Heavy Metals Enrichement in Deposited Particulate Matter at Abu Zaabal Industrial Area –Egypt

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Abstract: This study aims to assessment the impact of two major polluted industries in Egypt located in Abu Zaabal industrial area. Deposited particulate matter was monitored at Abu Zaabal industrial area around Awadalla lead smelter and abu Zaabal phosphorus fertilizer plant. This study also provides information on the distribution of trace elements in dust fall during different times and areas. Dust fall was collected monthly from November 2008 to October 2010. Heavy metals were extracted by nitric acid and measured using Perkin Elmer 6100 ICP/MS. Dust fall (DF) results revealed that the annual mean rate of deposited dust collected during the year 2009 was 29.49, 33.54, 35.64, and 36.83 g/m^2.30days for sites no. 1, 2, 3 and 4 respectively while during the year 2010, the annual mean rate of deposited dust was 28.53, 34.40, 164.46 and 295.65 g/m^2.30 days for sites no. 1, 2, 5 and 6, respectively. Sites no 5 and 6 recorded higher P_2O_5 concentration and deposition rate than sites 1 and 2 that is due to the impact of fertilizer plant. High enrichment factors for heavy metals (Pb, Cd, and Ni) were found in dust-fall samples, while Zn, Co and Cr showed minimal to moderate enrichment.

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Key words: Industrial area, Deposited particulate matter, Heavy metals.

1. Introduction:

Quality of life is a balance between technology progress and environmental risks. This balance can be controlled by analytical chemistry, which is in a central position. Elaboration and rapid determination of anthropogenically toxic elements is urgently required **(Rahmalan *et al.*, 1996)**. Many scientists believe that current concentrations of pollution-derived particulate matter (PM) in ambient air are deadly causing thousands of premature deaths annually **(Colburn and Johnson, 2003; Dockery *et al*., 1993; Dominici *et al*., 2003; Kjellstrom *et al*., 2002; Netherlands Aerosol Programme, 2002; Pope *et al*., 2002; Samet *et al*., 2000; Schwartz, 1991; U.S. EPA, 1997)**. Such premature deaths are thought to be due to both long-term and short-term exposure to ambient PM. Human exposure to trace metals occurs primarily through inhalation of air and ingestion of food and water. It was estimated that more than 15 10^9 kg of particulate matter from anthropogenic sources are emitted into the air each year **(EPA ,1976)**. Abu Zaabal industrial area is located in the north of Cairo city and comprise more than 700 industrial facilities beside Abu Zaabal for special chemicals and Abu Zaabal for fertilizers and chemicals industries. Awdalla lead smelters was transferred to Abu Zaabal since 2000 beside railways workshops.

The primary objective of this work is to put into perspective some of the current concepts with respect to trace metals distribution and emissions in air. This will reflect the potential adverse on health effect due to human exposure to trace metals.

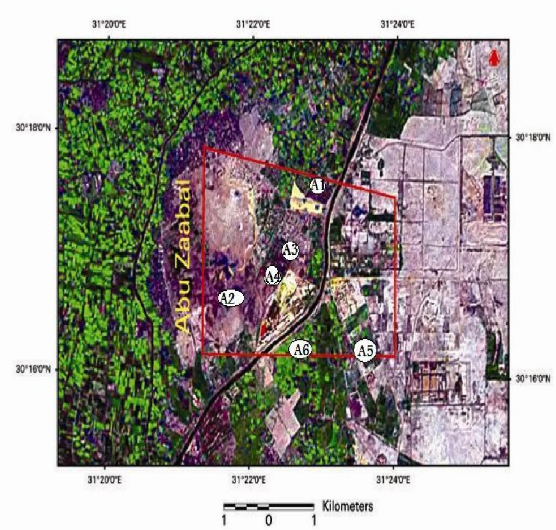
2. Material and Methods

Dust fall is monitored using the American Society for Testing and Materials standard method for collection of dust fall – **ASTM Method D1739**. Deposited particulates matter were collected monthly for two successive years from Nov. 2008 to October 2010 and dust fall collectors were used for collecting dustfall as previously used in Egypt. **(Ibrahim, 2000)** .The collector consists of cylindrical glass beakers 17 cm height and 8 to 9 cm diameter. The cylindrical glass beaker was mounted on a height of 150 cm above roof level to prevent dust from disturbances close by to have an impact. Dust fall jars were replaced at the beginning of each month and were investigated for heavy metals content. Jar content was transformed quantitatively carefully to a dry, clean weighed beaker using successive washing with distilled water till the inside of the jar become clean. Successive dry and weighing the beaker were made until constant weight, the differences in weight represent the amount of deposits dust during the corresponding month at each site of the present study. For heavy metals determination and P_2O_5 in deposited dust, method 3050B **EPA Standard Methods** was used for the digestion of samples by weighing definite weight of sample then digested with repeated additions of nitric acid (HNO) and hydrogen peroxide, hydrochloric acid (HCl) was added to the initial digestate and the sample was refluxed then filtrated and rinsed with hot HCl and concentrated by heating then completed to 25 ml volume flask and measured by inductively coupled plasma (ICP) but fluoride ion was determined by using selective ion electrode.

Table (1): Dust fall sites in Abu Zaabal industrial area

Sites NO.	UTM Coordinates		
		Northing	Easting
1	North of lead smelter	30172967	312255.42
2	Beside lead smelter	301642.50	312144.92
3	Central of Abu Zaabal	301707.10	312235.16
4	Railways hospital	301700.84	312214.22
5	200m Eastern of Fertilizer plant	301527.96	312224.16
6	100m Eastern of Fertilizer plant	301606.13	312211.75

Fig. (1): Coordination map of Abu Zaabal studied area



3. Results and Discussion:

Tables (2 and 3) summaries the annual mean rate of deposited dust collected during the year 2009, it was 29.49, 33.54, 35.64, and 36.83 g/m^2.30days in Abu Zaabal industrial area for sites no. 1, 2, 3 and 4 respectively while during the year 2010, the annual mean rate of deposited dust was 28.53, 34.40, 164.46 and 295.65 g/m^2.30 days for sites 1, 2, 5 and 6, respectively. Site no. 5 and site no. 6 was located in the Eastern side of Abu Zaabal Fertilizer plant .received higher deposition rate of particulates than other sites that is due to the impact of fertilizer plant on the surround area. Fugitive dust and stake emission especially during charging and discharging of rock mills are the main sources of particulate emissions. The rate deposition of dust is considered 4 and 8 times more than the rate of deposition recorded at shoubra El-Khima industrial area where rate deposition ranged from 39.5 to 44.6 **(Ibrahim, 2000)**. This rate of deposition is considered very heavy deposition according to Pennsylvania guidelines for dustfall **(Stern, 1986)**, moreover, these rates of deposition exceed in terrible amount of standards for dust deposits in many countries ,for instance, the air quality standards in USA is 5.7 g/m^2.30 days and is 1.93 g/m^2.30 days as a background value **(Stern, 1986)**. While it is 14 g/m^2.30 days for industrial areas according to Egyptian law 470 / (1971). **The Environmental Information and Monitoring Program of Egypt (2011)** reported that, western countries normally state that whenever dust fall values are less than10 g/m^2 per 30 days, the area may be considered clean and according to **SANS (2005)**, the new dust fall standard has been established and widely used in determination the potential of dust fall in residential and industrial areas. **SANS (2005)** standard threshold stated that deposited dust in industrial area lies between 18 and 36 g/m^2/30days (Table 6) so that only sites no. 5 and 6 show the vigorous increase of dust fall than other sites and also exceeding the alert limit to take action of 72 g/m^2/30days to immediate action and remediation required following the first incidence of dust fall rate being exceeded. Fig. (2 and 3) refer to seasonal variation of deposited dust rate in Abu Zaabal industrial area during years 2009 and 2010. Although the deposition rate is higher in sites no. 5 and 6 than other sites but the seasonal variation stile refers to the increase of deposition rate during winter than other seasons while summer season shows the lowest deposition rate during years 2009 and 2010.This finding can be attributed to several factors, the most important factors are lack of rain fall in summer which washout the dust particulate from atmosphere**.**

Heavy metals concentrations in dust fall:

Lead smelters were transferred from Shobra El-khima since 2000 to El- Safa desert in Abu Zaabal, beside railways workshops and Abu Zaabal phosphorus fertilizers plant. One of the objects of the current study is to evaluate the concentration of lead metal and companied heavy metals after transferring the lead smelters to Abu Zaabal. table (2 and 3) show the increment of Pb in site no. 2 beside lead secondary smelter than other sites .it can be noticed that lead and nickel levels (1215, 994 µg/g respectively) are much higher than the levels recorded at sites no. 1,3,4,5 and 6 , this is may be due to the factories which emit high concentration of metals to surrounded area and threaten the quality of life to those people live in this area. Lead level recorded in the present study was considered very high when compared to other cities for example in Amman, Jordan where lead level recorded was 74µg/g **(Kamal, 2000)** this means that Abu Zaabal lead level was more than 10 times the lead level in Amman but in Shobra El-Khima the level of lead was much higher than the level of lead in Abu Zaabal. Ni level in Shoubra El-Kima was 230µg/g **(Ibrahim, 2000)** this value was about 20% of Ni deposited over Abu Zaabal (table2). Chromium, zinc, cadmium, cobalt recorded the highest values at sites no. 5 and 6 located beside the Abu Zaabal fertilizer plant, which ensure the impact of this factory in contaminating the surrounding area with heavy metals .The concentrations of those elements were much high higher than the concentration found at site no. 1 which located upwind to sites no. 5 and 6. The annual mean concentrations of P_2O_5 during the year 2009 were 38.45 µg/g, 45.18 µg/g, 48.85 µg/g, recorded in sites no. 2, 3 and 4, respectively ,while the concentrations recorded for P_2O_5 in sites no. 2, 5 and 6 during the year 2010 were 34.26 µg/g, 84.6 µg/g, and 158.3 µg/g, respectively, those values are significantly higher than P_2O_5 level in site no. 1 .Site no. 1 located upwind to the investigated area and away from the impact of lead smelters and fertilizer plant. The annual mean concentration of hydrogen fluoride present in dust fall during the year 2009 was higher at sites no. 5 and 6 than that recorded at site no.1 (0.23µg/g) , while sites no. 5 and 6 recorded 7.06 and 8.98 µg/g (table2). This data clearly show the vigorously impact of Abu Zaabal fertilizer plant on the surrounded area.

Generally the impact of Abu Zaabal phosphorus fertilizer plant is responsible of increasing the of heavy metals, HF and P_2O_5 concentrations in deposited dust over the surrounding area. This finding is clearly confirmed by the values recorded for site no.1 (tables 2,3). The maximum concentration of HF and P_2O_5 recorded during the study period were 158.3 and 8.98 µg/g respectively, those results considered terrible when compared with the same results recorded at site1.

Table (2): Annual average of deposited dust (g/m^2.30days) and some trace elements (µg/g) in Abu Zaabal industrial area during the year 2009.

2009		1	2	3	4
DF	Mean	29.49	33.54	35.64	36.83
	SD	2.69	4.22	4.65	4.13
Cr	Mean	16.23	37.33	26.09	30.82
	SD	4.71	6.19	9.20	8.94
Ni	Mean	59.18	994	415	468
	SD	15.80	134.71	129.99	140.17
Pb	Mean	51.72	1215	242	316
	SD	19.95	234.	112	144
Zn	Mean	133.43	311.52	175.47	209.39
	SD	27.08	90.67	33.71	47.29
Cd	Mean	2.32	6.68	3.95	4.52
	SD	0.69	2.13	0.92	0.77
Co	Mean	14.49	28.18	19.97	21.54
	SD	3.45	6.50	2.24	2.05
HF	Mean	0.38	2.52	2.37	3.05
	SD	0.19	0.83	0.83	0.93
P2O5	Mean	0.41	38.46	45.13	48.86
	SD	0.20	11.24	19.48	18.80

Table (3): Annual average of deposited dust (g/m^2.30days) and some trace elements (µg/g) in Abu Zaabal industrial area during theyear 2010.

2010		1	2	5	6
DF	Mean	28.53	34.40	164.46	295.65
	SD	1.86	4.91	19.35	43.67
Cr	Mean	13.27	29.57	46.57	69.84
	SD	4.61	6.90	13.42	17.70
Ni	Mean	47.45	907.5	526.1	787.4
	SD	19.65	219.1	159.9	211.1
Pb	Mean	38.82	1102.	335.7	497.5
	SD	9.67	284.6	117.5	142.2
Zn	Mean	105.8	399.3	522.9	786.4
	SD	30.91	93.54	157.6	196.7
Cd	Mean	2.13	5.08	11.65	16.69
	SD	0.61	1.59	3.19	2.87
Co	Mean	13.78	26.20	35.54	53.30
	SD	2.83	5.78	8.93	11.26
HF	Mean	0.23	2.07	7.06	8.98
	SD	0.15	1.00	2.26	2.31
P2O5	Mean	0.53	34.27	84.61	158.3
	SD	0.27	11.10	16.73	24.46

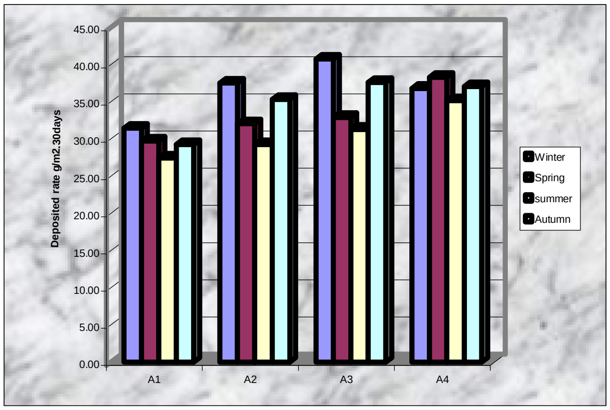


Fig. (2): Seasonal variation of deposition rate of Abu Zabal industrial 2009

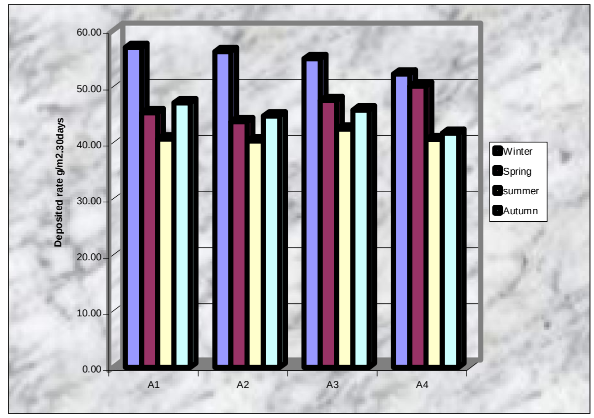


Fig. (3): Seasonal variation of deposition rate of Abu Zabal industrial 2010

Table (4): Correlation coefficient of duat fall and heavy metals in Abu Zaabal during the year 2009

	Cr	Ni	Pb	Zn	Cd	Co
Cr	1.00					
Ni	0.96	1.00				
Pb	0.86	0.96	1.00			
Zn	0.94	0.99	0.98	1.00		
Cd	0.98	1.00	0.95	0.99	1.00	
Co	0.98	1.00	0.94	0.98	1.00	1.00

Table (5): Correlation coefficient of duat fall and heavy metals in Abu Zaabal during the year 2010

	Cr	Ni	Pb	Zn	Cd	Co
Cr	1.00					
Ni	0.60	1.00				
Pb	0.15	0.88	1.00			
Zn	0.99	0.72	0.30	1.00		
Cd	0.99	0.51	0.04	0.96	1.00	
Co	1.00	0.63	0.19	0.99	0.98	1.00

Table (6): Air quality management guidelines for Dust Deposition – SANS 1929:2005

Band Number Band description	**Label**	**Dustfall rate (D) ($g/m^2/30day$)**	**Action taken**
1	Residential	D<18	Permissible for residential and light commercial
2	Industrial	24 < 0 < 36	Permissible for heavy commercial and Industrial
3	Action	36 < D < 72	Requires Investigation and remediation if two sequential months lie in this band, or more than three occur in a year.
4	Alert	72 < *D*	Immediate action and remediation required following the first incidence of dust fall rate being exceeded, Incident report to be submitted to relevant authority.

Determination of correlation coefficient:

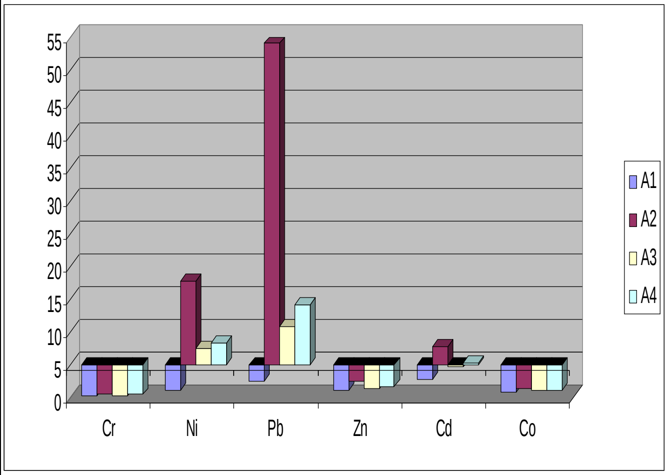
The correlation coefficient. between the heavy metals in dust falls at Abu Zaabal were studied . The correlation coefficients were evaluated as an index of dependency among metals and dust fall (DF). Tables (4&5) show a strong positive correlation between Cr, Ni, Zn, Cd, and Co this strong correlation between elements refers to probability of originating from the same origin. It can be concluded that heavy metals is a contaminants of fugitive dust emited from Abu Zaabal fertilizer plant and also emphasise the role of this plant in contaminating Abu zaabal area.

Determination of enrichment factor (EF) in dust fall:

To evaluate the magnitude of contaminants in the deposited dust, EF were computed for each location relative to the abundances of species in source materials to the control/background value and the following equation EF= (C_m/C_{Al}) sample/ (C_m/C_{Al}) control/background value was used Where (C_m/C_{Al})

sample is the ratio of concentration of trace metal (C_m) to the concentration of Al (C_{Al}) in the deposited dust samples and (C_m/C_{Al}) control/background value is the reference ratio in the control/background value. Al is selected as reference element because, it is mainly supplied from sediments and it is one of the widely used reference elements **(Sekabira *et al*., 2010)**. Cr is minimal enriched in all sites of abu zaabal during the years 2009 and 2010,cobalt also was minimally enriched in deposited dust except at site 2 during the year 2009 and sites 5 and 6 during the year 2010.

Ni, Zn and Cd are significantly enriched in site no. 2, located beside lead smelters area, the power of enrichment increase as the distance from smelter decrease that is why those elements are considered to be originated from industrial activities in Abu Zaabal ,while Pb, Ni, and Cd significantly enriched in sites 3 and 4. while pb was extremely high enriched in site no. 2 during the study period (2009 and 2010.). Generally, heavy metals in Abu Zaabal dust fall show the significant enrichment of Ni, Pb and Cd while other metals was minimal and moderate during the years2009 and 2010.



Fig(4): Enriched Heavy metals in Abu Zaabal dust fall during 2009 show the significant enrichment of Ni, Pb and Cd while other metals was minimal and moderate

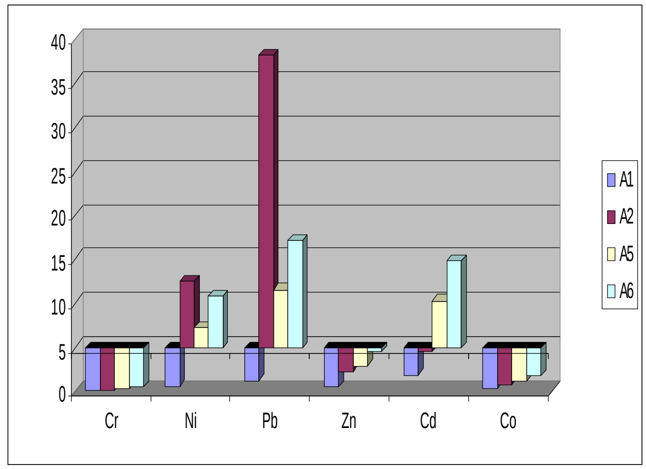


Fig (5): Enriched Heavy metals in Abu Zaabal dust fall during 2010 2009 show the significant enrichment of Ni, Pb and Cd while other metals was minimal and moderate

Conclusion

Lead smelters increased not only the concentration of lead in deposited dust but also increased other toxic heavy metals (Cd, Pb, Ni and Zn) in area near to lead smelters. Rate of deposited dust was exceeded the permissible limit of Europe But according to SANS new standard and alert limit only sites no. 5 and 6 exceeded the alert limit and need action to start mitigation in studied area. Pb , Ni and Cd were significantly enriched in dust fall during he years 2009 and 2010. Phosphurs fertilizer plant emit high amount of particulate matter contaminated with heavy metals beside HF and P_2O_5 , so that this factory has a big role in contaminating the surrounding area. Focusing and environmental consciousness must be taken into consideration in certain heavy metal.

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