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DETERMINATION OF HEAVY METALS IN CEMENT DUST, TOP SOIL AND TEFF AROUND HABESHA AND MUGHER CEMENT FACTORY, OROMIA REGIONAL STATE, ETHIOPIA

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ABSTRACT. In this study, the level of selected heavy metals in cement dust, soil and teff samples collected from around Mugher and Habesha cement factories, Ethiopia were determined using flame atomic absorption spectroscopy (FAAS). The collected samples were digested using properly optimized acid digestion using a mixture of 5 mL HNO_3:1 mL H_2SO_4:1 mL $HClO_4$ at 200 ºC for 2 h for the cement dust; 3 mL HNO_3:4 mL $HClO_4$:1 mL H_2O_2 at 300 °C for 3 h for the soil and 5 mL HNO_3:3 mL H_2O_2 for 1:30 h at 200 °C for the teff samples. The mean concentrations of metals determined (mg/kg) were in the ranges of Cu (450.26-471.79), Zn (1096.75-1103.10), Mn (3316-3419), Cr (242-404), Fe (31846-33836), Ni (1524-1727), Co (2492-2517), Cd (20.4-26.1), Pb (255-649) for cement dust; Cu (294-333), Zn (194-330), Mn (498-521), Cr (330-450), Fe (5283-5392), Ni (1138-3719) and Co (1439-1516) for soil, Cu (85.6-89.4), Zn (314-466), Mn (733-741), Cr (297-342), Fe (1327-1574) for teff. Cd and Pb were not detected in the teff and soil samples. The soil and teff samples collected from the two cement factories contained significant level of heavy metals. Except iron, the level of heavy metals in soil and teff samples were above the permissible limit of FAO/WHO.

KEY WORDS: Cement factory, Cement dust, Soil, Teff, Wet digestion, Heavy metals

INTRODUCTION

Human activities such as mining, coal processing, cement manufacturing, agriculture and transportation, etc. release high amounts of heavy metals into surface/ground water, soil and eventually to the biosphere [1]. These processes have frequently caused serious problems as the suppression of dust release could be very difficult. With the growing construction demands, mineral extraction has also increased in many countries such that emissions of particulate matter to the environment from crushing of limestone during the manufacture of cement have been of environmental concern. The dust, because of its fine particle size, travels over long distances and the total suspended particulate matter in the atmosphere is thus increased [2]. The deposition of these dust particles may harm the state of the ecosystem as finer particles which contain various toxic elements are deposited as the dust is transported away from emission source and has physical and chemical impacts on the environment [3].

Thus, cement factories along with many other anthropogenic activities are considered as a probable source of heavy metals such as cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), manganese (Mn), copper (Cu), and zinc (Zn) [4–6]. The majority of these heavy metals in a cement dust released from cement industries comes from the raw materials and have been overlooked in the past [7]. This dust can spread over large areas through wind and rain and are accumulated in and on soils and plants [8, 9]. Moreover, cement dust is largely made up of cement-kiln, a by-product that usually stored as waste in open-pit and unlined landfills [10].

The accumulation of the cement dust on top soil may have potential effect on human and animal health, vegetation and soil chemistry. Plant growth depends so much on soil micronutrient metals for the essential function and wellbeing of their organs. However, the concentration levels

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*Corresponding author. E-mail: birhanume@gmail.com and forms of the metals in the soil can be very critical to the plants; which may in turn affect the crop yield and contaminate the food chain and hence human health [11].

Particularly, toxic heavy metals such as cadmium and lead are toxic even at very small concentrations in the human body. These toxic metals frequently accumulate in the human tissues when they are not metabolized by the body for absorption and utilization. For instance, cadmium causes kidney damage and bone degradation because it affects calcium metabolism. Likewise, lead also causes numerous adverse health challenges in various organs of the human body. It can cause brain and kidney damage, decrease in hemoglobin production and male fertility. Lead enters human body by inhalation and ingestion, absorbed and carried by the blood; accumulated in liver, kidney, and bone up to about the fifth decade of life. There is substantial evidence that lead pollution can bring aggressive behavior in animals which can also occur in humans [4, 12, 13]. Thus, the analysis of these and other heavy metals in soil and food plants in potentially polluted areas in particular is vital.

However, only few studies have been reported on heavy metal accumulation and their potential health impacts around cement factories in Ethiopia. Yohannse and Eshetu have reported heavy metal pollution assessment in soil and barely crop grown around Mugher cement factory, Ethiopia. The results of the study indicate that high accumulation of all the heavy metals (Fe, Mn, Zn, Cu, Cr, Pb, Cd and As) investigated in the soil and barely crop except Cd and As for the later in samples collected from around Mugher cement factory, Ethiopia [14]. Similarly, Ermias *et al.* studied spectrophotometric determination of selected heavy metals (Cu, Cr, Cd, Pb and Ni) in some brands of Ethiopian cement (Mugher, Dangote, Capital and Derba) and soil sample collected from around Mugher cement factory. The study showed the presence of these metals in all the cement brands and soil samples analyzed. The result also confirmed the highest value of heavy metals in the top soil samples collected closer to the factory [15].

Therefore, the cement dust released from Mugher and Habesha cement factories may contaminate the surrounding environment including the soil and most widely grown cereal plant teff and other crops grown in the vicinity and hence might have a direct consequence of health impacts on the general public and those particular communities working in and living around the factories [11]. Teff (*Eragrostis tef*), a crop believed to have originated in Ethiopia, is among the primarily cultivated and consumed cereal crop around Mugher and Habesha cement factory. It accounts for about two-third of the daily protein intake in the diet of Ethiopian population. Very recently, teff have been receiving global interest as a healthy food due to the absence of gluten and gluten-like proteins [16, 17].

Thus, the study of the profile of heavy metals level in cement dust, top soil and teff grown near cement factory has significant value. On the other hand, no study has been reported on heavy metal levels in cement dust in any of the cement factories in Ethiopia and there is no report on the level of heavy metals in one of the most widely grown teff crop around Mugher and Habesha cement factory. The analysis of heavy metal levels in cement dust and soil around Habesha cement factory was not also produced to the best of our knowledge as it is a newer cement factory compared to Mugher cement which is one of the oldest factories in the country. Therefore, this study investigated the concentration of selected heavy metals (Cd, Pb, Cr, Cu, Zn, Mn, Fe, Ni and Co) in cement dust; top soil and teff seed cultivated around Mugher and Habesha cement factory using FAAS.

EXPERIMENTAL

Description of study area

The study area was found in West Showa Zone, Oromia regional state, Ethiopia, specifically located in Holeta for Habesha cement factory and Mugher for Mugher cement factory. Habesha cement factory is located 47 km West of Addis Ababa, Ethiopia. Holeta town lays at an elevation of 2, 600 m above sea level. Mugher cement factory is located at a distance of about 43 km furthest from Holeta town and 90 km West of Addis Ababa, Ethiopia. It lays at an elevation of 2,450 m above sea level. The average wind speed at height of 10 m above ground level was 1.0 km/h between October-November and 0.72 km/h between April-May [14]. The location map of the study area is shown in Figure 1.

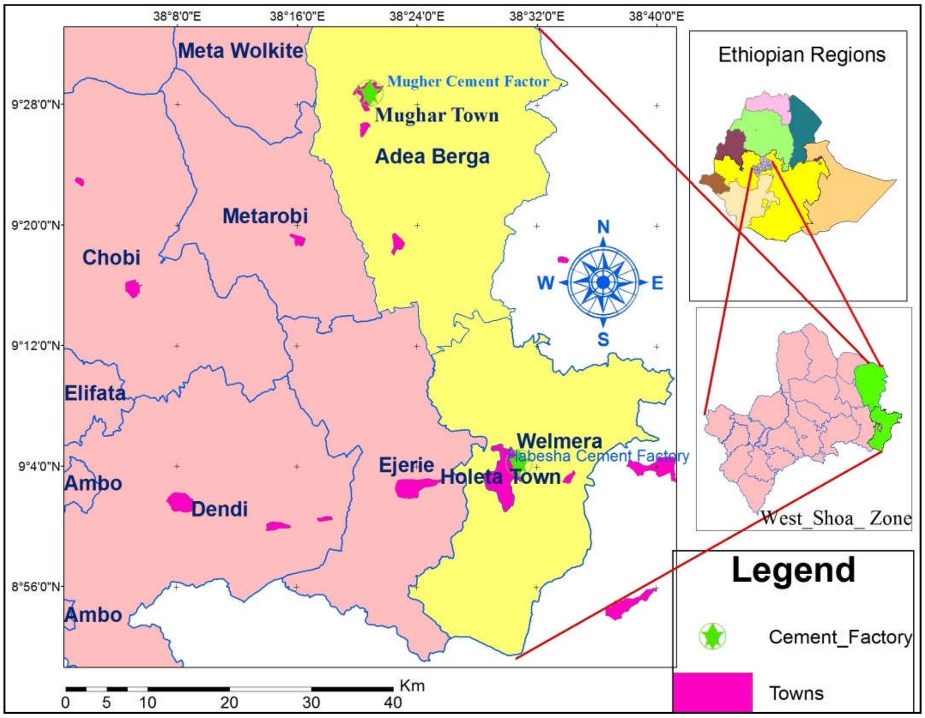

Figure 1. Location map of the study area.

Chemicals and reagents

All the chemicals and reagents used for sample digestions in this research work were of analytical grade. HNO_3 (69%), $HClO_4$ (70%), H_2SO_4 (98%) and H_2O_2 (30%) (all from UNI-CHEM® Chemical reagents, India). Stock standard solutions (1000 mg/L) of the target metal analytes (Pb, Cd, Cr, Zn, Mn, Fe, Co, Cu and Ni) were carefully prepared from their respective salts (nitrate salts) purchased from Sigma-Aldrich (Sigma-Aldrich Corp., St. Louis, USA) for the preparation of spiking and calibration standards. Double distilled water was used for diluting the digested samples and for preparation of intermediate metal standard solutions as well as for rinsing glassware and sample bottles.

Apparatuses and instrument

Polyethylene bags were used for packing the collected cement dust, soil and teff samples. Hot plate was used as heating apparatus during sample digestion. Borosilicate volumetric flasks were used during dilution of sample and preparation of metal standard solution. Mortar with pestle was used to mill the soil, cement dust and teff sample and sieve (0.5 mm mesh size) was used to separate larger sized particles. Analytical balance (Model E11140, Switzerland) with a precision of ± 0.0001 g was employed to weigh the processed samples, and measuring cylinders, pipette, and micropipette (Merck KGaA, Darmstadt, Germany) were used to measure different volumes of sample solutions, acid reagents and metal standard solutions. The digested samples were filtered with Whatman No.42, filter paper, and the digestion process was performed in a laboratory fume hood. FAAS (Model AAS AGELAND 2000 SIE) was used for the determination of target metals (Pb, Cd, Cr, Zn, Fe, Mn, Co, Cu and Ni) using air-acetylene flame. Oven (Model: DHG-9123A) was used for drying soil, teff and cement dust samples.

Sample collection and treatment

Samples were collected from both Mugher and Habesha cement factories in December, 2019. Cement dust samples were purposively sampled from within the factories at three different production stages (pre-heater, clinker cooler and cement mill) where excess generations of dusts are expected. The cement dust samples were collected by putting a wide plastic pan around these areas at an elevated place above the earth. The collected dust samples were composited and oven-dried at 105 °C for 2 h in the laboratory.

Soil and teff samples were collected from two locations around the two factories on the basis of dust accumulation. The first collection was made from within 1 km radius from the fence of the two factories where the accumulation of the dust particles is expected to be maximum. The sample collection was carried out by clustering the areas in to four directions (Northeast, Northwest, Southeast and Southwest). Then, soil and teff samples were randomly collected from each cluster and finally mixed to give a 1 kg composite of the four clusters.

The second sampling location was within 6–10 km radius distance from the fence of the factories. The accumulation of the dust particles is expected to be relatively low as compared to the samples collected from within 1 km radius and hence used as a control samples. The sampling procedure was the same as the samples collected within 1 km radius.

In both cases, the top soil (0–15 cm) and teff samples from the same area as the top soil were collected separately in a clean labeled polyethylene bags for storage and laboratory analysis. The soil samples were oven-dried at 105 °C for 2 h and ground using mortar and pestle, sieved with 0.5 mm nylon mesh size to make it homogenized. The teff samples were first cleaned, air-dried for 5 days, ground, and finally sieved with 0.5 mm nylon mesh size. The powdered samples were stored in clean polyethylene bags under airtight until digestion.

Optimization of digestion procedure

Table 1. Summary of the optimum conditions for the digestion of cement dust, soil and teff samples.

Sample type	Amount of sample (g)	Reagent used and volume (mL)	Digestion time (h)	Temperature (°C)
Cement Dust	0.5	5 mL HNO_3 1 mL H_2SO_4 1 mL $HClO_4$	2:00	200
Soil	1	3 mL HNO_3 4 mL $HClO_4$ 1 mL H_2O_2	3:00	300
Teff	0.5	5 mL HNO_3 3 mL H_2O_2	1:30	250

Different digestion procedures were assessed to figure out an optimum conditions for the digestion of the processed cement dust, soil and teff samples using HNO_3 (69%), H_2O_2 (30%), H_2SO_4 (98%) and $HClO_4$ (70%) acid mixtures by varying parameters such as volume of the acid mixture, digestion time and digestion temperature one at a time and keeping the others constant. The optimum digestion procedure was selected based on the usage of lesser reagent volume, shorter digestion time and reasonably mild temperature for obtaining clear solutions of the resulting digests. The summary of the optimum conditions for the digestion of cement dust, soil and teff samples were presented in Table 1.

Instrument working condition and preparation of standard solution

Stock standard solutions of 1000 mg/L of the metals of interest were prepared from their respective salts. Intermediate standards were used to obtain five point working standards for each metal of interest. Then, Pb, Cd, Cr, Zn, Fe, Mn, Co, Cu and Ni were analyzed by using FAAS equipped with deuterium background corrector and standard air–acetylene flame system. The calibration curves of each of the metal were constructed and the instrument response was found to be linear and sensitive with the corresponding correlation coefficients of $R^2 \geq 0.9969$. The calibration standard solutions were used to calibrate the instrument response with respect to analyte concentration [18]. The FAAS operating conditions, correlation coefficients and calibration equations for each metal are shown in Table S1 (supplementary information).

Method of validation

The efficiency of the analytical method was evaluated by spiking each sample with known amount of the analyte. The spiked samples were subjected to similar digestion procedure like the actual sample and the %recovery values were calculated. The obtained percentage recovery varied between 95.6–104% for all the metals analyzed in cement dust, soil and teff samples, which is within the accepted range of 80–120% for good recovery study [19]. The precision of analytical method was evaluated by using SD and %RSD of the replicate measurements. The %RSD values were < 10% for all the samples. The limit of detection (LOD, $3SD_b$) and limit of quantification (LOQ, $10SD_b$) were also determined from the standard deviation of seven replicates ($n = 7$) of blank samples digested following the same procedure utilized for digesting the cement dust, soil and teff samples. The limit of detection was found to be low enough to detect the metals at trace levels in the cement dust, soil and teff samples.

Metal transfer factor

The metal transfer factor (TF) is defined as the ratio of the concentration of metal in a plant (on dry weight basis) to the concentration of the same in a soil [20]. It is the bioaccumulation nature of the plant for heavy metals and is computed according to the method described by [21] using the formula:

$$\text{TF} = \frac{\text{Heavy metal concentration in the teff seed}}{\text{Heavy metal concentration in the soil}}$$

Statistical analysis

Descriptive statistics were used during data analysis. The recorded data were also subjected to ANOVA to investigate the effect of sample origin on the concentration of heavy metals. As the level of heavy metal concentration might vary with sample site, one-way ANOVA was used to test the existence of significant difference between the means [22]. Besides, correlation coefficients were calculated to examine association between objective metals. In all statistical analyses, confidence level was held at 95% (unless indicated) and the statistical calculations were made using SPSS software (23 versions).

RESULTS AND DISCUSSION

Concentration of heavy metals in cement dust, soil and teff

The results of the concentration of the heavy metals in cement dust, soil and teff samples collected within 1 km distance from Mugher and Habesha cement factories, and the control soil and teff samples collected within 6-10 km radius distance around the factories are provided in Tables 2-4. As it can be seen from the results of the cement dust, soil and teff samples from the two cement factories (Mugher and Habesha cement factory), varying concentration of considered heavy metals (Cu, Zn, Cd, Mn, Pb, Cr, Fe, Ni and Co) were determined.

All the analyzed metals were detected in the cement dust samples collected from Mugher and Habesha cement factories. Iron is the most abundant metal detected in the two cement factories while cadmium is the least among the metals studied. The trends in the variation of the metals in the cement dust samples were Fe > Mn > Co > Ni > Zn > Pb > Cu > Cr > Cd for Mugher cement factory whereas for Habesha cement factory the trend follows the order: Fe > Mn > Co > Ni > Zn > Cu > Cr > Pb > Cd. Currently, there are no guidelines for heavy metals in cement dust [6].

Table 2. Concentration of heavy metals (mg/kg) in cement dusts (mean ± SD, n = 3).

Metals	Sampling Sites	
	Mugher cement factory	Habesha cement factory
Cu	450 ± 14	472 ± 1
Zn	1103 ± 0.1	1097 ± 3
Mn	3316 ± 2	3419 ± 1
Cr	242 ± 2	404 ± 4
Fe	33836 ± 192	31846 ± 147
Ni	1727 ± 5	1524 ± 13
Co	2517 ± 4	2492 ± 6
Pb	649 ± 7	255 ± 1
Cd	20.4 ± 0.8	26.1 ± 0.1

Table 3 shows the mean concentration of heavy metals (mg/kg) in soil collected around 1 km distance radius and control sites (6-10 km) from both Mugher and Habesha cement factories. As can be seen from the Table, significantly elevated mean heavy metal concentrations were obtained in soil samples collected within 1 km distance from Mugher and Habesha cement factories except for Pb and Cd. The obtained concentrations of Fe were significantly higher than other metals with mean value of 5392 and 5283 mg/kg in soil samples collected around Habesha and Mugher cement factory respectively. Similarly, higher level of other analyzed metals were also detected with their concentration values following the decreasing order of Fe > Ni > Co > Mn > Cu > Zn > Cr, (for Mugher soil) and Fe > Co > Ni > Mn > Cr > Cu > Zn (for Habesha soil). Cd and Pb were not detected in both the soil samples collected from Mugher and Habesha cement factories.

The mean concentration of heavy metals in soil collected from the two control sites (Table 3) were relatively lower than the soil collected around cement factories which indicates considerable impact by the cement dust release from the factories. As can be seen from the results (Table 3), there is great significant difference between the concentration of heavy metals in soil samples collected around cement factory and that of the control samples. Pb and Cd were not detected in the soil samples collected from both sites which might be attributed to the dilution of the dust particles as it is released from the factory and travel a wide range of open areas and also mixes with the soil matter over which it resides. Thus, the concentration of Pb and Cd in the soil may be less (below MDL) than present in the dust sample collected directly from three points within the factory where the generation of cement dusts are very high. However, as the accumulation of dust particles continue, significant level of these metals will be detected in the future, if remediation measures were not taken in the future.

Table 3. Mean concentration of heavy metals (mg/kg) in soil collected around 1 km distance radius and control sites (6–10 km) from the factories (mean± SD, n = 3).

Metals	Mugher cement Factory		Habesha cement Factory	
	Within 1 km radius around the factory	Control soil sample (6-10 km distance)	Within 1 km radius around the factory	Control soil sample (6-10 km distance)
Cu	333 ± 1	232 ± 1	294 ± 0.5	234 ± 3
Zn	330 ± 8	170 ± 0.3	194.14 ±1.49	112 ± 0.3
Mn	521 ± 9	307 ± 43	498 ± 2	307 ± 0.1
Cr	330 ± 2	259 ± 5	450 ± 2	393 ± 8
Fe	5283 ± 4	3186 ±14	5392 ± 4	3843 ± 18
Ni	3719 ± 4	41.3 ± 3.9	1138 ± 3	44.1 ± 1.3
Co	1439 ± 29	1177 ± 19	1516 ± 1	1449 ± 2
Pb	ND*	ND*	ND*	ND*
Cd	ND*	ND*	ND*	ND*

*ND-Not detected.

Teff is the main cereal crop widely grown around Mugher and Habesha cement factories by the farmers leaving in the vicinity. As a result, the exposure of the plant to the cement dust is inevitable as the dust particles are carried by wind over several distances. As it can be seen from Table 4, significantly evaluated mean heavy metal concentrations were obtained in teff samples collected within 1 km distance from Mugher and Habesha cement factories. The obtained concentrations of Fe were significantly higher than other metals with mean value of 1574 and 1327 mg/kg in teff samples collected around Habesha and Mugher cement factory, respectively. Similarly, higher level of other analyzed metals were also detected with their mean concentration values following the decreasing order of Fe > Mn > Zn > Cr > Cu. Ni, Co, Pb, and Cd were not detected in any of the Teff samples analyzed. The metal concentrations of teff samples that are collected around cement factories were quantitatively higher than those from control sites. This could be as a result of large quantity of cement dust release from cement factories.

The mean concentration of heavy metals in teff samples collected from the two control sites were relatively lower than the teff samples collected around cement factories. As it can be shown from the results (Table 4), there is great significant difference between the concentrations of heavy metals in teff samples collected from around cement factory (within 1 km radius) and that of control sites (6-10 km radius) which might indicate serious pollution of the soil and plant by the cement dust emission. Cu, Zn, Mn, Fe, Cr were detected in teff samples collected from both control sites and around cement factories (within 1 km radius), whereas Pb, Cd, Ni and Co were not detected. The obtained concentration of Fe was much higher than the other metals with mean value of 1287 and 1171, respectively for teff sample from control sites of Habesha and Mugher cement factory.

The concentration of copper metal determined in soil samples collected from around cement factories were found to be 333 and 294 mg/kg in soil samples collected within 1 km radius around Mugher and Habesha cement factories, respectively. The corresponding result in the control site of the soil sample was 232 and 234 mg/kg. For the teff sample collected from the same area, the result was 85.6 and 89.4 mg/kg in samples collected close to the cement factories and 53.9 and 70.0 mg/kg in the control teff sample collected from around Mugher and Habesha cement factories. The concentration of Cu in soil samples collected from around and control sites of the cement factories were above FAO/WHO (100 mg/kg) [23]. However, it is below the recommended value of USEPA (4300 mg/kg) [24]. The concentration of Cu in teff collected from around the two cement factories within 1 km radius were above the permissible limit of FAO/WHO, but, in the teff samples collected from the control sites the copper level were below FAO/WHO (73.3 mg/kg). On the other hand, the concentration of Cu in cement dust collected from Mugher and Habesha cement factories were 450 and 472 mg/kg, respectively and this is significantly higher than 100 mg/kg reported by WHO [25].

Table 4. Mean values of heavy metals (mg/kg) in teff samples collected within 1 km radius and control sites (6–10 km) from Mugher and Habesha cement Factories (mean ± SD, n = 3).

Metals	Mugher cement Factory		Habesha cement Factory		WHO/FAO permissible level (mg/kg)
	Within 1 km radius around the factory	Control Teff sample (6-10 km distance)	Within 1 km radius around the factory	Control Teff sample (6-10 km distance)	
Cu	85.6 ± 1.9	53.9 ± 0.7	89.4 ± 0.7	70.0 ± 0.7	73.3
Zn	466 ± 1	98.5 ± 1.6	314 ± 3	85.9 ± 0.1	100
Mn	741 ± 2	453 ± 2	733 ± 2	414 ± 8	500
Cr	342 ± 2	39.8 ± 3.8	297 ± 2	34.7 ± 1.9	50
Fe	1327 ± 5	1171 ± 4	1574 ± 2	1287 ± 2	5000
Ni	ND*	ND*	ND*	ND*	10
Co	ND*	ND*	ND*	ND*	0.01
Pb	ND*	ND*	ND*	ND*	0.3
Cd	ND*	ND*	ND*	ND*	0.1-0.2

Generally, high exposure of copper can lead to the accumulation of excess metal into the body. At high concentration it may became toxic and produce a number of adverse health effects. Exposure to Cu can cause irritation of nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. High uptake if Cu may result in liver and kidney damage and even death [26]. Consequently, the workers and society living around these cement factories may be caused by disease such as sleep disorders, depression and other mental problems and learning disabilities.

The amount of zinc in the analyzed samples were found to be 330 and 194 mg/kg in soil collected from around cement factories, and 171 and 112 mg/kg in the control soils for Mugher and Habesha cement factories, respectively. The subsequent concentration of zinc in teff sample was found to be 466 and 314 mg/kg in teff samples collected within 1 km radius closer to the factories and 98.5 and 85.9 mg/kg in the control samples for the two factories. The concentration of Zn in all soil samples were below the recommended value of USEPA (750 mg/kg) [24]. The mean concentration of Zn in Teff collected from around the cement factories were above the permissible limit of FAO/WHO. However, for teff samples collected from the corresponding control sites the average level of zinc is below FAO/WHO limit (100 mg/kg). On the other hand, the mean concentration of Zn in cement dust was 1103 and 1097 mg/kg, respectively for cement dust from Mugher and Habesha cement factories. These mean values of Zn in the dust samples were above the permissible limit of WHO (300 mg/kg) [25].

In general, the concentration of Zn in all the samples analyzed is within the safe limit of FAO/WHO. But, high concentrations of zinc can cause acute effects such as vomiting and gastrointestinal irritation weakness, anorexia, anemia, diminished growth, loss of hair, lowered food utilization, changes in the levels of liver and serum enzymes, morphological and enzymatic changes in the brain, functional changes in the kidney [27]. Zinc toxicity is more often associated with direct toxicity of elevated concentrations rather than dietary or food chain toxicity [28]. Hence, continuous monitoring of zinc concentration in these samples is very important.

The mean value of manganese in the analyzed samples were found to be 521 and 498 mg/kg in soil samples and 741 and 733 mg/kg in teff samples collected from around Mugher and Habesha cement factories, respectively. The corresponding levels of Mn were 307 and 307 mg/kg in soil samples and 453 and 414 mg/kg in teff samples collected from the control sites. The mean concentration of Mn in teff collected around cement factories were above permissible limit of FAO/WHO while in teff samples collected from the control sites the levels of manganese were below FAO/WHO (500 m/kg).The concentration of Mn determined in the cement dust samples was found to be 3316 and 3419, respectively for dusts obtained from Mugher and Habesha cement factories. The mean level of Mn in the two dust samples was below permissible limit of WHO (5000 mg/kg). Mn concentration in teff samples collected from within 1 km radius is relatively higher than the FAO/WHO limit. Thus, farmers should be advised to avoid cultivating teff and other plants near the vicinity of the factory as prolonged inhalation of high levels of manganese negatively affects the central nervous system, visual reaction time, hand steadiness and eye-hand coordination [29]. In addition, the companies should be informed to reduce the dust release by using appropriate safety measures to protect the safety of the works and the community living around the factories.

The total concentration of chromium level in the analyzed samples were found to be 330 and 450 mg/kg in soil collected around cement factories, and 59.3 and 92.9 mg/kg in control soils; whereas the total level of chromium determined were 342 and 297 mg/kg in teff samples collected around cement factories and 39.8 and 34.7 mg/kg in control teff samples for samples collected from Mugher and Habesha cement factories, respectively. The mean concentration of total chromium in soil and teff collected around cement factories (Table 2 and 3) were above the recommended value, 100 mg/kg by FAO/WHO. On the other hand, the mean concentration of chromium in soil and teff samples collected from the control sites (Table 2 and 3) were below the permissible limit of FAO/WHO (50 mg/kg) for teff.

The mean concentration of chromium in selected cement dust samples was found to be 242 (Mugher) and 404 mg/kg (Habesha). The minimum is detected in Mugher cement dust and still this value is above the permissible limit set by WHO (50 mg/kg). About 75% of chromium in cement dust is obtained from limestone and coal ash [30]. Hence, the workers and communities living around these factories may have the chance to be affected by diseases such as; chronic bronchitis and sinusitis, allergic skin reactions, skin irritation or ulceration and eye irritation and damage. In cement industry the linings for the rotaries contain chromium, which could be liberated by wear and friction [30].

Iron is the most accumulated heavy metals in all the samples investigated in this study. Iron is an essential element for both plant productivity and nutritional quality. It is present in soils in higher concentrations than any other nutrient. The concentration of Fe in the analyzed samples were found to be 5283 and 5392 mg/kg in soil and 1327 and 1574 mg/kg in teff samples collected around Mugher and Habesha cement factories, respectively. The amounts of iron in the corresponding control sites were found to be 3186 and 3843 mg/kg in soil samples, and 1171 and 1287 mg/kg in teff samples (Table 3 and 4), respectively, for samples collected from Mugher and Habesha cement factories. The mean concentration Fe in all analyzed samples were below the permissible limit of FAO/WHO (50 g/kg) for soil and (5 g/kg) for teff. The average concentration of Fe determined in the cement dust in the present study were 33836 and 31846 mg/kg for Mugher and Habesha cement factories, respectively.

The average concentration of nickel determined in the analyzed soil samples was found to be 3719 and 1138 mg/kg around the cement factories, 41.3 and 44.1 mg/kg in the control sites (Table 3), respectively for Mugher and Habesha cement factories. The mean concentration of Ni in soil collected around cement factories were above the permissible limit of FAO/WHO (50 mg/kg). However, the level of Ni in the control sites was below limit of FAO/WHO. Nickel was not detected in any of the Teff samples investigated in this study. The level of Ni detected in the studied cement dust samples ranged between 1727 mg/kg in Mugher and 1524 mg/kg in Habesha cement factory. The value obtained is above the permissible limit (200 mg/kg) set by WHO. Therefore, people who are exposed to these cement dust can be affected by disease like nickel allergy, lung fibrosis, cardiovascular and kidney diseases and cancer of the respiratory tract. The main concern in handling nickel is its ability to produce allergic dermatitis. Ni exposure effects vary from skin irritation to damage to lungs, the nervous system and mucous membranes. It is also a known carcinogen [31].

The mean concentration level of cobalt in the analyzed soil samples were found to be 1439 and 1516 mg/kg in soil samples collected from around Mugher and Habesha cement factories, respectively. The result in the corresponding control sites were determined to be 1177 and 1449 mg/kg in the soil samples (Table 3 and 4). The mean concentration of cobalt in the analyzed soil samples were above permissible limit of FAO/WHO (50 mg/kg). However, the level of cobalt in all the teff samples collected from both Mugher and Habesha cement factory was below the method detection limit. Though cobalt is characterized by significant mobility in plants, but it depends on the species and the various forms of cobalt present, most often in the form of di- and trivalent cations. Usually, its largest amounts accumulate in the roots, smaller amounts in the stems, and the smallest amounts in the leaves. As the present study focuses on the consumed seed part of the teff, the concentration of Co might be very low. Moreover, the application of an alkaline fertilizer to the soil increases the pH and reduces the solubility in the soil and the availability of cobalt and other trace elements for plants [32, 33].

The mean level of cobalt in analyzed cement dust was found to be 2517 and 2492 mg/kg in Mugher and Habesha cement factories, respectively. The obtained concentration of Co in cement dust was above permissible limit reported by WHO (50 mg/kg), but it is below the MDL in both soil and teff samples. Human exposure to Co takes place through air, drinking water and food. Health effects from Co arise due to exposure to radiations from radioactive cobalt isotope which causes sterility, hair loss, vomiting, bleeding, diarrhea and even death when this radiation is used in cancer-patients [34].

The level of cadmium and lead in the present study was below the method detection limit for all the analyzed soil and teff samples. However, significant amount of cadmium (20.4 ± 0.8 and 26.1 ± 0.1 mg/kg) and lead (649 ± 7 and 255 ± 1 mg/kg) were detected in the dust samples collected from both Mugher and Habesha cement factories, respectively.

The concentration of Cd in cement dust was 20.4 (Mugher) and 26.1 mg/kg (Habesha), which is considerably higher than 3 mg/kg reported by WHO. Thus, the workers and society living around these cement factories may be susceptible to diseases such as; high blood pressure, damage the lungs and may cause death. The level of lead detected in the studied cement dust samples were found to be 649 and 255 mg/kg in Mugher and Habesha cement factory respectively, which were also higher than the permissible limit 5 mg/kg reported by WHO. As a result, people who exposed to these cement company may be affected by diseases like headache, fatigue, nausea, abdominal cramps, joint pain, and etc. The minimum was detected in dust from Habesha cement and the maximum was detected in Mugher cement. Lead can be distributed into cement from raw material of cement such as limestone, clay and sand as reported by Cipurkovic and co-workers [30]. Even though the toxic heavy metals lead and cadmium were not detected in teff and soil samples as opposed to high level of these metals in the cement dust samples collected from both factories in the present study, the overall result on the dust clearly shows that serious attention should be given by the factories on ways of monitoring the free release of cement dusts to the local environment concerning the safety of their workers and the local communities living around the factory. As such, great efforts on the part of the occupational and public health should be taken to curb the dangers of these metals.

Comparison of level of heavy metals in the soil and cement dust collected from Mugher Cement factory with Habesha cement factory

Generally, the mean concentration of Zn, Pb, Fe, Ni and Co in cement dust collected from Mugher cement factory is significantly higher than that of cement dust collected from Habesha cement factory. The reverse is true for the mean concentration of Cu, Cd, Mn and Cr in cement dust samples. This might be possibly attributed to the usage of raw materials from different sources or places. The mean concentration of heavy metals such as Cu, Zn, Mn and Ni determined in soil sample collected around Mugher cement factory were higher than that of the soil sample collected from around Habesha cement factory which may be due to high dust discharge from Mugher cement factory to the surrounding environment. Whereas the mean concentration of Cr, Fe and Co determined in soil samples collected around Habesha cement factory were higher than that of soil sample collected from around Mugher cement factory. This is because the soil found around Habesha cement factory is red clay type soil which contain high amount of Fe in nature.

Comparison of levels of heavy metals in cement dust samples with literature

The concentrations of heavy metals in dust samples considered in this study were compared with some literature reports conducted in some other parts of the world. The results reported in the literature (for USA, Nigeria and Iran) and the values obtained in the current study are presented in Table 5. Except for Cr, the levels of other heavy metals Cu, Zn, Cd, Mn, Pb, Fe and Ni in the present study are much higher than the literature reports presented for comparison in Table 5. The level of Cr reported in the present study is less than these literature reports indicated in Table 5 with the exception of the report by Ogunbileje and his co-workers [5] in Nigeria.

Table 5. Comparison of level of heavy metals (mg/kg) in cement dust with literature values.

Metals	Country			
	USA	Nigeria	Iran	Ethiopia
Cu	23.7 ± 7.2	6.92 ± 0.86	NR	472–450
Zn	475 ± 29	422 ± 18	NR	1097–1103
Mn	2526 ± 223	381 ± 23	409–432	3316–3419
Cr	598 ± 65	91.7 ± 19.9	21571–26197	242–404
Fe	23586 ± 1268	17557 ± 1116	NR	31846–33836
Ni	47.5 ± 3.2	17.3 ± 1.0	13.0–15.2	1727–1524
Co	NR	NR	NR	2492–2517
Pb	3.03 ± 0.55	3.86 ± 0.56	51.3–59.3	649–255
Cd	0.05 ± 0.01	0.57 ± 0.04	3.84–6.16	20.4–26.1
Ref.	[5]	[5]	[6]	[This study]

NR: Not reported.

Transfer factor

Table 6. TF of heavy metals analyzed in teff samples from Mugher and Habesha cement factory.

Metals	Mugher cement factory	Habesha cement factory
Cu	0.26	0.30
Zn	1.41	1.62
Mn	1.42	1.47
Cr	1.04	0.66
Fe	0.25	0.29
Ni	ND*	ND*
Co	ND*	ND*
Pb	ND*	ND*
Cd	ND*	ND*

The metal transfer factor (TF) from the soil to the plant is presented in Table 6 for teff plant grown around Mugher and Habesha cement factory. The transfer factors are computed for the metals to quantify the relative differences in the bioavailability of metals to the plant or to identify the efficiency of the plant to accumulate these metals [35]. The result shows that the ratio of metal concentration in the edible parts of the teff plant to the extractable metal in the soil varied among the metals investigated. As shown in Table 6, Zn and Mn have a transfer factor > 1 for teff samples collected from both factories whereas Cr has a metal transfer factor of > 1 at Mugher cement factory. Zn has the highest bioaccumulation factor followed by Mn with TF factor of 1.41 and 1.62 for Zn and 1.42 and 1.47 for Mn in Mugher and Habesha cement factory, respectively. The result also shows significant bioaccumulation of Cr by the teff seeds analyzed. Generally, TF for the detected heavy metals is in the order of Mn > Zn > Cr > Cu > Fe and Zn > Mn > Cr > Cu > Fe for Mugher and Habesha cement Factory, respectively. The result of the TF confirms that the uptake of metals by plants does not necessarily increase linearly with increasing concentrations of the metals in the soil which is in accord with the finding results of Rattan and colleagues [36].

Analysis of variance

The variations in the mean concentration of each metals between the samples were tested using one-way ANOVA in order to determine whether it was just from a random error, the treatment the experimental procedure, or it is from heterogeneity amongst the samples such as difference in the mineral composition of the raw material used for cement production, mineral content and type of the soil, climatic conditions, soil inputs like fertilizers, pesticides or herbicides, or variations in soil parameters such as the pH [37]. The results of one-way ANOVA of the present study indicated that significant differences in the mean values were observed among the sampling sites for the detected heavy metals at 95% confidence levels ($p < 0.05$) for Cu, Zn, Cd, Mn, Pb, Cr, Fe, Ni and Co in cement dust, soil and teff sample collected from Mugher and Habesha cement factories. Hence, it can be concluded that the mean values of all of the metals analyzed in this study were significantly different among and within the sampling sites.

Correlation coefficient analysis

Correlation study is important to see the effect of the concentration of one metal on the concentration level of the other metal [37]. Hence, the Pearson correlation matrices using correlation coefficient (r) for the samples were employed for metals determined in the samples of this research study. Pearson correlation coefficient is a number between -1 and +1 that measure the degree of association between two variables (call them concentration of metal X and Y). A positive value for the correlation implies a positive association (large values of X tend to be associated with large values of Y and small values of X tend to be associated with small values of Y) and vice versa [38]. If a correlation coefficient is > 0.7, there is a very strong positive relation whereas r value of < -1 confirms a strong negative relationship. A correlation coefficient closer to zero shows a weak relationship or no association. Generally, from statistical analysis it can be predicted that a very strong positive correlation value between the mean concentrations implies that there is possibility of these metals have the same or common source. Whereas, a very strong negative correlation implies the source of these metals are independent of each other.

CONCLUSIONS

Consuming the foods contaminated within heavy metals has different determinant effects on human health; therefore, monitoring contamination of heavy metals will allow for avoiding unnecessary exposures. The result of this study has revealed that various concentrations of the heavy metals: Cu, Zn, Cd, Mn, Pb, Cr, Fe, Ni and Co were detected in dust samples collected from Mugher and Habesha cement factories. However, only Cu, Zn, Mn, Cr and Fe were detected in teff seed samples collected from the same sampling sites. The trace toxic heavy metals Cd and Pb were not detected in any of the soil and teff samples. Ni and Co were also below the method detection limit in any of the teff samples analyzed. The concentration of some of the analyzed heavy metals in soil and teff samples collected from Mugher cement factory were slightly higher than that of the same samples collected from Habesha cement factory. The levels of heavy metals determined in the control sites are lower than samples collected closer to the cement factories. The result shows significant contamination by cement dust from the cement factories on the nearby environment. The concentration of the detected heavy metals in soil and teff samples collected from both factories were above the permissible limit of WHO except for Fe, which is below the recommend limit set by FAO/WHO. Thus, the factories should apply the use of modern plants that have the closed pits and back filter motions which absorb and recycle the dust to reduce the dust disposal to the environment. Moreover, the implementation of waste management policies must be enforced by the stakeholders to keep the safety of the workers and the communities leaving around the factories from hazardous cement dust. The study also appears to indicate the need for further investigation of the toxicity of heavy metals in cement dust on human health, particularly these working in cement factories and the community living in the vicinity of the factory.

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