#### Health risk assessment of workers exposed to heavy metals in cement kiln dust (CKD)

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Abstract: Cement kiln dust (CKD) like cement itself is not considered to be hazardous material under EPA regulations. However, this does not mean that CKD does not contain anything that could pose a hazard to the environment. Therefore, the objectives of this paper were to: 1) evaluate the concentration of six hazardous metals; arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni) and zinc (Zn) in CKD. 2) Carry out health risk screening analysis for occupational exposure in the cement plants. CKD samples were collected from the biggest three companies for Portland cement production, which are located at Helwan governorate south of Cairo, Egypt. In the present study concentrations of the six metals were measured using Atomic Absorption Spectrometry techniques. The obtained average daily and lifetime average daily doses for each metal were calculated to evaluate the health risk assessment (HRA) among workers exposed to hazardous metals detected in CKD. Moreover, the results of the current work showed that Cr represents a high risk in the three cement plants comparing to the others measured ones. It might be attributed to high content of this metal in CKD and its carcinogenicity characters.

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#### 1. Introduction

The rising problem of air pollution over the last few decades as a consequence of the various developmental activities, especially in cement industry and transportation, is catching attention of the policymakers and common man in Egypt. Despite some effective steps have already been taken in Egypt to tackle the air pollution problem, Egypt is still suffering from this problem. Cement industry is one of the biggest dust producing industries in Egypt. One kilogram of cement manufactured daily generates about 0.07 kilogram of dust in the atmosphere (Hindy and Attia, 1988). Cement dust and associated chemicals can spread over a large area through wind and rain, becoming accumulated in lichens, plants, animals and and consequently, negatively soils, affecting environment and human health. (Carreras and Pignata, 2002; Grantz et al., 2003; Schuhmacher et al. 2009; Al-Saleh et al. 2010).

Cement plants are important emission sources of pollution of both organic and inorganic chemicals, and produce an input of metals. There are about 17 trace elements in cement dust; antimony, arsenic, lead, cadmium, chromium, cobalt, copper, manganese, nickel, thallium, tin, vanadium, zinc, beryllium, selenium, tellurium and mercury (Hg) (Achternbosch and Bräutigam, 2001). As, Cd, Hg and Pb, are known neurotoxins to which workers can be exposed (Quandt et al., 2010). Lead and some species of Cd, Cr and Ni compounds are classified as human carcinogens (International Agency of Research on Cancer (IARC), 1993; Das et al., 1997; Grimsrud et al., 2005). Arsenic is known to cause skin lesions and cancer of the brain, liver, kidneys, and stomach (Tchounwou et al., 2004; Yoshida et al., 2004; Yoon et al., 2010).

Metals are diverse substances, with different properties and characteristics, considered important in Life Cycle Impact Assessment (LCIA) because of their toxicity to humans and ecosystems (Pizzol et al., 2010). Several metals, such as Pb, Cd, Cr and cobalt are considered hazardous contaminants that can accumulate in the human body, with a relatively long half-life (Onder and Dursun, 2006). For example, Cd has a halflife of 10 yr in the human body (Salt et al., 1995). Women are more susceptible to the adverse effects of Cd and have higher body burdens due to the long halflife of Cd and increased dietary absorption of Cd in menstruating women (Mijal and Holzman, 2010). Cd is long-lived in the body and low-level cumulative exposure has been associated with changes in renal function and bone metabolism (Mijal and Holzman, 2010).

Some of the heavy metals emitted by cement industry are known to be toxic for human and plants, even at low concentrations (Forstner and Wittmann, 1983; Kabata-Pendias and Mukherjee, 2007). For instance, Pb low level exposure can be harmful to enzyme systems, brain and blood production for human body. While high Pb level may affect blood Pb level and intelligence (Li et al., 2001; Sezgin et al., 2003). While long-term exposure to Pb can increase the probability of mentally retarded children and slow down the mentality development of children (Ahmed and Ishiga, 2006). Exposure to Cr results in the increased production of reactive oxygen species (ROS), lipid peroxidation, and enhances the excretion of urinary lipid metabolites (Bagchi et al., 2002; Caylak et al., 2007 and 2008).

Moreover, the wildlife populations around the cement plant also might be experiencing toxic metal effects. For example, Bobak, (2000) and Yang et al. (2003) found that cement dust air pollution has an impact on an adverse pregnancy outcome (preterm delivery) in many counties. The prevalence of delivery of preterm birth infants was significantly higher in mothers living within 0-2 km of a cement plant than in mothers living within 2-4 km (Yang et al., 2003). Concentrations of Pb and Zn in top soils were influenced by the cement plant faraway 18 km (Bermudez et al., 2010; Al-Saleha et al. 2010).

Heavy metals in cement raw materials and fuels may be discharged through three separate streams. These include emissions from a kiln through exhaust stacks, incorporation into CKD and cement clinker; these latter two solids are continuously withdrawn from the kiln (Guo et al., 1996). CKD is a similar, in appearance, to Portland cement, and it is fine-grained particulate material composed of oxidized, anhydrous, micron-sized particles collected from electrostatic precipitators during the high temperature production of clinker. 75% of CKD is fine particles that consider within the respirable range (Siddique, 2006).

Exposure to hazardous air pollutants (HAPs) at sufficient concentrations and durations may increase cancer risk or cause toxicity to the immune, neurological, reproductive, developmental, and respiratory systems (Roels et al., 1992; National Toxics Program, 1993; Tam and Neumann, 2004). It is usually estimated by measurement of the airborne pollutants or by biomonitoring. Metal in hepatitis patients with chronic hepatitis (B, C) and healthy control was higher at Egyptian polluted areas (Edfu) than an unpolluted area (Daraw) (Rashed et al., 2010). Exposure to HAPs may pose both short-term and long-term health risks. It concerns workers and subpopulations living in urban and industrial areas or in houses built on abandoned contaminated industrial sites (Grandjean et al., 1988a; Heinzow et al., 1991). Mothers and their newborns might jeopardize the health risk of heavy metals even they are non-occupational (Bermudez et al., 2010; Al-Saleha et al. 2010).

Exposure to CKD has long been associated with respiratory symptoms and varying degrees of airway obstruction for exposure (Yang *et al.*, 1996; Noor *et al.*, 2000). Exposure to CKD may result in DNA damage and lipid peroxidation through oxidative stress owing to the existence of heavy metals and silica particles, which is a principal compound of CKD (Siddique, 2006; Liu *et al.*, 2009). Therefore, the present work aimed to: 1) evaluate the concentration of some metals (As, Cd, Cr, Ni, Pb and Zn) in CKD collected from the biggest three companies for Portland cement production in Helwan, Egypt; 2) present the scientific knowledge of the possible health risk of these metals on occupational exposure to CKD.

# 2 .Materials and methods

The present study was executed in three Portland cement production companies located in Helwan governorate south of Cairo, Egypt. Helwan Portland Cement Company and Qawmia Cement Company locate inside Helwan industrial area, about 27 km to the south-east of Cairo. Whereas Tura Portland Cement Company locates 13 km the north of Helwan industrial area. The qualifications of the companies are exhibited in Table 1.

Parameter	Cement company		
	Tura	Helwan	Qawmia
Established date	1927	1929	1956
Production date	1929	1930	1960
Total area in million m <sup>2</sup>	10	1	2.2
Number of quarries	69	548	72
No. of productions lines	9	10	2
Number of workers	2500	4000	3000
The regular used fuel	Mazout*	Mazout	Mazout
The secondary used fuel	natural gas	natural gas	natural gas
First annual production in million ton	0.16	0.1	0.3
Annual production in million ton	3.0	4	2.4
CKD damping area in million m <sup>2</sup>	0.34	2.7	0.36
Total discarded CKD in million ton	0.3	0.4	0.24

Table (1) Qualification of the investigated companies for Portland cement production.

Mazout\*: The cheapest type of heavy oil in Egypt

Sources: Web site of the three Egyptian cement plants and EEAA (2005).

#### 2.2 Sampling and analytical procedures

CKD samples were taken from the center of two different hoppers of ESPs installed on cement dry kilns through three consecutive days of September, 2009, for each company. Each investigated CKD sample represented a mixture of the six samples gathered from the individual company. CKD samples were kept all time in a dessicator then samples were dried in an oven at 95 °C for two days and then size differentiated physically by sieving. The size fraction < 20 µm of CKD was then chemically analyzed. A fixed portion of CKD sample (0.05 gm;  $< 20 \mu$ m) was completely decomposed by hydrochloric, nitric and hydrofluoric acid mixture according to the procedure described by El-Ghandour et al. (1982). The concentrations of As, Cd, Cr, Pb, Ni and Zn were determined by Atomic Absorption Spectrometry (Perkin Elmer) model 3300 manufactured by U.S. Instrument Division, Norwolk, CT 06859 USA.

### 2.3 Human health risk assessment

The risk estimates generated using the risk model, as a general case in risk assessment, are

presented in numbers, which look very similar to both cancer risk and non-cancer toxic risk estimates. Fundamentally, "Carcinogenic Risks" are statement of probability and represent a judgment of how likely is the specified exposure will lead to cancer in the exposed individuals. Cancer risk is expressed as the likelihood of occurring cancer due to pollutant intake through different routes (e.g. ingestion, inhalation, dermal) over the entire exposure duration and parameters which presented in Table 2. The carcinogenic risk was calculated by multiplying the estimated dose by the cancer potency factor. In contrast, the estimates for "Non-Cancer Toxic Risks" are numbers on a scale that reflect whether the exposure was larger or smaller than a specified 'safe' level of exposure. This critical level represents the threshold below which assumed adverse effects will not occur. Non-cancer risk is expressed by the hazard quotient (HQ), which compare the exposure the RfD/RfC (Reference Dose/Reference to Concentration) (Han et al., 1998).

parameter	Exposure estimate					
General Parameters						
Body Weight	70.00 kg					
Lifetime	70.00 years					
Exposure Period	30 years					
Specific Parameters						
Event Frequency	350 events/per year					
Event Duration	8 hours/per event					
Oral Amount Ingested	100 mg/event					
Oral Fraction concentration	100%					
Inhalation Breathing rate	$2.2 \text{ m}^3/\text{hour}$					

 Table 2
 Exposure parameters used to generate exposure estimates for adults

### 2.4 Model parameters and risk estimate

In the present study, human exposure and risks were assessed by using Risk\*Assistant multimedia model, the description of this model is written elsewhere (Hassanien et al., 1999). Briefly, the computer software (Risk\*Assistant, 1997) is a powerful set of tools and databases for estimating the health risk of various chemicals in the environment, in particular, settings. It was first developed by the Hampshire Research Institute. The most updated version of Risk\*Assistant for Windows (1995) offers more features for a variety of assessors to perform risk assessments, especially at the local level, where risk occurs. Default input parameters provided by the model are used, whenever possible, instead of a site-specific information. Default parameters for calculating exposure have been extracted from the USEPA exposure factor's handbook (Konz et al., 1989; USEPA, 1991).

It was assumed that exposure frequency, exposure levels and exposure duration do not change in a lifetime and that the human activities remain the same. It is apparent that the probability of this is extremely small. To illustrate this, people spend only a fraction of their lifetime in one location (Paustenbach *et al.*, 1992). The main exposure pathway for this research study was through the direct ingestion and inhalation of the contaminated cement dust. Many EPA risk assessments have assumed an adult soil ingestion rate of 100 mg/day.

### 3. Results and discussion

Figure 1 presents concentration of the six metals (mg/kg) determined in CKD collected from the

three Egyptian companies for Portland cement production. The following conclusions can be extracted; concentration of Cr was the predominant (30.7, 33.9 and 43.4 mg/kg) followed by Zn (26.7, 27.8, and 36.0 mg/kg), Ni (14.9, 15.5, and 16.0 mg/kg) and Pb averaged 12.5 mg/kg at Helwan, Tura and Qawmia, respectively. While As and Cd concentrations were less abundant with concentration averaged 1.27 and 1.02 mg/kg, respectively. As recorded the same value at all sites, concentration of all pollutants was higher at Qawmia compared to the other areas, and Cr was the highest value (43.35 mg/kg) comparing to the others measured ones.

Concentration of Cd and Cr were higher than the values (0.3 and 25.0 mg/kg, respectively) reported in the similar study done by Achternbosch *et al.* (2003) in the raw meal used in Portland cement production. Meanwhile, concentration of Zn, Ni, Pb, and As were lower than the values (53.0, 25, 22, 20, 5, and 0.3 mg/kg, respectively) founded in the raw meal in the same study.

The increase in Cd and Cr concentration may be attributed to their emission during the fossile fuel fired in the kiln which contains trace amounts of heavy metals (Serclerat and Moszkowicz, 1997). While the decrease in other metals concentrations could be related to the high temperature inside the kiln. Where the row meal is must be heated up to  $1450^{\circ}$ C which is an emergency for cement manufacturing operation. Thus an increase in metal evaporation would be expected especially some metals consider semi-volatile metal, such as lead (Dellinger *et al.*, 1993; Sarotim *et al.*, 1994). It might be also due to a difference in the specification of the raw meal used in Egyptian cement plants.

The sum average of the studied metals represented 0.01% by weight. This ratio is in close to the corresponding value found in cement plants that alternative waste derived fuels (WDF) was not used (similar to our case) nor other hazardous waste feed rates to the kiln and reported by Dellinger *et al.* (1993); Sarotim *et al.* (1994); Siddique (2006). Average concentration of Cr, Ni, Pb, and Cd for the three plants was in agreement with the range from three regions of the United States for CKD which were between (11.5 – 81.7; 6.9–39; 5.1–1490; and 0.89–80.7 mg/kg, respectively). While the average concentration of As was less than corresponding range (2.1- 20.3 mg/kg) at the same three American regions (EPA, 1993).

The low metal concentration, particularly of As and Cd does not deny or moderate its health a hazardous effects. In some cases, low-level exposures can be more harmful than high-level exposures of the same pollutant (Schmidt, 2001). In addition, there is still a potential for long-term contamination since heavy metal is known to be an accumulation within biological systems (Waly et al., 2007). Interest in the biological effects of toxic metals such as Pb, Cr, Ni and the metalloid arsenic has increased since 1985. The reason is that large amounts of toxic and carcinogenic elements have been released into the environment, particularly in industrial areas (Vahter, 1986; Järup et al., 1989; World Bureau of Metal Statistics, 1990; American Bureau of Metal Statistics, 1991). As is one of the worst cancer-causing chemicals distributed widely in the environment from both natural and anthropogenic sources, (Moon et al.,

2004; Wang and Duan, 2009). In soil As can a pose risk to human health either by ingestion via the food chain or through secondary pollution of air and water due to dust and leaching loss (Zeng *et al.*, 2008; Wu and Chen, 2010).

Estimated average daily dose (ADD) and lifetime daily dose (LADD) of inhaled and orally ingested heavy metals by adult workers besides the total carcinogenic risk (CR) and total hazard quotient (HO) in the three cement plants are presented in Table 3. The assumption upon which these values are based is explained in the methodology. ADD values of dust oral ingestion of Cd, Zn, Ni and Cr are high at Qawmia, while ADD corresponding values for Pb and As are equal in all sites. The highest values of ADD among all data recorded were reported for Zn and Cr metals. Regarding LADD ingestion of dust is a bit different from ADD. LADD values of Pb and Ni were similar in all sites. The corresponding values of Cd, Zn and Cr were higher at Qawmia. The results of total exposures to these metals during the daily exposure were used for computing the associated cancer risk is summarized in Table 3. The Table clarifies CR and HQ conducted for all pollutants had the same value at the three cement companies. This can be attributed to the very close amount of investigated pollutants, the same method of cement manufacturing and technology were used, and applying the same condition.





		Metals					
Company	Parameter	Cr	Zn	Ni	Pb	As	Cd
nia	ADD (mg/kg/d)	5.90E-05	4.90E-05	2.20E-05	1.70E-05	2.00E-06	2.00E-06
	LADD (mg/kg/d)	2.50E-05	2.10E-05	9.00E-06	7.00E-06	7.30E-07	6.80E-07
ШW	CR	3.00E-06					
Qa	HQ	0.02					
	ADD (mg/kg/d)	4.60E-05	3.80E-05	2.10E-05	1.70E-05	2.00E-06	1.00E-06
ra	LADD (mg/kg/d)	2.00E-05	1.60E-05	9.00E-06	7.00E-06	7.30E-07	6.20E-07
	CR	3.00E-06					
Πu	HQ	0.02					
ц	ADD (mg/kg/d)	4.20E-06	3.70E-05	2.00E-05	1.70E-05	2.00E-06	1.00E-06
	LADD (mg/kg/d)	1.80E-05	1.60E-05	9.00E-06	7.00E-06	7.70E-07	5.10E-07
lwa	CR	3.00E-06					
He	НО	0.02					

Table (3) The estimated average daily dose (ADD) and lifetime average daily dose (LADD) in mg/kg/d of metals detected in CKD of the three Egyptian companies of Portland cement production.

CR: Total Carcinogenic Risk from all pollutants;

HQ: Total Hazard Quient from all pollutants.

### **Uncertainty analysis**

Uncertainties exist in the risk assessment of exposure could be due to many factors such as uncertainties in measurement analysis (Fritz and Schenk, 1987), variations in exposure values assigned to examined population (Wallace, 1991), and variations in concentrations from place to another (Kim et al., 2002). While chemical analysis uncertainties can be arisen from the number of possibilities such as poor sampling, incomplete samples extraction and weighting errors, the potency calculations are an important factor responsible for uncertainties in assigned exposure values. Furthermore, uncertainties in the general extrapolation to toxicity information are responsible for the highest uncertainty (Asante-Duah, 2002).

In general, the basic process and hazards including CKD and associated metal concentration is still the most important occupational hazards in the cement industry. In Egypt most exposures to these metals are from CKD sources and its uncontrolled damping close to the company. Rather, the primary sources during most processes of a cement manufacturing operation in plant which are close to them too.

# 5. Recommendation

Undoubtedly, extermination of air pollution source roots is better and chipper than its impact treatments. So reutilization of CKD is a feasible solution to mitigate air pollution levels in Egypt. The handy and convenient usage of CKD may be in highway establishment as well as mineral filler in asphalt concrete mixes. Fortunately, Egypt has recently

witnessed a great interest in enhancing and upgrading the highway and main road networks to cover all the country, and it is estimated to have reached to double during the next decade.

# 6. Conclusion

In light of this study, cement plant workers would be under the threat of heavy metal health risk. It is of even greater concern if the carcinogenic metal concentration in cement dust reaches an amount that cannot be ignored. Consequently, the results of the current work showed that Cr represents the high risk in the three cement plants comparing to the others measured ones due to its high content in CKD and its carcinogenicity character. Transportation of the big amounts of CKD into the damping area, and water required to granulate it cost the company a lot of unprofitable money and effort. Besides CKD occupies a large area which can be used in other modern projects and investment with high economic profit. Briefly, CKD poses a very challenging task of safe handling, proper disposal and utilization. Therefore. environmental concerns related to Portland cement production, emission and disposal of CKD must be progressively significant.

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