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Spectrophotometric Determination of Heavy Metals Levels in Ethiopian Cement and Soils Around the Cement Factories

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Abstract
The current boom in construction sector of the country has aroused scientific concern about the safety of construction workers who regularly work with cement. The aim of this study was to determine the levels of selected heavy metals (Cr, Pb, Cd, Cu and Ni) in branded cement samples (Mugher, Dangote, Capital, and Derba) and soils around the Mugher cement factory. The level of the selected heavy metals in cement and soil samples were analyzed by Flame Atomic Absorption Spectroscopy. The detected range of metal concentrations (mg/kg dry mass) in different cement sample were Cu (0.131 ± 0.021-0.302 ± 0.004), Cd (0.02 ± 0.008-0.023 ± 0.008), Pb (0.187 ± 0.042- 0.353 ± 0.016), Cr (0.185 ± 0.017 - 0.765 ± 0.017), Ni (0.233 ± 0.002 - 0.906 ± 0.290) in ppm. Among the tested heavy metals Ni was found in highest concentration and it was in Capital cement sample. The heavy metal levels in the studied samples not comply with international standards. The detected range of the heavy metals in soil samples collected at different distances from the target cement factory were Cr (7.317 ± 0.501 - 25.558 ± 0.055), Cu (1.269 ± 0.003 - 45.317 ± 0.014), Pb (0.45 ± 0.0433 - 9.867 ± 0.011), Cd (0.492 ± 0.076 to 2.442 ± 0.063), Ni (13.383 ± 0.638 - 49.958 ± 0.0205) in subsoil and that of layer soil sample were Cr (1.292 ± 0.052 to 24.141 ± 0.476), Pb (0.058 ± 0.039 - 6.942 ± 0.284), Cu (0.537 ± 0.003 - 32.725 ± 0.083), Cd (0.108 ± 0.072 to 0.883 ± 0.014), Ni (11.183 ± 0.341-49.517 ± 0.892) in mg/kg. The measured physicochemical parameters in soil sample ranged pH (7.393 ± 0.061 - 8.483 ± 0.014), Electrical Conductivity (0.613 ± 0.005 - 2.918 ± 0.072) mS /cm. The level of heavy metals in soil samples was found to increases as sampling distance from the factory decreases. This study indicates that all of the metals are concentrated on the surface soil, and decreased in the lower part of the soil, this due to reflect heavy metal's mobility and physical properties of soil and its alkaline pH values.
Keyword: Cement, FAAS, Heavy metals, physicochemical parameters

Introduction

Production of cement starts with the extraction of the raw materials and their subsequent pre-crushing in the quarry located in the vicinity of cement works. With the ratio of raw materials being specified exactly, a mixture is produced, if necessary, by adding correction materials, such as sand, iron ore and clay. Apart from natural raw materials, waste materials containing lime, aluminates, silicate, and iron are used as raw materials substitute. This mixture of raw materials is milled to raw meal and, at the same time, dried with the residual heat of the kiln of gases[1, 2].

Cement dust spreads along large areas through wind rain etc. and are accumulated in soils, plants and animals and can affect human health badly[3, 4]. Heavy metals are known to pose serious health problems to humans, affect plant growth and general damage to ecosystem. Heavy metals are among the most relevant substances emitted during the process of cement manufacture [5-7]. Among the metals especially known to have toxic effect in environmental studies are arsenic, cadmium, lead, mercury and thallium, aluminum, beryllium, chromium, copper, manganese, nickel and zinc, among others, have been identified in the emission from cement plants[8].

As a general this research is proposed to determine content of selected heavy metals in Ehiopian cement factory of Derba, capital, Mugher and Dangote that possessed through their raw material, during processing and to access whether waste material emitted from Mugher cement industry can pollute the soil around the industry, using Spectrophotometric method. And deal uses and health effects of these metals.

Transfer of trace elements into cement and concrete, the primary raw materials represent the most important, but not only major input path for all trace elements. Also secondary input materials contribute to the trace element content of cement. Their share, however, differs from trace element to trace element. Based on the distribution pattern of the trace element input for the different classes of input materials into Portland cement, four categories can be distinguished[9].

2. Materials and Methods

2.1 Study area

Different cement samples were bought namely; Derba, mugger, Dangote, randomly from different super market of Hawassa town. Additionally, soil samples were collected from around Mugher Cement Factory; it is state owned cement producing industry in Ethiopia. Its geographic location is (9°40'60")N latitude, (37°58'60")E longitude at an altitude/elevation of 2496m above sea level, 90 kilo meter away west of the capital city, Addis Ababa. The factory has an average daily production capacity of five thousand tone of clinker with three production lines

2.2. Sampling

2.2.1. Sampling and Sample Pre-treatment of cements

Three of each cement samples namely Derba, Mugher, Dangote and capital were bought; randomly from three different store of Hawassa town and 1g of each sample were taken in clean plastic bag as soon as cement bag is opened to avoid surface contamination and keep for further analysis.

2.2.2. Sampling and sample pre-treatment of soil samples

Soil samples were collected in polythene bags using auger (or stainless steel spatula) from cultivated soils around the Mugher Cement Factory near Addis Ababa. Samples were taken randomly round the factory starting from the fence and proceeding away from the factory at 500 m by 100 m intervals in every direction (East, West, North, and South) of the reference point until 2.5 km radius is covered round the factory. Soils from depths of 0-15 cm and 15-30 cm were taken at each sampling point. A total of 40 soil samples Mugher cement factory area were brought to the laboratory for analysis. Stones and foreign objects were removed by hand. Soil samples were air dried before being crushed in a ceramic mortar and sieved in a 2 mm screen sieve.The major sampling points which are indicated in Figure 1. This sample point may help to evaluate the effect of factory effluent for the soil quality.

2.3. Sample Preparation for Physico-chemical analysis

2.3.1. Analysis of pH and Conductivity

The pH of the sample was measured with a portable pH meter (Model HI9024, HANNA Instrument) calibrated with pH 4.0, 7.0 and 10.01 standard buffer solutions. Conductivity was analyzed using portable digital conductivity meter (model 4200, Jenway, England instrument). It has been calibrated with0.001 M KCl standard conductivity buffer solution to give a value of 14.7 µS/m at 25 ºC.

2.4. Instrument and Apparatus

In this research work; electro thermal heating mantle (BI Barnestead). G. A refrigerator (Hitachi, Japan). All the cement and soil samples were weighed on a digital analytical balance (ADAM, Model AFP-110L, England) with 120 g loading capacity and ± 0.0001 precision. Flame atomic absorption spectroscopy (Buck Scientific, Model 210VGP AAS, USA). Drying oven (Digit heat, J. P. Selecta, Spain) Measuring cylinders (Duran, Germany), pipettes and micro pipettes (Pyrex, USA), were used.

2.5. Chemicals and reagents

Reagents that were used in the analysis were all analytical grade. (69-72 %) HNO_3 (Spectrosol, BDH, England), 37% HCl and 70% $HClO_4$ (Aldrich, A.C.S. Reagent Germany) were used for digestion of Cement and Soil samples. The standard solutions of metals Cr, Cu, Ni, Cd and Pb (Buck Scientific Puro-Graphic^{tm} calibration standards, USA) were used.

2.6. Sample digestion

2.6.1. Digestion of cement sample

The optimized digestion procedure for cement samples was used. 1 g of well homogenized cement samples were accurately weighed on an analytical balance. For the digestion purpose each samples in quartet of dried powdered Ethiopia cement samples (Derba, Mugher, Dangote and capital) were weighed on a digital analytical balance and directly transferred in to 250 ml round bottom flask followed by the addition of HNO_3 (10 mL), $HClO_4$ (1 mL) and H_2SO_4 (2 ml) for each sample. Then the mixture was stirred using glass rod stirrer carefully until the solid materials dissolved. The mixture was swirled and refluxed with optimized digestion conditions. The mixture cooled and filtered with a whatman filter paper (110 mm), then diluted into 25 ml volumetric flask to the mark.

2.6.2. Digestion of soil sample

The optimized digestion procedure for soil samples was used. Soil samples were mixed thoroughly to achieve homogeneity and sieved (< 2 mm). 1 g (dry weight) was weighed by using digital balance and transferred to 250 ml refluxing flask. 6 mL of NHO_3, 2 ml of $HClO_4$ and 2 ml HCl was added to the sample and refluxed for optimized condition then allowed to cool. The digest were filtered through a Whatman filter paper (110 mm) and the filtrate were collected in 25 mL volumetric flask and made up to the mark with de ionized water.

2.6.3. Digestion of Blank Samples

Digestion of blank solution was also performed in parallel with the root samples keeping all digestion parameters the same. For the analysis of the root samples ten reagent blank samples were prepared for each. All the digested blank samples were stored in refrigerator until analysis. The solutions of the digested blank samples were used to determine the concentration of each element by FAAS.

2.7. Instrument Operating Conditions and Calibration

In this study a total of five metals for each root sample were analyzed using FAAS with external calibration curve after the parameters such as burner and lamp alignment, slit width and wavelength adjustment were optimized for maximum signal intensity of the instrument (Table1). For each metal, the respective hollow cathode lamp was inserted in to the atomic absorption spectrophotometer, and the solution was successively aspirated into the flame. Three replicate determinations were carried out for each sample.

Calibration curves were prepared to determine the concentration of metals in soil and cement sample solutions. The correlation coefficients of the calibration curve for the entire metals were greater than or equal to 0.999 which assured the linearity of instrumental response for individual analytes.

2.8. Method Detection Limit (MDL)

Method detection limit is the minimum concentration of analyte that can be identified, measured and reported with 99 % confidence that the analyte concentration is greater than zero [10]. Ten blank samples were digested and analyzed for cement and soil samples. Then the standard deviation of the ten blank samples (S_B) was calculated for each metal. Finally, the detection limits were obtained by three times of the standard deviation of the reagent blank ($3S_B$). As shown in Table 2.

2.9. Recovery analysis

For spiking of cement samples, 0.1 mg/L of Pb and Cr were spiked at once in to round bottom flask that containing 1 gram of cement sample. 0.1 mg/L of Ni, Cu, and Cd were spiked at once in another round bottom flask containing the same amount of cement sample. The spiked samples were digested in the same manner and with the same reagents as described above for cement samples.

For spiking of soil samples, 0.1 mg/L of Cr, and Pb were spiked at once in to 250 ml refluxing flask that containing 1 gram soil sample. 0.1 mg/L of Cd, Cu and Ni were spiked at once in other round bottom flask containing same amount of soil sample and were digested in the same manner and same reagents as described above for soil samples. Each recovery test for cement, and soil samples were performed in triplicates. Each sample was determined for their respective spiked metals by FAAS.

2.10. Determination of the pH and EC.

10 gm of air dried grind was weighed into 100 mL beaker. And 25 mL of de ionized water was added to the beaker, then after stirring by a magnetic stirrer for 30 minutes the sample was allowed to equilibrate by standing for 1 hr. The pH of the suspension sample was measured with a portable pH meter (Model HI9024, HANNA Instrument) calibrated with pH 4.0, 7.0 and 10.01 standard buffer solutions.

10 gm of dried sample was transferred in to 100 ml beaker containing 50 ml of deionised water, then after stirring by a magnetic stirrer for 30 minutes the sample was allowed to equilibrate by standing for 1 hr. Conductivity were analyzed using portable digital conductivity meter (model 4200, Jenway, England instrument). This instrument was also used to cross check the temperature of the water sample, it has been calibrated with 0.001 M KCl standard conductivity buffer solution to give a value of 14.7 µS/m at 25 ºC.

2.11. Data analysis

As the study is aimed at assessing the degree of contamination of cement and soil samples using heavy metals analysis, data obtained were analyzed by a computer program to analyze tabulated data using Microsoft Excel 2007 and origin 8 Software. Analysis of variance commonly abbreviated as ANOVA. One-way ANOVA (alpha = 0.05) was used to assess the significance difference between the sample sites. t- test was used to check whether there was a significant difference or not between the impacted soil sample and reference sample.

3. Results and Discussion

3.1. Physicochemical Characterization

Physicochemical characterization of the soil has always been used to define quality of soil and often with biological processes influence soil fertility in a variety of ways, each of which can have an ameliorating effect on the main soil-based constraints to productivity. The pH value is measured for all samples and ranging in narrow interval (6.383 to 8.483), indicating that the soils are originally acidic except for the activities of cement which suggests neutral to sub-alkaline conditions for the top soil samples, which is consistent with similar work done at some Cement industry sites in[11]. The maximum and the minimum value are recorded for the samples taken at a distance of 100 m and 500 m, respectively. For layer soil samples the value ranges from 5.83 - 8.377 and also showing maximum and minimum value at similar distance with top soil samples, these values were obtained in eastern direction. Usually pH influences the CEC of soil composition, which in turn affects the heavy metal mobility and distribution in the soil samples. The moderately acidic soil tends to have an increased micronutrient solubility and mobility as well as increased heavy metal concentration in the soil[12].

The EC value of top soil samples is higher than the layer soil sample. It is found in the range of (0.613 - 0.892) mS/cm. The highest value was recorded at 300m in east direction and the lowest value was recorded at 500m in southern direction from the factory. For the layer soil sample the values of EC ranged between (4.10 - 0.801) ms/cm. The maximum and the minimum value of EC are found in the same distance and direction as top soil samples.

High EC value is due to concentration of salt in the soil. Industrial saline wastes and irrigation are the main human activities that add salts to the soil[13]. There are no irrigation activities around study area other than gardening. Higher values of EC have to be related the dust emission from cement factory.

On the other hand, as indicated by (Table 3) the pH of selected Ethiopian cement samples are ranged between 12.48 ± 0.07 and 12.543 ± 0.031. The value of pH obtained for all the studied cement samples were similar. However the maximum value was recorded for Dangote cement and the minimum value was recorded Capital cement. Since the cement are very alkaline they can easily cause severe skin burns if not promptly washed off with water and also dry cement powder in contact with mucous membranes can cause severe eye or respiratory irritation. Therefore cement users need also to wear appropriate gloves and protective clothing.

3.2. Determination of Heavy metals in Cement Samples

Heavy metals are very toxic substance to humans and environment when they exceed their permissible limit. According to preveviously done research [14, 15] cement is manufactured from raw material consists of heavy metals, in Ethiopia most people exposed to cement during production of cement and construction work is proceeded, without taking necessary care for heavy metal present in cement and dust form of cement released from cement factory. For this reason, in this study to give awareness to people, determination of level of selected heavy metals (Cr, Pb, Cu, Cd and Ni) in selected Ethiopian cement sample is important.

Chromium (Cr)

About 75%input of Cr is from limestone and ash [14]. The mean concentration of Cr in selected cement samples was found in the range of (0.185 ± 0.017 - 0.765 ± 0.017 ppm).The minimum is detected in Mugher cement and the maximum is detected in Derba. This value is above permissible limit set by WHO (0.05 ppm). Therefore the users of this cement and the workers of Derba cement factory may have the chance to be affected by disease discussed in literature review section such as; chronic bronchitis and sinusitis, allergic skin reactions, skin irritation or ulceration and eye irritation and damage. Cement samples are significantly different in sampling sits (at 0.05 levels). In cement industry the linings for the rotaries contain chromium, which could be liberated by wear and friction [16].

Lead (Pb)

The level of Pb detected in the studied cement samples ranged between 0.187 ± 0.042 and 0.353 ± 0.016 ppm which is higher than the permissible limit 0.005ppm reported by WHO. As a result, people who use and exposed to this cement may be caused by disease like headache, fatigue, nausea, abdominal cramps, joint pain, and etc. The minimum was detected in Dangote cement and the maximum was detected in Derba cement. Cement samples are significantly different in sampling sites (at 0.05 levels). Pb can be distributed into cement from raw material of cement such as limestone, clay stone, marl lime, sand and trass as reported by [14].

Copper (Cu)

The concentration of Cu in soil ranged from 0.131 ± 0.021to 0.302±0.004 mg/kg and this is significantly higher than 0.01ppm reported by WHO. The minimum was detected in Dangote cement and the maximum was detected in Derba cement. Consequently the users of the cement may be caused by disease such as sleep disorders, depression and other mental problems and learning disabilities, Cement samples are significantly differ in sampling sits (at 0.05 levels).

Cadmium (Cd)

The concentration of Cd in cement ranged from 0.02 ± 0.008to 0.023 ± 0.008 mg/kg, which is significantly higher than 0.003 reported by WHO. Thus, the users and the workers of this cement in construction sectors and that cement factory can be caused by disease such as; high blood pressures, damage the lungs and may cause death. The minimum was detected in Capital cement and the maximum was detected in Mugher cement. There are no significantly different in sampling sits (at 0.05 levels)

Nickel (Ni)

The level of Ni detected in the studied cement samples ranged between 0.233 ± 0.002 ppm and 0.906 ± 0.290 ppm. The minimum was detected in Derba cement and the maximum was detected in Capital cement. The value obtained is above the permissible limit (0.02ppm) set by WHO. So people who exposed to this cement can be affected by disease like nickel allergy, lung fibrosis, cardiovascular and kidney diseases and cancer of the respiratory tract. Cement samples are significantly different in sampling sites (at 0.05 levels). Heavy metal contents of selected cement factory in order of decreasing order; Derba> Capital >Mugher> Dangote except for Ni .Cement samples are significantly differ in sampling sits (at 0.05 levels),

3.3. Determination of Heavy metals in soil Samples

In Ethiopia there are about 15 cement factories are present now days, Cement factory through the release of air pollutants such as heavy metals (HM), generated in the process of crushing limestone, bagging, and transportation of cement are carried by wind and deposited on soil, plants and water bodies [17]. Globally, the problem of environmental pollution due to heavy metals has begun to cause concern in most cities since this may lead to geo accumulation, bioaccumulation and biomagnifications in ecosystem[18]. Some researchers investigated the impact of cement dust on soil properties and plant growth [18-20]. The study, therefore, is aimed at determination of heavy metal levels in soil around Mugher cement factory since it is the largest Ethiopian cement factory which has the capacity of producing large amount of cement 2,140,000(ton/yr) next to Derba. Unlike Derba, there is no mining area around Mugher cement factory. Calibration curves for each heavy metal were set to ensure the accuracy of the Atomic Absorption Spectrophotometer (AAS) as set for cement sample.

The comparisons of metal concentrations in upper soil sample of Mugher cement factory with reference soil were listed in Table 5. The recorded value of Cu (1.181 ± 0.0059), Cr(0.0912 ± 0.0046), Pb(0.0548 ± 0.0081), Cd(0.021 ± 0.00239) and Ni (0.179 ± 0.0018) (Table 5) lower than upper soil sample of Mugher cement factory. All samples in four direction (WTS, NTS, STS and ETS) are significantly higher (at 0.05 levels). whereas, the concentrations of Cu in ETS, Pb in WTS and Cd in STS sample of Mugher cement factory there is no significant differ with reference soil samples (at 0.05 levels),

3.4 Results of upper soil samples collected from the area of Mugher cement factory

All the five elements display their presence in all the soil and cement samples used for the study.

Chromium (Cr)

The concentration of Cr in top soil ranged from 4.083 ± 0.210 to 25.558 ± 0.055 mg/kg and this is significantly lower than 100 mg/kg reported by EU (2006) and FAO/WHO. The minimum was detected at 500 m from the factory in Western direction .The maximum was detected at 100m from the factory in Northern direction. The range of Cr in this study reflected a significant pollution impact compared to 0.38 ± 0.04mg/kg observed in Lithuania [21]. The value obtained in this study was almost similar in some values with result reported by [22, 23]. Soil samples are significantly differing in sampling sites (at 0.05 levels).

Lead (Pb)

The concentration of Pb in the upper part of soil varies from 0.45 ± 0.0433-9.867±0.011 mg/kg which is lower than 100 mg/kg reported by EU (2006) and FAO/WHO. The minimum value was recorded at 500 m from the factory in Eastern direction. The maximum was recorded at 100 m from the factory in southern direction. The mean values of lead in the analyzed soils are much lower than those reported for the ones from different land use areas in the world (i.e. London, Aberdeen, urban playground in Hong Kong, Hong Kong and central Jordan). In this study, it has been noted that the concentrations of metals are highest around the cement factory [22, 23].

Copper (Cu)

The level of Cu detected in the studied soil samples ranged between 1.269 ± 0.003 mg/kg and 45.317 ± 0.014 mg/kg which is below permissible limit 100mg/kg set by ME and FAO/WHO. The minimum was detected at 500m from the factory in southern direction. The maximum was detected at 100m from the factory in southern direction.

Cadmium (Cd)

The mean levels Cadmium of ranged from 0.492 ± 0.076 to 2.442 ± 0.063 mg/kg in the soil samples from the Mugher. These values are lower than the natural limits of 1 and 3 mg/kg in soil as given by EU (2006) FAO/WHO Guidelines, respectively.

Nickel (Ni)

The critical level for Ni in soil have been investigated by many researchers [24] and estimated to be in the range of 2-50 µg/g. The mean concentrations of Ni in the Mugher soil varied between 13.383 ± 0.638 mg/kg and 49.958 ± 0.0205mg/kg, which was consistent with critical permissible level which is 50 mg/kg for soil recommended by EU (2006) and FAO/WHO. The highest mean concentration was detected at 100 m from the factory in Northern direction. The lowest mean concentration was detected at 500 m from the factory in southern direction. Based on the results presented, the overall degree of contamination by the five metals in distance terms is of the order 100 m>200 m>300 m>400 m>500 m. And also this table provides information which indicated that the order of contamination is E>N>W>S in terms of directions from the cement facility.

3.5. Results of layer soil samples collected from the area of Mugher cement factory

The mean concentration of metals in both soil depths (top and layer) are found to be higher than their

corresponding mean values in the reference area.
Chromium (Cr)
The mean concentration of Cr in layer soil ranged from1.292 ± 0.052to 24.141675 ± 0.476 mg/kg and this is significantly lower than 100 mg/kg reported by EU (2006) and FAO/WHO. The minimum was detected at 500 m from the factory in Southern direction .The maximum was detected at 100m from the factory in Northern direction.
Lead (Pb)
The concentration of Pb in the upper part of soil varies from 0.058 ± 0.039- 6.942 ± 0.284 mg/kg which is lower than 100 mg/kg reported by EU (2006) and FAO/WHO. The minimum value was recorded at 500m from the factory in Eastern direction. The maximum was recorded at 100m from the factory in southern direction.
Copper (Cu)
The level of Cu detected in the studied cement samples ranged between 0.537 ± 0.003mg/kg and32.725 ± 0.083 mg/kg. The minimum was detected at 500m from the factory in southern direction. The maximum was detected at 100m from the factory in Northern direction.
Cadmium (Cd)
The mean levels of ranged from 0.108 ± 0.072 to 0.883 ± 0.014 mg/kg in the soil samples from the Mugher. These values are lower than the natural limits of 1-3 mg/kg in soil as given by EU (2006) FAO/WHO Guidelines. The minimum was detected at 100 m away from factory in northern direction and the maximum concentration was found at 400 m from factory in western direction.
Nickel (Ni)
The mean concentrations of Ni in the Mugher soil varied between 11.183 ± 0.341 mg/kg and 49.517 ± 0.892 mg/kg, which was lower than the critical permissible level which is 50 mg/kg for soil recommended by EU (2006) and FAO/WHO. The highest mean concentration was detected at 100 m from the factory in Northern direction. The lowest mean concentration was detected at 500 m from the factory in southern direction.

4. Conclusions

The data obtained in this study demonstrate that the metals concentrations of soil around the Mugher cement factory were below the toxicity limit set by WHO, FAO and EPA. Only for nickel metal, the value obtained at 100m in Northern direction was nearly equal to the permissible limit. However highest value of both physicochemical parameters and heavy metal concentration were found for the top and layer soil in the area close to the cement factory. Long term exposure and deposition of this metal can cause an effect on both living things and soil properties. For the cement samples based on results of the study the concentration of all studied heavy metals were above the permissible limit. From the studied cement samples Dangote cement is better in its heavy metal content. There was significant variation between each concentration value of cement samples and soil sampled in all direction. The level of metals concentration in cement samples of Mugher, Dangote, capital, and Derba are Ni > Pb > Cr > Cu > Cd, Ni > Cr > Pb > Cu > Cd, Ni > Cr > Cu > Pb > Cd, Cr > Pb > Cu > Ni > Cd respectively, while level the soil sample metals concentration are Ni > Cu > Cr > Pb > Cd in four side. Secondary input materials contribute to the total trace element concentration of cement. Although primary raw materials (Limestone, marl lime, clay stone, sand and trass) represent the most important input pathway, they cannot be considered the only relevant source of trace element concentration in cement. An increase of the trace element concentration of cement due to the use of waste as input material [25].

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***Conflict of Interest*:** The authors declare that they have no conflict of interest.

Reference

1. Brandt A. M, *Cement-Based Composites Materials. Mechanical and Performance*. 1st ed. 1995, London: E& FN Spon.
2. Barnes P, *Structure and Performance of Cements*. 1983, London and New York: Applied Science Publishers.
3. Bayhan, Y.k. and O.I. Özbay, *Cadmium exposure from the cement dust emissions.a field study in a rural residence.* Chemosphere, 2006. **63**: p. 1546-1552.
4. Demir, T.A., Isikli, B., , S.M. Urer, Berber, A., Akar,T, and M. Canbek, Kalyoncu, C., *Nickel exposure and its effects.* Biometal, 2005. **18**: p. 7-13.
5. Schuhmacher, M., Bocio, A., Agramunt, M. C., Domingo, J. L. and de Kok, H. A. M., *PDCC/F and metal concentration in soil and herbage samples collected in the vicinity of a cement plant.*

Chemosphere, 2002. **48**: p. 209-217.
6. Al-Khashman, O.A.a.S., R. A. , *Metal distribution in soils around the cement factory in Southern Jordan.* Environmental Pollution, 2006. **140**: p. 387-394.
7. Domingo, J.L., *Metal-induced developmental toxicity in mammals: A review.* Journal of Toxicology and Environmental Health, 1994. **42**: p. 123-141.
8. Chang, L.W., *Toxicology of metals*. 1996, Boca Raton, FL, USA: CRC Lewis Publishers.
9. Carter, M.R., *Soil Sampling and Methods of Analysis.* . 1993, Lewis, Boca Raton: Canadian Society of Soil Science.
10. Miller, J.N., & Miller, J. C., *Statistics and Chemometrics for Analytical Chemistry*. 5th ed. 2005, England: Pearson Education Limited.
11. Abatyough T. Michael, U.D.D., Uttu Jibrin, Abatyough Benard B., *Distribution and Variation of Heavy Metals and Soil Properties around a Mega Cement Factory in Gboko, Benue State,.* Nigeria International Journal of Science and Technology, 2015. **4**: p. 4.
12. Odu CTI, E.O., Nwaboshi IC, Ogunwale JA, *Environmental study (Soil and Vegetation) of NigeriaAgip Oil Company Operation Area* A report submitted to Nigeria Agip Oil Company Limited, Lagos, Nigeria, 1985: p. 102-107.
13. Hrinch, L.B., Brian, L.M. and George, A.O.canner, *"Soil chemistry" John wiley and sons. Inc. USA third edition.* 2001.
14. Cipurkovic., A., I. Trumic., Z. Hodžic., V. Selimbašic., and A. Djozic., *Distribution of heavy metals in Portland cement production process.* Advances in Applied Science Research, 2014. **5**: p. 252-259.
15. Ibrahim H.H., B.-Y.U.A., Muhammad C. and Umar A., *Assessment of Pollution Potentialities of some Portland Cement.* Nigerian Journal of Basic and Applied Science, 2012. **20**: p. 182-184.
16. Banat K.M., Howari F.M., and Al-Hamad A.A., *Heavy metals in urban soils of central Jordan: Should we Worry about their environment risks.* Environmental Research **97**: p. 258-273.
17. Will., P., Ogbonna C., and A.N. Nwosu., *Metal concentration in soil and plants in abandoned cement factory.* International Conference on Biotechnology and Environment Management 2011. **18**: p. 1-3.
18. Kabir, G. and A.I. Madugu, *Assesment of environmental impact on air quality by cement industry and Mitigating measures.* Acase study environment Monit Assess, 2010. **160**: p. 91-99.
19. Muhammad. I. and S. Muhammad, *periodical effect of cement dust pollution on the growth of some plant species.* Turkish Journal of Botany, 2001. **25**: p. 19-24.
20. Olubunm, E. and E. Olarunsolaola., *Evaluation of the status of heavy metal pollution of soil and plant (chromolaenaodorat) of Agababu Bilumen deposit area, Nigeria.* American- Eurasian Journal of scientific Research, 2010. **5**: p. 241-248.
21. Sakalauskaite, J., Kupčinskiene, E., Kviklys, D., Duchovskiene, L., Zinkute, R., Sakalauskiene, S., and P. Duchosvskis, *Nutritional diagnosis of apple-tree growing in the cement factory region.* Sodininkyste IR Daržininkyste, 2009. **28**: p. 29-37.
22. Omar A. Al-Khashman. and R.A. Shawabkeh, *Metals distribution in soils around the cement factory in southern Jordan.* Environmental Pollution, 2006. **140**: p. 387-394.
23. Estifanos, S. and A. Degefa, *Assessing the effect of cement emission on the physicochemical Nature of soil around Messebo area, Tigray, North Ethiopia.* International Journal of economy Environmental Geology, 2012. **3**: p. 12-20.
24. Shallari, S., C. Schwartz, A. Hasko, and J.L. Morel, *Heavy metals in soils and plants of serpentine and industrial sites of Albania.* science of Total Environment, 1998. **209**: p. 133-142.
25. Achternbosch, M., Bräutigam, K.-R., Hartlieb, N., Kupsch, C., Richers, U., and P. Stemmer mann, *Heavy Metals in Cement and Concrete Resulting from the Co-incineration of Wastes in Cement Kilns with Regard to the Legitimacy of Waste Utilisation* 2003.

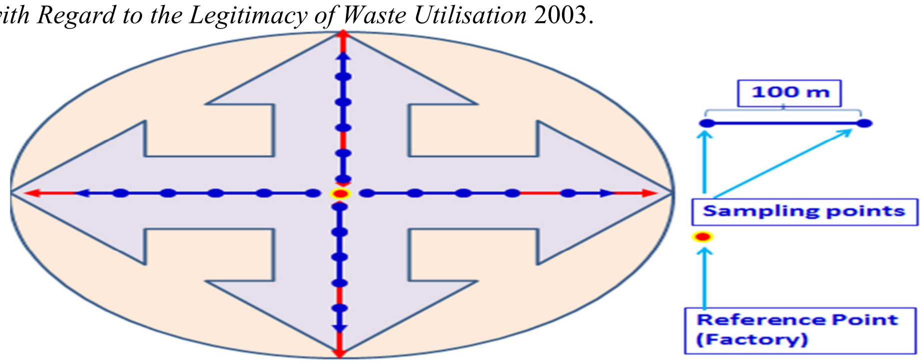

Figure 1: Schematic representation of soil sampling

Table 1: Instrumental operating conditions for determination of selected metals in cement and soil sample using FAAS

Elements	**Parameters**				
	Wave length (nm)	**Slit width (nm)**	**Lamp current (mA)**	**Energy (eV)**	**Flame, Oxidant and Fuel Type**
Cr	357.9	0.7	2.0	3.271	A-A, rich yellow
Ni	232	0.2	7.0	3.162	A-A, lean blue
Cu	324.7	0.7	1.5	3.938	A-A, lean blue
Pb	283.2	0.7	2.0	2.874	A-A, lean blue
Cd	229	0.7	2.0	3.214	A-A, lean blue

Note: A-A = Air and Acetylene

Table 2: Method detection limit for metals of interest determined in soil and cement sample.

Metals	**MDL for Soil (mg/L)**	**MDL for cement (mg/L)**	**IDL for selected metals (mg/L)**
Cr	0.06461	0.08617	0.040
Pb	0.0511	0.04873	0.040
Cd	0.01275	0.01400	0.010
Cu	0.03637	0.01301	0.005
Ni	0.04237	0.03590	0.020

Note: MDL = Method Detection Limit, IDL = Instrument Detection Limit

Table 3: Result of pH cement samples

No	Cement samples	pH
1	Mugher	12.523 ± 0.021
2	Capital	12.48 ± 0.07
3	Dangote	12.54 3 ± 0.031
4	Derba	12.523 ± 0.168

Table 4 : Heavy metal concentration in cement samples with their permissible limit in ppm

Sites	Cr(0.05)	Pb(0.005)	Cu (0.01)	Cd(0.003)	Ni(0.02)
Mugher	0.185 ± 0.017	0.214 ± 0.025	0.132 ± 0.0196	0.023 ± 0.008	0.323 ± 0.079
Dangote	0.194 ± 0.002	0.187 ± 0.042	0.131 ± 0.021	0.020 ± 0.006	0.359 ± 0.034
Capital	0.247 ± 0.077	0.218 ± 0.075	0.230 ± 0.079	0.02 ± 0.008	0.906 ± 0.290
Derba	0.765 ± 0.017	0.353 ± 0.016	0.302 ± 0.004	0.022 ± 0.007	0.233 ± 0.002

Table 5: Heavy metal concentration(mg/L) of reference soil

Metals	Maximum Concentration	Minimum	Mean
Chromium (Cr)	0.103±0.0021	0.085±0.001	0.0912 ±0.0046
Lead (Pb)	0.0591±0.0034	0.0513±0.0037	0.0548±0.0081
Copper (Cu)	1.187±0.0091	1.179±0.0077	1.181±0.0059
Cadmium (Cd)	0.021±0.0057	0.018±0.0029	0.021±0.00239
Nickel (Ni)	0.181±0.0079	0.177±0.0084	0.179±0.0018