Evaluation of accumulated heavy metals in the area surrounding suk AL-Khamees cement Factory (case study)

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ABSTRACT

In recent years, there has been emphasis on environment pollution problems such as water, air and solid pollutions resulted from waste and heavy metals disposal in cement industry where, the dust emitted from cement factories is estimated to be about millions of tons and is accumulating annually at domestic cement plants. However, Heavy metals are considered extremely pernicious because they are toxic, none degradable and environmentally persistent and can be readily absorbed by agriculture and directly enter the human food chain, thus presenting a high health risk to consumers.

In this paper, an evaluation of accumulated selected heavy metals in the soil caused by Cement Kiln Dust (CKD) emitted in the area surrounding Suk Al – Khamees -Emsehel Cement Factory was conducted. Samples were collected from soils sites at four directions around the factory from top soils (0-10 cm) and deep soils (30 cm and 60 cm) at distances 250 m, 1000 m and 3000 m then analyzed for Fe, Zn and Pb using Atomic absorption spectrophotometer as major pollutants, together with control sample.

The results showed that, top surface soil iron (Fe) concentrations ranged between 920 - 1170 ppm at all direction where, the background concentration (control sample) of Fe at 25km ranged between 1003 -1202 ppm which is within the values of the background concentration.

Soil lead (Pb) levels in test and control sites were 890±43 ppm and 105.75±3.76ppm respectively and it was found that lead concentrations on top soils were elevated by six folds than background concentrations. Zink (Zn) concentration in soils was 28.75±6.57 ppm;these figures for Zn showed little analytical significance and are below the toxic limit. Zinc (Zn) levels are also within the excepted normal values except in the North side of the Factory.The average range of Enrichment factor for Fe, Zn and Pb were 0.91-0.97, 0.8-1.20 and 8.3-8.5 respectively.

These results concluded that, the concentration of iron and zinc within the range but lead is high compared with European Union standard which is a wild life destroyed and has reverse effects on environmental & human health.

Keywords: environment pollution, Heavy metals, Cement Kiln Dust

1. Introduction

Cement industry is one of the sources of environmental pollution. Cement dust contains heavy metals (HMs) pollutants which are hazardous to the biotic environment with adverse impactsonvegetation, human health, animal health, and ecosystems[1-2].

There are 35 metals that are of concern because of occupational or residential exposure; 23 of these are the heavy elements or "heavy metals": antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc [3]. Interestingly, small amounts of these elements are common in our environment and diet and are actually necessary for good health, but large amounts of any of them may causeacute or chronic toxicity (poisoning).

According to Kumar et al., cement industry is one of the 17 most polluting industries listed by the Central Pollution Control Board (CPCB).Different norms and guidelines are given for all the industries depending upon their pollution potentials[4].

Many ofthe scientific data as well as maps showing different levels and patterns of pollution have been published and there has been emphasis in the last few years on such environment pollution problems as water pollution, solid waste disposal, air pollution and soil pollution by heavy metals.

In industrial cities, metallurgical industry seems to contribute substantially to the heavy metal burden of the soils where it is possible to refer most peak concentrations control could significantly reduce health risks related to urban food production and human health. However, in some areas, the metal concentrations in the soil are lower than expected may be due to potential leaching due to sandy soil texture [5].

Heavy metals and other toxic pollutants are considered extremely pernicious because they are toxic, non-degradable and environmentally persistent;electroplating, metal finishing and leather tanning are producing wastewater streams contaminated with heavy metals such as copper, chromium, zinc, cadmium, lead, nickel and mercury. The cement industry also emits largequantitiesof pollutants [5].

In Egypt alone, the dust emitted from cement factories is estimated to be about two million tons per year and is accumulating annually around domestic cement plants; this finely divided dust is emitted from cement kilns and must be disposed of at waste disposal sites. However, the cost of storage, transportation and disposal are still high. To minimize the undesirable environmental impacts and to conserve materials, many researches have been conducted for recycling or reusing the cement kiln dust (CKD) as raw materials, fertilizers, constructing materials and improving the sand soil properties [6].

The pollution problems has received considerable attention in recent years, primarily due to the concern that heavy metals can be readily absorbed by plants from soil and directly enters the human food chain, thus presenting a high health risk to consumers [7].Cadmium, for example, damages the kidneys; lead adversely affects red blood cells andthe nervous system. [8].Those metals are described as "heavy metals" which, in their standard state, have a specific gravity (density) of more than about 5 g/cm^3. Under the new guidance of United State Environmental Protection Agency, Washington, DC, USEPA (2010)dust is a fraction passing 0.063 mm (63 microns) [9].

Well-known environmentalist Yellappa Reddy, on 24th June, 2010in Mahusudhan, expressed that the dust contains toxic particles such as silicon, fluoride, iron and other heavy metals and pointed that if the fine dust got into the lung, it might cause diseases such as lung cancer, allergic bronchitis and other breathing problems where toxic heavy metals and their reverse effects on environmental & human health are given in table (1).

Table 1: Toxic heavy metals and their adverse reverse effects on environmental & human health [10]

Heavy metals	Effects
Cadmium	Replaces zinc bio-chemically causing high blood pressure, kidney damage, destruction of testicular tissue
Chromium	Essential trace metallic element: Possibly carcinogenic as Cr
Copper	Essential trace metal not very toxic to plants and algaecide algae at moderate and high levels
Lead	Toxic (anemia,kidney disease nervous disorder) wild life destroyed
Manganese	Relatively non- toxic to plants at higher levels stains material (bath clotting)
Mercury	Highly toxic to human and animals
Zinc	Essential in many metalloids enzymes buttoxic to plants at higher levels
Nickel	Causes dizziness, headaches, nausea and carcinogenesis

In a toxicity study conducted by Chauhan 2014 on heavy metals (Fe, Zn, Cu, Pb, Cd, Mn and Cr) contaminationofvegetables (Spinach, Cabbage, Cauliflower, Brinjal, Lady's Finger, Tomato and Radish) grown atthe vicinity of cement factory, he found that . Thetoxicity levels of tested vegetables grown in contaminated Cementfactory area was significantly higher than that of the vegetables grown in the reference clean (control) area.

Tiimub, et.al, 2015 also determined the amount and types of heavy metal pollutants associated with the dust and also identified the probable adverse effects they have on human health and the environment. The statistical programme revealed appreciable amounts of As, Hg, Mn, Cu, Zn, Pb and Fe which differ from one site to another. Atomic absorption spectrometry (AAS) analysis revealed relatively higher concentrations of As, Ag, Cu and Zn in both dust sites. However, concentrations ofMn, Fe and Pb were higher in secondary dust site (more far from source) and dust away from the primary site(more closest from source).

The Guideline for maximum limit of selected studied heavy metals (Fe, Znand Pb) in soil was adopted from the reference by European Union Standard and United State Environmental Protection Agency is shown in Table 2.

Table 2: Guideline for safe limits of heavy metals in soil [10]

samples	Standards	Fe	Zn	Pb
For soil (ppm)	European union standard (2002)	Not applicable (NA)	300	300
	United State Environmental Protection Agency, Washington, DC.USEPA (2010)	(NA)	200	300

2. Study area

Suk AL-Khamees cement Factory is located in the southeast of the capital Tripoli approximately 50 Km. The investigated area has a Mediterranean climate characterized by a little hot in summer and nearly cool, rainy winters where the annually rain approximately 75mm , which might increase the dissolution of the emitted heavy metals. Figure 1 shows the location of study area and the sites of the Factory and the samples.

The factory was established in 1974 to meet the needs of construction works in the Northeastern part of Libya. It has an installed capacity of one million ton per year.

3. Methodology

Nine soil samples were collected from sites at each direction of four directions in the neighborhood of the factor east to West, as well north to south where, from each site samples collected at distances of 250 m, 1000 m and 3000 m from the Factory. From each of these sites three samples were also collected at three different depths as shown in figure 1. On top or ground surface level to 10 cm below ground surface level (0-10 cm), 30 cm and 60 cm below ground surface level and also one sample wastaken as a control to determine the background concentrations. This sample was taken 25 Km from the Factory). All the collected samples were duplicated.

In an attempt to understand the pattern of metal contamination in the area surrounding the factory, useful tools including Enrichment Factor were also employed to indicate the sources of soil contamination were anthropogenic in character.

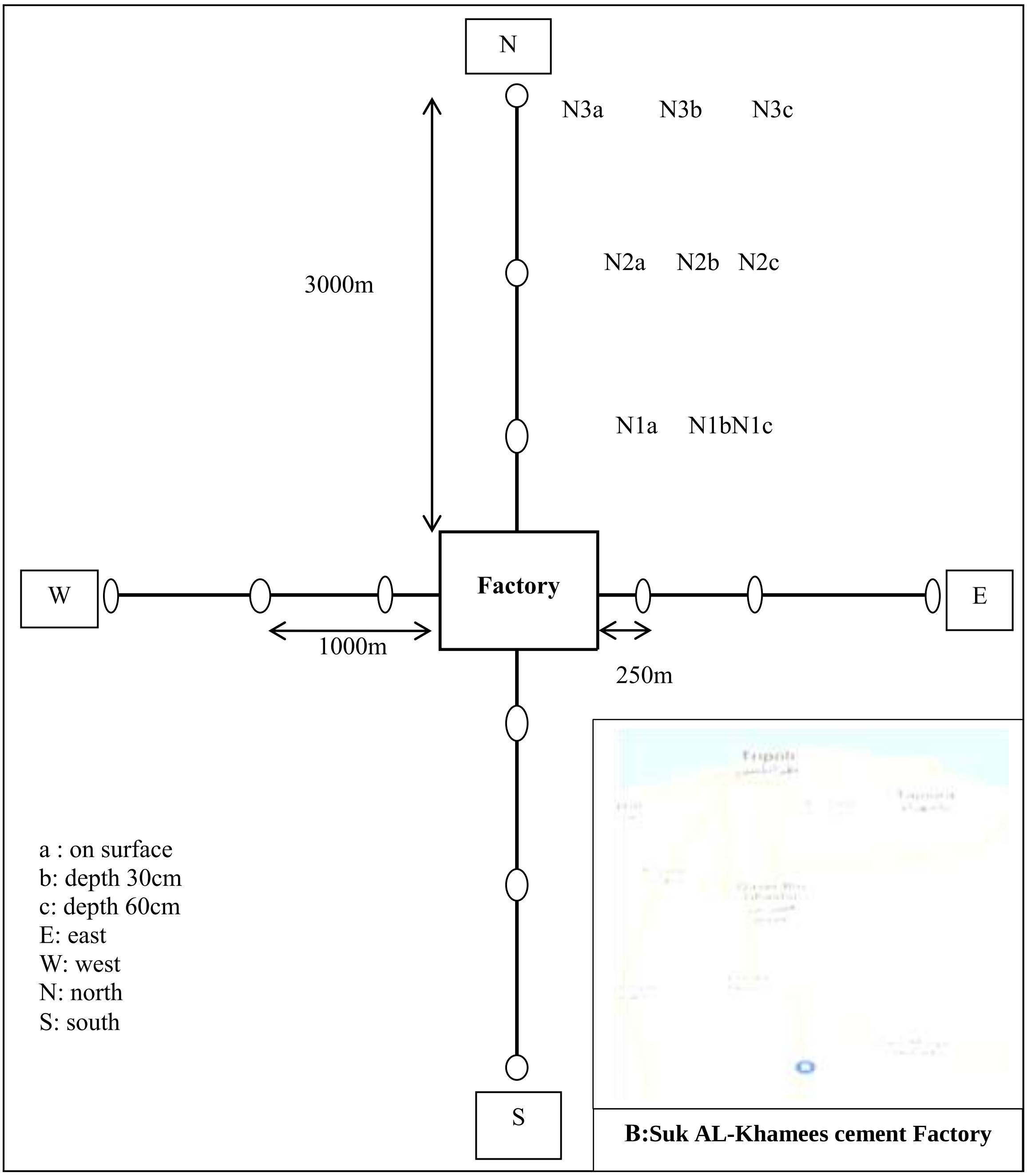

Figure1.Map of factory location and test samples

3.1. Enrichment factor (EF):

The enrichment factor (EF) has been calculated to derive the degree of soil contamination and heavy metal accumulation in soil (Kisku et al., 2000).

And according to Ergin et al., (1991) the metal enrichment factor (EF) is defined as follows:

$$\text{Enrichment Factor } (EF) = [Mx \ / \ \text{Mref}]_{\text{samples}} / \ [Mx \ / \ \text{Mref}]_{ckground}$$

Where:

EF: the enrichment factor.

M: Metal Concentration in soil sample

$(Mx/Mref)_{sample}$ is the ratio of metal or heavy metal concentration of a sample.

$(Mx/Mref)_{background}$ is the ratio of metals and heavy metal concentration of a background.

The background concentrations of metals were taken from an undisturbed area and five contaminationcategories are recognized on the basis of the enrichment factor as follows:

EF < 2 is deficiency to minimal enrichment

EF < 2-5 is moderate enrichment

EF < 5-20 is significant enrichment

EF 20-40 is very high enrichment

EF > 40 is extremely high enrichment

Despite certain shortcomings, the enrichment factor, due to its universal formula, is relatively simple and an easy tool for assessing enrichment degree and comparing the contamination of different environments. [11]

All the collected samples were duplicated. Figure 1 shows the map of the sites of the Factory and the samples.

3.2. Experimental procedure

Soil samples were collected from the site and allthe results are related to dried soil from the site directly, the metal concentrations were determined in the lab as follows:

The soil samples (5g) were introduced into 100ml beaker and were treated with concentrated nitric acid (25 ml) for 2 hrs. at 75^{o}C on a hot plate.

Hydrogen peroxide (5ml) was then added and the solution was heated for one more hour at the same temperature. The contents of the beaker were dissolved in 5M HNO_3 (3ml) and filtered with filter paper NO.42 into a 100 ml volumetric flask. The beaker was washed with distilled water and volumetric flask was made to volume with distilled water for analysis with graphite tube atomic absorption spectrometry and the following are steps for each HMs:

1. **Determination of Total Iron as Fe2O3 lead and Zinc:**

The total iron as Fe_2O_3, lead and Zinc contents were determined by the graphite furnace atomic absorption spectrophotometer by using the stock solution:

2. **Standard Stock of 1000 ppm for Fe:**

Pure iron metal (1g) was dissolved in minimum amount of HCL and was made to volume with deionized water in and liter volumetric flask (The blank was 1% HCL)

3. Standard Stock Solution of 1000ppm for Pb:

Lead nitrate Pb $(NO_3)2$ (1.598g) was dissolved in 1% HNO_3 and was diluted to 1 liter with deionized water (The blank was 1% HNO_3)

4. Standard Stock Solution of 1000ppm for Zn:

Zinc oxide ZnO (1.244g) was dissolved in 0.5% HNO_3 and was diluted to 1 liter with deionized water. (The Blank was 1% HNO_3)

5. Standard stock solution of 100ppm:

10ml of 1000ppm standard stock solution was taken into 100ml volumetric flask and was made to the volume with deionized water for all samples.

6. Working Standard Solutions:

0.5 ,1 ,2 ,4 , 6 and 8ppm of working standards were prepared by taking 0.5 ,1 ,2 ,4 ,6 and 8ml of 100ppm stock solution in a series of 100ml volumetric flasks and volume was made to the mark with deionized water.

7. Spectrophotometric Measurements:

The atomic absorption spectrophotometer was set according to the following conditions for all three elements as shown in table 3.

Table .3 the atomic absorption spectrophotometerconditions

	Fe	Pb	Zn
Mode	Absorption	Absorption	Absorption
Wave length	248.3nm	217nm	----
Slit width	0.2nm	0.4nm	0.4mm
Air flow	5liter/min	------	----
Fuel flow	1liter/min	5l/m	5l/min
Burner height	10mm	10mm	10mm

The instrument was calibrated with the iron working standard solutions of 4 and 8 ppm. The working standards 1, 2, 4 and 8 were then run as unknown. After verification of accuracy, the stock solution A of both certified rock standards and samples were run on the instrument. After making sure that the instrument is properly calibrated the rest of the sample solutions were run on the atomic absorption and the results of iron as fe2o3 were determined.

4. Results and Discussion

Tables 4 showsa summary of average range of heavy metal concentrationandaccording to obtained values of the studied heavy metals, soil lead (Pb) levels in test and control sites were 890±43 ppm and 105.75±3.76ppm, respectively, and for contaminated soils fell within the range of toxic levels (500-1000ppm).

Zn concentration in soils was 28.75±6.57ppm. These figures for Zn showed little clinical significance and are below the toxic limit. Zinc (Zn) levels are also within the excepted normal values except in the North side of the Factory.

The results values show that topsoil iron (Fe) concentrations ranged between 1170 to 920ppm at all directions from East to West and North to South. The background concentrations at 25Km away from the factory ranged between 1003 and 1202 ppm . Therefore the iron (Fe) concentrations are within the values of the background concentrations. This result is normal as the iron soil concentration is high in all Libyan Soils On going from South to East, the iron concentration increased at the topsoil[12].

Table 4: average range of heavy metal concentration

	average range of heavy metal concentration		
sample	Fe	Zn	Pb
For soil ppm	920-1170	28.75—35.32	850-935

This is normal as well, as the winds usually blow from West to East and more cement kiln dust (CKD) settles on top of the East side soils of the factory. In certain areas, the iron concentrations at depths of 30cm or 60cm were higher than in top soils. This is correlated with high iron (Fe) content of the Libyan soils.

It was found that lead (Pb) concentrations on top soils were elevated by six folds than background concentrations, which was measured at 25 Km away from the site of the Factory. These high values could be attributed to the winds blowing from East to the winds blowing from East to West and from South to North.

Part of the higher lead (Pb) concentrations in the vicinity and in certain areas along the roads, may be due to the heavy traffic on these roads emitting tetraethyl lead that might be used as gasoline additive and antiknock agent.

In addition, table 5 displays a summary of the EF values for each heavy metal in all direction as average values. According to Zhang and Liu, EF values between 0.5 and 1.5 indicate that a metal is entirely from crusted material or natural processes, whereas EF values greater than 1.5 suggests that the source were more likely to be anthropogenic. The result of the present study showed that, the enrichment factor for Fe and Zn in all studied sites were within 0.5 and 1.5, indicated that factors mostly from natural sources.

Enrichment factors for Pb showed that lead is the only metal with significantly enriched (EF>5-20) Since the EF values of the metals are less than 1.5 (except for Pb) this indicated that the environment under the study is minimally/ moderately enriched to significantly enrich with leadmetals.

Table 5: The average range of enrichment factor in all directions

Average range of Enrichment factor in all directions(Dimensionless)		
Fe	Zn	Pb
0.91-0.97	0.8-1.20	8.3 -- 8.5

5. Conclusions

In this paper, an assessment of the environmental pollution caused by accumulation of heavy metals in the soil caused by Cement Kiln Dust (CKD) emitted in the area surrounding Suk Al – Khamees -Emsehel Cement Factory has been conducted using graphite tube atomic absorption spectrometry. Fractionation of the metals species in soils around the cement factory shows higher percentages of Pb metal. Lead (Pb) levels in test and control sites were 890±43 ppm and 105.75±3.76ppm respectively.

Zn in soils was 28.75±6.57ppm. These figures for Zn showed little analytical significance and are below the toxic limit.

Topsoil iron (Fe) concentrations ranged between 920 to 1170 ppm at all direction from East to West and North to South .The background concentrations at 25Km away from the factory ranged between 1003 and 1202 ppm. Therefore the iron (Fe) concentrations are within the values of the background concentrations. This result is normal as the iron soil concentration is high in all Libyan Soils.

These results conclude that the cement kiln dust is a source of pollution in the area surrounding the Suk Alkhamees factory; the levels of lead were higher than those mentioned in guideline which makes the factory emission a potential hazard to human health and the environment.

The cement kiln dust pollution is hazardous and more heavy metals need to be investigated, however, due to the globally growing demand of cement results in the production of largequantities of CKD, the disposal of this fine dust is difficult and possesses environmental and human threat.

Many technologies such as cyclones and electrostatic precipitators has been applied to reduce the emitted amountof CKD a cross the world but in this factory no such technologies has been applied yet.

However, an economical evaluation study is needed to evaluate introducinga such technologies to minimize the waste or other choice which is the relocation of the Cement Factory Away from residential areas if it becomes impossible to relocate man and animals.

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