DETERMINATION OF SOME HEAVY METALS IN THE ENVIRONMENT OF SADAT INDUSTRIAL CITY

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The aim of this study was to assess the heavy metal concentration in the soil and the groundwater of Sadat City in Egypt and its relation to the highly developed industrial activities in that area. The levels of Pb, Cr, Cu, Cd, Zr, and V were determined in the groundwater samples (as drinking water supplies) and also the same elements in the soil samples.

10 soil samples and 18 groundwater samples were collected from the city. The soil and the groundwater samples were analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The concentration of Pb, Cr, Cu, Cd, Zr, and V measured (in ppm) in the soil samples ranged from 0.48 to 11.3, 0.36 to 2.56, 43.7 to 304.0, 0.34 to 2.64, 0.209 to 21.7, and 0.10 to 17.0, respectively. The concentration of Pb, Cr, Cu, Cd, Zr, and V measured (in ppb) in the groundwater samples of all studied wells ranged from 0.11 to 41.32, 0.10 to 2.63, 0.14 to 5.76, 0.03 to 21.7, 11.4 to 134, and 0.08 to 5.08, respectively. The levels of Pb and Zr exceeded the threshold limits set by the WHO health-based guideline for drinking water in some studied groundwater wells.

2. INTRODUCTION

The levels of heavy metals in the environment have been seriously increased during the last few decades due to human activities. Since the toxicity of the heavy metals is related to their existing species, the speciation of them is increasingly attracting more attentions [1]. There is an increasing need to determine concentration of contamination rapidly and precisely, in particular those of toxic heavy metals. Most available methods utilize expensive equipment or consist of time consuming laboratory analyses, resulting in the need for fast and in situ methods [2]. Around the world several studies have evaluated the heavy metal concentrations in groundwater and soils using ICP-MS.The most interesting publications in that area are the papers of [3-5].

The objective of this study is to determine the concentration of some trace metals in environmental samples from the industrial city of Sadat in Egypt by using ICP-MS.

3. METHODOLOGY

3.1 Study area:

Sadat city is the second new industrial city built in Egypt. It is located in the north-west of Cairo at the point 93 km on Cairo-Alexandria road with a total area of 500 km^2. Sadat city was built as residential, industrial, and agriculture city. The main water source for drinking and irrigation is the ground water from the wells in the city [6]. Figure (1) shows the map of the location of the collected samples for the studied area.

3.2 Soil sampling

The soil samples were collected from the industrial area of Sadat city. A total of 20 sampling sites not affected by anthropogenic activities were chosen for sampling. The sampling procedure was intended to obtain a representative average sample made of 5 sub–samples collected at each site. Samples were extracted by using a stainless steel template sampler of dimension 25cm ×25cm ×5cm (depth).

3.2.1 Soil sample preparation for ICP-MS analysis

Fifty mg of soil (hand crushed to < 60 mesh) was dissolved in 3Ml ultra pure HF in Teflon bombs on a hot plate for 24 hours. The lids were then removed and samples were dried completely at low temperature 40 $^{\circ}$C in a laminar flow box. Samples were then brought into solution using 1 Ml ultra pure concentrated HNO_3. The liquid was then transferred to 100 Ml PTFE bottle and brought to 99 ml in 18.2 mΩ water. To this solution we added 2 ppb ^{115}In as an internal standard. Instrument configuration included the MCN100 nebulizer but, due to the high concentration of rare earth element (REE) in the solid samples, we did not use the guard electrode. External precision was calculated using external standardization based on measurements of a range of REE standards (1 ppb, 10 ppb, 100 ppb, 1 ppm, and 10 ppm). All sample preparation was performed in a class 100 clean laboratory at W.H.O.I. All acids used were ultra pure. Soil samples were diluted 1:100 prior to spiking with indium.

3.3 Groundwater sampling

Eighteen ground water samples were collected from the ground water wells of Sadat city. The samples were collected from the well in polypropylene containers. The pH were measured at the sampling time by using a pH meter model H18424. About 40mml of the samples was taken for the analysis.

3.3.1 Groundwater sample preparation for ICP-MS analysis

Groundwater samples were filtered through 0.45 µm filters and acidified to pH less than 2 using ultra pure HNO_3. Elemental composition of the waters was measured using a Finnegan Element sector field inductively couple plasma mass spectrometry (ICP-MS). All samples were spiked an internal standard (2 ppb ^{115}In) prior to analysis. These samples were then aspirated directly into the sector field ICP-MS. In terms of instrumental configuration, a MCN100 nebulizer was used in tandem with a guard electrode which enhances signal and decreases oxide interferences, particularly BaO and lanthanide oxides. External precision was calculated using external standardization based on measurements of a range of REE standards (1 ppt, 10 ppt, 50 ppt, 100 ppt, 500 ppt, and 1 ppb). No chemistry blanks are associated with the liquid samples aside from that attributable to the filtration process. Filtration blanks were too low to calculate. Water samples were directly nebulized into the instrument using an MCN600 desolvating nebulizer.

3.4 Apparatus

The samples were analyzed by using ICP-MS (Finnigan element 2).

The measured isotopes by ICP-MS with total concentration based on linear calibration of elemental standards with these isotopes selected for monitoring to reduce isobaric interferences 115In was used as an internal standard. These isotopes are given in the following Table (1).

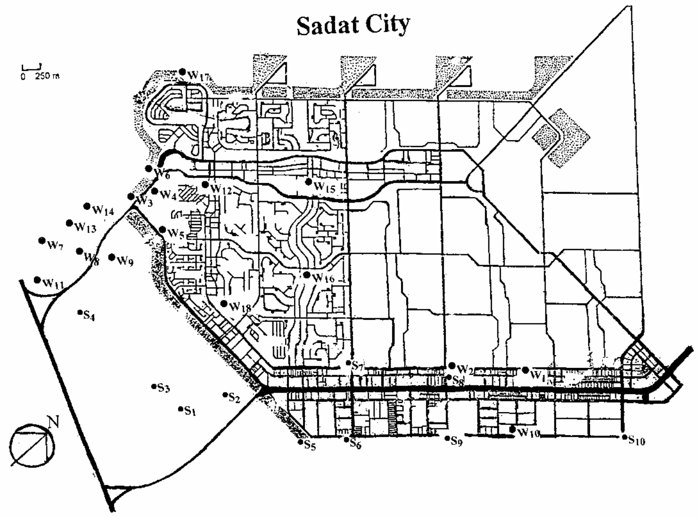

Figure 1. Map of Sadat city showing the locations of the collected samples.

Table 1. The resolution of the measured isotopes of the heavy metals.

Element	Isotope	Mass Resolution
Pb	208	Low Resolution
Cr	52	Medium Resolution
Cu	63	Medium Resolution
Cd	111	Medium Resolution
Zr	91	Low Resolution
V	51	Medium Resolution

4. RESULTS AND DISCUSSION.

4.1 ICP-MS Mass Spectrometry Results of Soil Samples.

The results of the concentration of the heavy metals for all the measured soil samples were given in Table 2. The measured concentration of lead in soil samples ranges from 0.67 to 11.30 ppm with an average value of 5.89 ppm. Our results are in the lower range of the world values (2-300 ppm) given by B. J. Alloway [7] as shown in table 4. Chromium contents vary between 0.61 to 1.87 ppm with an average of 1.24 ppm. Our results are in the lower range of the world values (5-1500ppm) given by B. J. Alloway.

Copper contents in the measured samples is much higher than the other elements. The concentration ranges from 50.0 to 304 ppm with an average value of 140.1 ppm. Samples S3, S6, and S7 showed higher concentration of Cu than the other samples. Our results are in the world range given by B. J. Alloway (2-250 ppm).

Cadmium contents vary between 0.34 to 2.01 ppm with an average value of 1.20 ppm. Our results are in the world range given by B. J. Alloway (0.01-2.0 ppm).

Zirconium contents vary between 0.21 to 2.2 ppm with an average of 0.78 ppm. For comparison, our results are in the lower range of the data given by M. Pinta [8] , up to 300 ppm.

The measured concentration of Vanadium in the studied soil samples ranges from 0.10 to 3.37 ppm with an average value of 1.87 ppm. Our results are in the lower range of the world values given by B. J. Alloway (3-500 ppm).

The values of concentrations calculated by external calibration. V, Cr, Cu, and Cd were measured in medium resolution-analytical uncertainty ~ <1%. Analytical uncertainty for trace metals was < 0.5%.

Table 2. Analysis Results of Heavy Metals in Soil Samples Collected from Sadat and October city (ppm).

Site No.	Area Classification	Pb	Cr	Cu	Cd	Zr	V
S1	Agricultural area (A)	8.01	1.2	73.0	2.01	0.209	2.14
S2	A	8.34	1.87	91.1	1.32	0.921	2.57
S3	A	11.3	1.54	253	1.25	0.211	1.27
S4	A	9.64	1.67	137	1.64	0.528	3.37
S5	Industrial area (I)	2.36	1.2	110	0.912	0.742	3.33
S6	I	9.31	0.871	239	0.335	0.212	0.888
S7	I	2.93	0.61	304	1.32	1.39	0.099
S8	I	0.67	1.25	50.0	1.11	0.843	3.09
S9	I	2.65	0.942	93.5	0.874	2.20	0.439
S10	I	3.64	1.23	50.0	1.22	0.524	1.48

4.2 ICP-MS Mass Spectrometry Results of Ground Water samples.

The results of the concentration of the heavy metals for all the measured groundwater samples were given in Table 3. Level of lead in the ground water samples was found to be much higher than the other elements except Zirconium. The concentration of lead ranges from 2.61 to 41.32 ppb with an average of 20.48 ppb in the ground water samples of the industrial part of the city. The higher amount of lead were found in the three wells of the industrial area well Delta, well R, and well AH. Lead contents in the agricultural area vary between 0.105 to 24.9 ppb with an average of 3.31 ppb. The higher concentration of lead in the ground water samples of the agricultural area were found in well SH. Lead contents in the ground water samples of the residential area were found to be in the ranges from 0.38 to 0.82 ppb with an average of 0.556 ppb.

From the obtained results it is clear that the average values for all the three areas are different. The found higher amount of lead in some wells of the industrial area is likely a contamination issue and seems to have origin of release from the industrial activities. However, the concentration of lead in well AH is below the Egyptian guidelines for drinking water quality (50 ppb) and four times higher than the international guidelines for drinking water quality [9] given by the World Health Organization (WHO) which is 10 ppb (see Table 5). Taking into account that lead is a mobile element in the aqueous phase, the increase of lead in the wells of the industrial area might be attributed to the industrial releases or due to the erosion of the natural deposits. The purification methods should be applied for all three wells specially for the higher concentration of lead in well AH to remove the excess of lead in this well.

Most of samples show lower concentration of Chromium except sample well AH. The average concentration of Chromium in the three areas are almost the same. Chromium contents in the studied ground water samples of the industrial area ranges from 0.42 to 2.63 ppb with an average of 1.199 ppb. The concentration of Chromium in the ground water samples of the agricultural area ranges from 0.10 to 1.22 ppb with an average of 0.365 ppb. Chromium contents in the ground water samples of the residential area vary between 0.18 to 1.51 ppb with an average of 0.622 ppb. The national and the international recommended value of Chromium to be in water is 50 ppb as shown in table 5. It is indicated that Chromium is naturally occurring metal in all the analyzed samples. Chromium do not constitute a risk to human health from the studied wells. The correlation between Chromium and lead were found to be 0.574 which indicates that both Cr and Pb are directly and related between themselves concerning the concept of there origin.

Copper content in the ground water samples shows low concentration in all the studied ground water samples. Copper contents vary between 0.25 to 5.76 ppb with an average of 2.255 ppb. The concentration of Copper in the studied ground water samples of the agricultural area ranges from 0.19 to 1.28 ppb with an average of 0.534 ppb. Copper contents in the studied ground water samples of the residential area ranges from 0.14 to 1.37 ppb with an average of 0.454 ppb.. It is clear that the average value of the concentration of Copper in the industrial area is noticeably higher comparing with the concentration values in the other two areas. The level of Copper in all samples (see Table 5) shows lower concentration below the national guidelines (1000 ppb) and the international guidelines (1000 ppb). We indicate that the wells have not been contaminated with copper by any industrial activities in the city. The correlation between copper and lead is found to be 0.725. Also the correlation between Copper and Chromium is 0.700.

Cadmium in the ground water samples is relatively higher than the other elements in the studied samples. Cadmium contents vary between 0.19 to 16.0 ppb with an average of 5.83 ppb. The concentration of Cadmium in the ground water samples of the agricultural area ranges from 0.13 to 21.70 ppb with an average of 3.691 ppb. The concentration of Cadmium in the ground water samples of the residential area ranges from 0.03 to 11.80 ppb with an average of 2.307 ppb. The higher concentration of Cadmium were found in the agricultural area well 95 and well M, well AH in the industrial area and well Us in the residential area. The national guidelines of Cd to be in water is 5 ppb while the international level of Cd given by WHO is 3 ppb as shown in table 5. The higher concentration of Cd in the four wells agricultural area is higher than the national and the international recommended value (Table 5) and will affect the human exposure from the daily intake of the ground water, plants, vegetables and from the food stuff which use the water from these wells. Cd is immobile aqueous element. It was found that the correlation between Cd and Cu is 0.678.

Zirconium contents in the ground water samples of the industrial area ranges from 14.5 to 24.2 ppb with an average of 20.17 ppb. The concentration of Zirconium in the ground water samples of the agricultural area ranges from 11.4 to 134.0 ppb with an average of 30.655 ppb.

The concentration of Zirconium in the ground water samples of the residential area ranges from 20.3 to 79.6 ppb with an average of 34.42 ppb.

The Egyptian guidelines and the WHO have no recommended data concerning Zirconium concentration in water. Generally, the source of Zirconium to the water will be bedrock and refractory soil minerals. The authors of FWQP reference sheet [10] found the concentration of Zirconium in the studied ground water is less than 1 ppb. The highest concentration of Zirconium were found in well 2 (134 ppb) in the agricultural area. The concentrations of Zirconium in all analyzed samples are very high likely due to the nature of the aquifer material (sands and gravels).

Vanadium contents vary between 0.08 to 3.43 ppb with an average of 2.14 ppb. The concentration of Vanadium in the ground water samples of the agricultural area ranges from 0.12 to 5.08 ppb with an average of 2.35 ppb. The concentration of Vanadium in the ground water samples of the residential area ranges from 1.11 to 3.52 ppb with an average value of 2.22 ppb. The Egyptian guidelines [11] and the WHO have no recommended data concerning Vanadium concentration in water as shown in table5. The authors of FWQP reference sheet 11.2 (Table 5) found the concentration of Vanadium in the studied ground water is in the range from 0.1 to 100 ppb [10]. It is indicated that Vanadium is naturally occurring metal in all the analyzed samples.

The concentration values were calculated by external calibration. Analytical uncertainty for trace metals was < 2 %. Cr, Cu, Cd, and V were measured in medium resolution-analytical uncertainty < 3 %.

Table 3. Analysis Results of Heavy Metals in Ground Water Samples Collected from Sadat City (ppb)

Site Description & No.	Area Classification	Pb	Cr	Cu	Cd	Zr	V
Well Delta (w_1)	Industrial area	17.509	0.42	0.25	0.188	14.5	0.08
Well R (w_2)	Industrial area	2.607	0.552	0.754	1.30	21.8	3.43
Well 2 (w_3)	Agricultural area	0.105	1.221	0.478	0.237	134	4.54
Well 1(w_4)	Residential area	0.615	1.51	0.228	0.044	79.6	3.52
Well Mubarak (w_5)	Residential area	0.674	0.850	0.139	0.029	31.9	2.26
Well 93.5(w_6)	Agricultural area	1.231	0.302	0.306	0.393	22.6	3.24
Well 95(w_7)	Agricultural area	0.360	0.167	0.935	6.63	16.5	1.48
Well SH (w_8)	Agricultural area	24.900	0.174	0.252	0.462	16.0	0.972
Well Mahmoud Amin (w_9)	Agricultural area	0.393	0.188	0.189	0.241	24.5	1.09
Well AH (w_{10})	Industrial area	41.317	2.627	5.76	16.0	24.2	2.91
Well 3 (w_{11})	Agricultural area	0.648	0.685	0.269	0.134	16.7	3.53
Well Hassan Alam (w_{12})	Residential area	0.821	0.308	0.192	0.152	24.6	1.11
Well M (w_{13})	Agricultural area	1.123	0.096	1.28	21.7	15.1	0.115
Well I (w_{14})	Agricultural area	0.621	0.227	0.622	2.16	19.1	5.08
Well Ms (w_{15})	Residential area	0.380	0.182	0.489	1.66	20.3	1.17
Well Us (w_{16})	Residential area	0.421	0.202	1.374	11.8	24.3	1.73
Well D (w_{17})	Agricultural area	0.381	0.226	0.475	1.26	11.4	1.09
Well N (w_{18})	Residential area	0.423	0.679	0.289	0.156	25.8	3.52

Table 4. Concentration of heavy metals in soils samples.

Element	Normal range in soils (ppm)
Pb	2-300**
Cr	5-1500**
Cu	2-250**
Cd	0.01-2.0**
Zr	300***
V	3-500**

**Data mainly from B.J.Alloway 1995 " Heavy Metals in Soils " Second edition, Blackie Academic & Professional.

***Data from M. Pinta 1978 " Modern Methods For Trace Element Analysis"

In general the data in this study is connected to the previous study of the rare earth elements [12] in frame of comprehensive investigation of influence of the non nuclear activities on the environment.

Table 5. Comparison of regulations after WHO [9], Egyptian guidelines [11], and FWQP Reference [10]

Element	WHO data in Water (PPb)	Egyptian guide lines (PPb)	FWQP Reference (PPb)
Pb	10	50	0.1-100
Cr	50	50	0.1-100
Cu	1000	1000	0.1-100
Cd	3	5	0.1-100
Zr	---	---	<1ppb
V	---	---	0.1-100ppb

CONCLUSION

The results of the heavy metal elements in the ground water and soil samples will be used to establish the environmental Guid levels for various heavy elements in Egypt. All the chemical pollutants in the ground water wells are within the Egyptian and the WHO guide lines except for lead in three wells in the industrial area. The use of water obtained from these wells must undergo some measures to limit the possible chemical hazard. This study has highlighted the need for further research, in order to determine the permitted levels of metals in water and soil samples as well as to identify areas of potential toxicity and the drinking water quality.

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