 1, near to the factory, is a medium content soil category and significantly differ from the respective treatments. The content of phosphorus increases and significantly different when the pH changes from moderately acidic (pH: 5.86) to neutral (pH: 7.02). This can be due to fixing of available P content in acidic soil with cations like Al.

Sulfur (S) exists in soil and soil solution mainly as the sulfate (SO_4-S) and Plants absorb sulfur in this form. Along with N and P, potassium (K) is also of vital importance in crop production. It has categorized that medium content of potassium.

Heavy metals in Barley crop
Arsenic (As) and Cadmium (Cd) were not detected in any of the cereal samples analyzed in the study area. The levels of heavy metals determined in the analyzed cereal samples were found to be below the permissible limit set by FAO/WHO [38].The heavy metal transfer factor of each heavy metals from soils to barley crop is calculated using the formula [39]:- $TF = \frac{MP}{MS}$; Where: TF – transfer factor, Mp – metal content in plant (mg kg^{-1}), Ms – metal content in soil (mg kg^{-1}). By using the data of Table 4 for Mp and Table 2 for Ms, the result for all heavy metals analyzed are below one. If the ratios >1, the plants have accumulated elements, the ratios around 1 indicate that the plants are not influenced by the elements, and ratios <1 show that plants exclude the elements from the uptake [40]. Therefore the selected cereal crop (barley) in the study area are safe for consumptions.

5. Conclusion
Consuming the cereals contaminated with heavy metals has different detrimental effects on human health; therefore, monitoring contamination of heavy metals will allow for avoiding unnecessary exposures. The result of this study has revealed that the various concentrations of the heavy metals Cu, Fe, Zn, Mn, Cr, As, Pb and Cd in Barley collected from Mugher site around Mugher cement factory of the Oromia Regional State, central Ethiopia. The concentrations of heavy metals determined were Fe, Mn, Zn, Cu, Cr, Pb ; As and Cd were not detected in any of the cereal crops. Generally, the levels of heavy metals obtained in barley are within the acceptable ranges and calculated values of transfer factor shows the crop not influenced by heavy metals that uptaked from the dust polluted fields in study area. Therefore this crop harvested from cement dust polluted experimental fields do not pose toxic effect to the health of their consumers, may as well serve as sources of trace metals to the population. Further studies recommend to carried out on the yield of cereal crops grown in the study area.

From soil data-Igeo values were calculated for each heavy metal with respect to control (≈4000m far from the factory). The value indicated Igeo< 0 that the soil quality is practically unpolluted. According to soil interpretation guide, the major nutrient status (i.e. phosphorus, nitrogen, and potassium) are medium to high category. The phosphorus, organic carbon, total nitrogen, potassium and sulfur contents of soil polluted with cement dust are decrease/significantly differ in contents than the control (≈4000m from the factory). In general, the factory should monitor the dust pollution emanates during cement production that changes the physico-chemical properties of soil by enhancing the pH level. Its recommend that carrying out further studies on speciation of heavy metals in soil and yields of cereals crop.

Conflict of interest

The author have not declared any conflict of interest.

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