Assessment of heavy metal Levels in the Environment, Egypt

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Abstract: The air pollution in Cairo is a matter of serious concern. Particulate and heavy metals are particularly high air pollutants. Soil represents a huge sink for heavy metals ions, which can then enter the food chain through plants or leach into ground water. The present study was designed to investigate heavy metals in the environment. Samples were collected from three compartments, air, soil, and the selective cultivated plant (cucumber), at three different districts of Egypt, and their contents of heavy metals, including Lead (Pb), Copper (Cu), Zinc (Zn), Aluminum(Al) and Cadmium (Cd), were analyzed. The six heavy metals were selected from points of public concern .The concentrations of heavy metals were determined using atomic absorption. The study showed differences in metal concentrations according to the plant part (root, leaf, and fruit).

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1. Introduction

A heavy metal is a member of an ill-defined subset of elements that exhibit metallic properties, which would mainly include the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed; some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity.

Examples of heavy metals include Chromium, Arsenic, Cadmium, Lead, Mercury, and Manganese. Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies through foods, drinking water and air. As trace elements, some heavy metals such as Copper and Zinc are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination such as Lead pipes, high ambient air concentrations near emission sources, or intake via the food chain. The inorganic elements such as Pb, As, Ni, Cd, Cr, Cu, and Al were selected to assess the environmental quality.

The heavy metal contamination is partly due to emissions from metallurgical industries in various chemical forms during the smelting of non-ferrous metals. These potentially toxic elements accumulating in soils induce a potential contamination of food chain and endanger the ecosystem safety and human health (***Reynders et al., 2008; Shah and Nongkynrih, 2007***).

In recent years, environmental problems such as air and soil pollution have become increasingly important issue in everyday of life. The widespread contamination with heavy metals in the last decades has raised public and scientific interest due to their dangerous effects on human health (***Gilbert, 1984***). They are toxic and harmful even at low concentrations. Metals are a ubiquitous class of agents both in the natural environment and at the workplace. There are numerous natural and artificial forms of metals. The common occurrence of metals in the human environment is dictated both by their wide natural distribution and by their intensive use in an ever-growing number of industrial processes. Metals have played a critical role in industrial development and technology. Heavy metals falls to environment from different sources: industry, energetic objects, agriculture, roads and railway transport. Excessive levels of heavy metals can be introduced into the environment by fertilizers. They are toxic and harmful even at low concentrations. The environmental and human health effects of heavy metals depend on the mobility of each metal through environmental compartments and the pathways by which metals reach humans and the environment. The degree of concern about human and environmental health varies with each metal. Some metals are toxic and others are known to be essential micronutrients for humans and animals. Respiration and ingestion with food are two pathways for many metals entering humans. Most metals are not destroyed; indeed, they are accumulating at an accelerated pace, due to the ever-growing demands of modern society. A fine balance must be maintained between metals in the environment and human health. Metals have been classified as essential, beneficial, or detrimental. Trace elements recognized as essential for human health include iron, Zinc, copper, Chromium, iodine, cobalt, molybdenum, and selenium

(***WHO/FAO/IAEA, 1996***). For essential elements, it is obvious that the balance between risks of deficiency and risks of toxicity must be considered. The objective of this study was to assess environmental risks of heavy metal pollution in the environment (Soil, plant and air).

2. Material and methods:

Air, soil and cucumber samples were collected from three sites varied in their activities: one Industrial site heavily influenced by road traffic north of Greater Cairo, The second is downwind industrial l site and the third is local background site remote from the city away from pollution activities

Determination of heavy metals in Air:

The concentrations of selected trace metals were determined at three locations .site 1 located at the industrial area with high traffic density north Cairo (Shoubra El Kheima) site 2 located at the industrial area south Cairo (Helwan). Site 3 located at rural area (ELmonofia governorate away from pollution source (90km)). Particulate matter was calculated gravimetric of heavy metals in the filters were extracted using an ultrasonic extraction method in a mixture solution of HNO_3: HCl (1:1 v/v). The solution was then boiled at 80ºC for 1 h in a water bath to extract the heavy metals. The extracted solution was filtered using a GF/C filter with a 0.45 μm pore size. The solution was filtered into a 100-ml volumetric flask, diluted to the mark with de-ionized water. One unexposed filter was prepared as a blank using the same procedure as that followed for the air-exposed filter. For the determination of the heavy metal concentrations, calibration curves for each metal were prepared with five standard solutions at different concentrations. Metal solutions were aspirated into the flame of the Atomic Absorption Spectrometer (AAS). Perkin-Elmer model 2380 with double beam and deuterium background correction. Hollow cathode lamps of Pb, Cd, Cu, Al and Zn were used at specific wave length of every metal.

Blank correction was performed by preparing field blanks using the same procedure as that for the SPM samples. An AAS was used to determine the concentrations of heavy metals Al, Cd, Cu, Pb, Zn, the concentrations of each metal were determined from the standard calibration curve of the individual metal.

Determination of heavy metals in Soils:

Trace metals are useful indicators of contamination in surface soil environments. Such elements tend to accumulate in top soils, and may affect population health if they reach levels such that they constitute toxic pollutants. Nine soil samples were collected from three different sites. The soil samples were obtained with a hand auger from topsoil only (to a maximum depth of 25cm). These samples were suitably packaged and conveyed into the laboratory for sample preparation and analysis. For determination of heavy metal concentrations, a wet digestion of the dried samples was done using concentrated H_2SO_4 and 30% H_2O_2 mixture. To a 0.5 g of dry-ground sample placed in 100-ml beaker, was added 3.5 ml of 30 % H_2O_2. The content of the beaker was heated to 100 ◦C, and the temperature was gradually increased to 250 ˚C, and left at this temperature for 30 min. The beaker was cooled and more 1 ml of 30 % H_2O_2 was added to the digestion mixture and the contents were reheated again. The digestion process was repeated more than one time until clear solution was obtained. The clear solution was transferred into 50-ml volumetric flask, and completed to the mark with deionized water. A blank digestion solution was made for comparison. A standard solution for each element under investigation was prepared and used for calibration. Measurements were done against metal standard solutions.

Determination of metal concentration in plant:

The roots, stems, leaves and fruits of the collected plant collected from different sites (cucumber) were separated and used as separate samples. The fresh samples were washed with tap water and rinsed twice with distilled water, then dried first with absorbent papers and further at 70 ^{O}C for 24 h. After the measurement of dry weights, they were pulverized with a micro hammer mill. Then 1.0 g of sample powders were weighed into 100 mL Pyrex beakers, and treated with 10mL concentrated HNO_3 (ultrapure 65%). The beakers were covered with watch glass, and the suspensions were heated to 130 ^{O}C for 1 h. A total of 4ml 20% H_2O_2 were added in four aliquots of 1mL each. After cooling to the room temperature, the suspensions were filtered and the filtrates were collected in 50mL flasks. The filtrates were diluted with deionizer double-distilled water to 50 ml. An AAS was used to determine the concentrations of heavy metals (Zn, AL Cu, Pb, Ni, and Cd).

3. Results and discussion:

Atmospheric heavy metals:

Primary pathway for human health exposure to heavy metals is inhalation of air particulates containing heavy metals. Industrialization and urbanization are the two major causes of deteriorating air quality. The average concentrations (mean ± standard deviation) of heavy metals, including Al, Pb, Cu, Zn, and Cd in air from different areas are presented in Table (1). Results revealed that the concentration of heavy metals in ambient air of Cairo (the largest city in Egypt) was high. On the other hand, rural area received the minimum amount of heavy metals.

At majority of sampling sites, concentrations of Zn were found to be maximum than other heavy metals. The mean concentrations of Zn in atmosphere were 4.167, 10.60, 8.50 µg/m^3, for site 1, 2 and 3, respectively. The usage of Zn for protective coating on iron, steel etc. in the industry at Cairo city could be the main reason for the higher concentration of this heavy metal in (site 2) atmosphere. Generally, the results demonstrated that the minimal concentration of heavy metals was detected in rural area (site 3) while it was maximum in the industrial area with heavy traffic density (site1).

The mean concentration of Lead (Pb) at site (1) was 1.2 ±0.04 µg/m^3.This concentration exceeded both the Egyptian standard for lead (1 µg/m^{3}as annual mean, *EEAA, 1994*) and the World Health Organization (WHO) air quality standard (0.5-1 mg/m^3, *WHO, 1992*). However, this mean concentration of Lead is much lower than that found by *Shakour et al. (2001)* (4.1mg/m^3) The decrease of Lead concentration measured in the present study may be attributed to the relocation of many Lead smelters outside Shoubra El-Kheima north of Cairo city, in addition to the use of unleaded gasoline in automobiles. The monitoring results suggest that traffic is the major source of Pb missions. *Shakour (1991*) found that Lead comprise about 43%of the particulate matter emitted in the auto exhaust. The observed increase on the Pb concentration, due to traffic Impact, averages in site 1, about 166% on the level recorded at site 2

The mean concentration of Pb at site (2) was 0.45 µg/m^3, Table (1). This value is approximately half the Egyptian standard (1 mg/m3; *EEAA, 1994*). However, it meets the WHO air quality standard (0.5 – 1 µg/m^3; *WHO, 1992*).Mean while the value of Pb at site 3 (rural area) was 0.09 µg/m^3. As mentioned before, site (1) was located at an area north Cairo which characterized by heavy traffic beside the industrial activity. The main source of Lead was the heavy traffic emission beside that transferred under the effect of winds from the industry. This is in agreement with *Ibrahim (2000)* and *Fang et al. (2005)*.

Site (1) shows the maximum amount of atmospheric Cadmium. The mean concentration measured at site (1) was 0.007 µg/m^3. Although this level is much lower than the value recorded for atmospheric level (up to 0.06 µg/m^3) in industrial areas (*WHO 1992*), this concentration is approximately one and half time higher than the guide value proposed by the World Health Organization (*WHO, 2000*) for Cd (0.005 µg/m^3). The high concentration of Cd at site (1) may be attributed to industrial activities beside the density of vehicular traffic emissions especially diesel engine. This is in agreement with *Wang and Huang (2003)* and *Fang et al. (2005)*. However, this value is lower than that measured by *Shakour et al. (2001)* at Shoubra El Kheima and *Lim et al. (2005)* at the industrial area of Brisbane, Australia. Cd concentration recorded at the rural area was 1 µg/m^3 (table1) this concentration is much lower than the atmospheric levels of Cadmium range up to (5 µg/m^3) in rural areas (*WHO 1992*).

The maximum mean concentration of Ni was 0.004 µg/m^3, recorded at site (1). This high concentration of Ni at site (1) may be attributed to the local emission from the industrial processes at Shoubra El-Kheima beside to the emission from the heavy traffic road. *Shakour (1991)* reported that the particulate matter emitted from gasoline powered vehicles contain approximately 0.7% Ni and added that automobile exhaust appears to be a source of atmospheric Nickel in Cairo City. This finding isalso in agreement with *Khoder, (1997)* and *Ibrahim (2000).*

At site 2 the mean value of Ni was 0.003 µg/m^3. Ni at site (2) may be attributed to the local emission from the industrial processes especially from combustion of oil, metallurgical operations (steel and Ni alloy manufacturing and metals smelting). However, this concentration was about half that found by *Shakour et .al. (2010)*.The order of average concentrations of heavy metals in Cairo atmosphere was Zn>Pb>Cu>Ni>Cd>Al.

Heavy metal contamination of soil:

Excessive levels of heavy metals can be introduced into the environment, for example, by industrial waste or fertilizers. Atmospheric inputs of heavy metals to agricultural systems can be significant contributors to metal loading in soil. Soil represents a major sink for heavy metals ions, which can then enter the food chain via plants or leaching into ground water. he most important heavy metals with regards to potential hazards and the occurrence in contaminated soils are: Cd, Pb, and Zn. The concentration of these toxic elements in soils may be derived from various sources, including anthropogenic pollution, metal deposits, and agriculture as well as natural activities. Chemical and metallurgical industries are the most important sources of heavy metals in the environment. The present study, therefore, examines the concentrations and distribution of heavy metals in the soils at three sites Shoubra al khima industrial zone with heavy traffic (1), Helwan industrial zone south Cairo (2), and rural area far from Cairo (3). Concentrations of various heavy metals in soils of the study area are given in Table (1). Compared with the rural site results, it was found that vehicle exhaust and smelters were the main sources of soil heavy metals. These metal-laden soils constitute a major health risk to the local population and a cause for concern. The higher levels of metals Zn, Pb, Cu, Cd, Ni and Al were found in the samples from industrial area with heavy traffic (site1). Zn and Pb were found at higher levels in all soil samples. Zinc belongs to a group of trace metals, which are essential for the growth of humans, animals and plants and are potentially dangerous for the biosphere when present in high concentrations. Zn was detected as the highest in all samples. The levels of this essential element were 426.7 µg/g, 313.3 mg/kg and 195.3 mg/kg for sites1 .2 and 3, respectively. These values exceed the back ground 114 mg/kg. It also exceeds the value reported in India (*Gowd et.al, 2010*).

The maximum concentration of lead was 42.67 mg/kg recorded in site (1) µg/g. The main sources of pollution are industries and the use of liquid manure, composted materials and agrochemicals such as fertilizers and pesticides in agriculture (*Romic, 2003*). Copper values were found to be moderate in the study area. The copper levels in soil samples ranged from 5.17to 28.6 µg/g while the normal threshold value prescribed in soil is 30 µg/g.Copper accumulation in the soil of the study area is due to the industries like steel manufacture, blast furnace, and application of agrochemicals in the agro-based industry. Cadmium is a byproduct of the smelting of lead and zinc. It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. It can be found in soils as insecticides, fungicides, sludge, and commercial fertilizers that use cadmium are used in agriculture. Cadmium levels ranged from 1.4 to 6 µg/g in the study area (table1).

Table (2) summarized the relationship between the investigated metals at the studied areas. The data shows that there is a positive correlation between anthropogenic factors that made the soil heavy metal concentrations increase. Most heavy metals are cations, meaning they carry a positive charge. Soil particles and loose dust also carry charges. Most clay minerals have a net negative charge. Soil organic matter tends to have a variety of charged sites on their surfaces, some positive and some negative. The negative charges of these various soil particles tend to attract and bind the metal cations and prevent them from becoming soluble and dissolved in water (*Vaicys M., 1997*).

Heavy metal contamination of plant:

With time, Heavy metals get accumulated in soils and plants causing a negative influence on physiological activities of plants (e.g. photosynthesis, gaseous exchange, and nutrient absorption). In small concentrations, the traces of the heavy metals in plants are not toxic. Lead, Cadmium and mercury are exceptions being toxic even in very low concentrations. The contamination of vegetables with heavy metals due to soil and atmospheric contamination poses a threat to the vegetables quality and safety. The accumulation of heavy metals through soil into the plant might cause pollution to the fruit. Cucumber quality was assessed based on the contents of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn). This study shows the concentrations of heavy metals in fruits, leaves and roots are high when grown in industrial areas (1). Plants are able to accumulate and tolerate extraordinarily high concentration of heavy metals. The occurrence of heavy metals according to their distribution in various parts of the plant is considered, taking into consideration the cultivated area and its environment. Comparison is made with respect to metal contents in soil. Content of heavy metals in different organs of the cucumber plant (fruits, leaves ad roots) varies. The overall distribution of each of the six heavy metals Cd, Cr, Cu, Ni, Pb, and Zn in each plant part is presented in table (1). Highly significant differences were found in Cd accumulation among plant parts analyzed. Pb was higher in the roots and leaves and Ni was higher in edible and feeder roots. Except for Ni, Cu and Al, concentrations in edible fruit tended to be the lowest concentrations, compared to concentrations in other plant parts. There are always more heavy metals in cucumber root grown in industrial area than in the rural area. The mean concentration of Lead in cucumber root was 13.07µg/g, 12.6 µg/g and 5.63 µg/g at site 1, 2 and 3 respectively. These levels decrease to1.50 µg/g, 0.70 µg/g and 0.330 µg/g in the fruit. The same pattern was applied for the investigated heavy metals (table 1). Average contents of heavy metals in cucumber at site 1 and 2 were much higher than that found by *Wiesław et al.(2007)*, (0.013 µg/g Pb, 0.007 µg/g Cd, 0.141 µg/g Ni, 1.84 µg/g Zn, 0.336 µg/g Cu, µg/g of fresh matter). However, there are always heavy metals in smaller or larger quantities in cucumber even in rural area (site 3). The results revealed that there is always a smaller degree of dangerous heavy metals Pb, Ni and Cu in cucumber .Metal accumulation in the plant tissues was found to be proportionate to the level of soil concentrations for Pb and Cd. The values ranged from 1.50 µg/g, 0.403 µg/g, 0.577 µg/g, 0.005 µg/g to 9.530 µg/g, the order of Pb>Cd >Ni> Cu>Al > Zn

from most to least toxic. The present study shows that there is a good relationship between most of collected data
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Table (1) Concentration of heavy metals in the environment of Cairo city

Sites	Air ($\mu g/m^3$)	Soil ($\mu g/g$)	Root ($\mu g/g$)	Leaf ($\mu g/g$)	Fruit ($\mu g/g$)
Site1 (industrialand,Traffic)					
Pb	1.200	42.67	12.6	7.83	1.50
Cd	0.007	5.97	5.2	3.83	0.403
Zn	4.167	426.67	115.1	163.3	9.530
Cu	0.027	28.60	7.83	2.6	0.577
Ni	0.004	17.67	6.8	1.267	0.267
Al	0.005	2.00	0.17	0.11	0.005
Site 2 (industrial)					
Pb	0.450	23.03	13.07	5.83	0.70
Cd	0.002	3.13	1.87	1.67	0.18
Zn	10.60	313.30	71.80	45.30	3.53
Cu	0.086	16.77	3.5	2.0	0.427
Ni	0.003	13.7	2.27	1.13	0.320
Al	0.002	2.03	0.24	0.12	0.002
Site 3 (rural)					
Pb	0.09	14.87	5.63	2.73	0.330
Cd	0.001	1.37	0.2	0.23	0.039
Zn	8.5	195.3	31.06	14.50	1.700
Cu	0.005	5.17	1.63	1.67	0.170
Ni	0.004	1.4	0.93	0.90	0.113
Al	0.0018	0.9	0.18	0.08	0.002

Table (2) Correlation coefficient between air and soil

Site	Pb	Cd	Zn	Cu	Ni	Al
Industrial and Traffic	0.2	0.76	- 0.83	- 0.733	0.779	- 0.974
industrial	0.69	0.866	0.965	- 0.835	0.999	0.912
rural	- 0.91	0.97	0.99	0.95	0.803	- 0.24

Table (3) Correlation coefficient between soil and root

Site	Pb	Cd	Zn	Cu	Ni	Al
Industrial and Traffic	0.887	- 0.565	- 0.553	0.733	0 .568	0.803
industrial	- 0.334	- 0.756	0.995	- 0.427	0.877	- 0.585
rural	0.859	0.00	0.814	0.803	0.982	0.756

Table (4) Correlation coefficient between Leaf and Fruit

Site	Pb	Cd	Zn	Cu	Ni	Al
Industrial and Traffic	-0.327	0.675	0.885	0.652	0.277	-0.945
industrial	-0.709	0.5	-0.74	0.874	0.906	0.86
rural	0.999	0.999	-0.982	0.00	-0.176	0.945

Conclusion:

Heavy metals presence in the atmosphere, soil and plant, even in traces can causes serious problems to all organisms, and heavy metal bioaccumulation in the food chain especially can be highly dangerous to human health. Some of the heavy metals (Lead, Cadmium, and Ni), even in trace concentrations, are toxic to plants (*Ioan et al., 2008*). Heavy metal pollution of soil enhances plant uptake causing accumulation in plant tissues and eventual phytotoxicity effects and can change plant communities (*Gabriella et al., 2005*). The high levels of Pb, and Cd were detected in air, and the Pb, Cd and Cu and Al in root when comparison was made with other parts of plants epically for site 1 & 2. Soil represents a major sink for heavy metals ions, which can then enter the food chain via plants or leaching into groundwater. The heavy metal concentrations in the topsoil of Egypt are mostly comparable with the background values. Traffic and smelting contribute greatly to the increase of Pb, Zn and Cu in the soil, especially in the industrial area (site1). The heavy metal concentrations in the topsoil of Egypt are mostly comparable with the values recorded for plant tissues. Traffic and smelting contribute greatly to the increase of Pb, Zn and Cu concentrations in the air and soil. Anthropogenic activities such as agriculture, industry and urban life increase these elements contents in soils and air.

Generally, the concentration of all measured metals in the two selected areas except site (3) which considered as a remote or a background levels to those polluted area were significantly higher in the industrial area associated with high traffic density. This shows the extent to which this automobile and industries release those metals as pollutants into the environment. The results of the present study confirm that the main reason of high concentration of heavy metals localized in the industrial area is either related to the industrial activities or the density of traffic.

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