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ASSESSMENT OF INDUSTRIAL CONTAMINATION OF AGRICULTURAL SOIL ADJACENT TO SADAT CITY, EGYPT

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Abstract: Assessment of the environmental impact of El Sadat City, a Cairo satellite, known for its clustered enterprises, on the neighbourhood water supply El Manashi Tawfikia Canal was undertaken through soil analysis. A total of 20 agricultural soil samples were collected along the El Manashi Tawfikia Canal. Neutron activation analysis was implemented to determine heavy metal contents of such elements as As, Ba, Co, Cr, Ni, and Zn. Multivariate statistical analysis was applied to the results obtained. The metal pollution index and enrichment factor were calculated. It was shown that the content of toxic heavy metals in soil samples does not exceed the worldwide-published values, except arsenic which considerably exceeds normalized to the content of the same element in the Upper Continental Crust. The metal pollution index is high compared with the calculated ones for similar soil samples from the Nile Delta, and the enrichment factor varied from moderate to high enrichment ($5 < EF < 10$).

Keywords: El Manashi Tawfikia Canal, Sadat City, soil, instrumental neutron activation analysis, trace elements, heavy metals

Introduction

The largest industrial city in the country, El Sadat city, is among of the first generation, which the Urban Communities Authority formed in 1978. There are 94 factories of, chemical and metallurgy industries, textile, plastics and paper production [1]. Sadat City is located 93 km to the North-West (30.6°N , 30.22°E) from Cairo. The nearest to El Sadat City fresh drinking water source - El Manashi Tawfikia canal - is located 25 km east of El Sadat City (30.28°N , 30.48°E). Its water is also used for irrigation purposes in the adjacent agricultural area. The possible anthropogenic pollution produced by the industrial

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enterprises located in Sadat City was studied along the El Manashi Tawfikia canal. Published elemental concentrations of Pb, Cr, Cu, Cd, Zn, and V in the industrial area in El Sadat City showed great scatter of data [1]. For Pb the content in ppm ranged from 0.48 to 11.3; for Cr - from 0.36 to 2.56; for Cu - from 43.7 to 304.0; for Cd - from 0.34 to 2.64, for Zn - from 0.209 to 21.7, and for V - from 0.10 to 17.0. In our previous study [2] of the elemental concentrations in 40 surface soil and sediment samples collected in the Nile delta and in the Egyptian section of the Nile River Valley the content of the elements in question: As, Ba, Co, Cr, Ni, and Zn was much lower (5.3, 332, 18, 103, 43, 63, respectively) than in the present study. The aim of the present work was to identify the pollution sources responsible for emission of toxic heavy metals along El Manashi Tawfikia canal by means of non-destructive, multi-element instrumental neutron activation analysis (INAA) [3]. According to the modern trends in the field of risk assessment using equidosimetric parameters [4], both chemical and radiological issues [5] need to be considered.

Material and methods

Sample collection and preparation

El Manashi Tawfikia canal represents the eastern boundaries of El Sadat City as shown in the map of the sampling locations in Figure 1.



Fig. 1. A Google Earth image indicating the positions of the 20 sampling sites. The map insert shows the position of El Manashi Tawfikia canal with relation to Egypt

A total of 20 soil samples (≈ 1 kg each) were collected along El Manashi Tawfikia canal with an interval of 500 m. The total length of the studied area was ≈ 10 km.

The samples were collected at different depths of 0-5, 5-10 and 25-30 cm, air-dried, cleaned from vegetation, well mixed, crushed (with non-iron grinder to avoid the contamination of samples with iron) and sieved to get homogeneous grain size of particles ≈ 2 mm mesh for 20 soil profiles.

Each sample was a mixture of soils from the three different depths to consider the migration of elements vertically in soil profile as a result of rains or water level in the canal. Sampling procedures are given elsewhere [6].

Instrumental Neutron Activation Analysis (INAA)

INAA of soil samples was carried out at the reactor IBR-2 of FLNP, JINR, in Dubna, Russia. Characteristics of neutron flux density in the two irradiation channels of the pneumatic system are shown in Table 1.

Table 1

Flux parameters of irradiation positions [7]

Irradiation position	$\Phi_{th} \cdot 10^{12} [n \cdot cm^{-2} \cdot s^{-1}]$ $E = 0-0.55 \text{ eV}$	$\Phi_{th} \cdot 10^{12} [n \cdot cm^{-2} \cdot s^{-1}]$ $E = 0.55-10^5 \text{ eV}$	$\Phi_{fast} \cdot 10^{12} [n \cdot cm^{-2} \cdot s^{-1}]$ $E = 10^5-25 \cdot 10^6 \text{ eV}$
Ch1 (Cd-screened)	0.023	3.3	4.2
Ch2	1.23	2.9	4.1

The gamma spectra of the samples were measured with a HPGe detector with a resolution of 1.9 keV for the ^{60}Co 1332 keV line and analysed using Canberra software Genie 2000. The contents of the elements were calculated using software developed in the Frank Laboratory of Neutron Physics [7, 8].

Samples with masses of around 100 μg were heat-sealed in polyethylene foil bags for short time irradiation and in aluminium cups for long time irradiation. More details about the procedure of sample preparation for irradiation can be found elsewhere [9].

Usually two sets of elements (short and long-lived isotopes) were determined in this study. To determine long lived isotopes (LLI): Na, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zr, Sb, Ba, La, Ce, Sm, Eu, Tb, Dy, Hf, Ta, W, Th, and U, cadmium screened channel 1 was used. Samples were irradiated, repacked and measured, using high purity germanium detectors, twice, after 3-4 days and 20-22 days of decay, measurement time was 30 min and 90 min respectively. To determine short lived isotopes (SLI): Mg, Al, Cl, K, Ca, Ti, V, Mn, and Br irradiation channel 2 was used. Samples were irradiated for 1 min and measured 15 min of decay. In the present work, long-lived isotopes (LLI): As, Ba, Co, Cr, Ni, and Zn were determined to investigate the content of these elements due to the waste of different industries in the neighbored industrial city and corresponding levels of investigation and intervention for possible required actions for cleanup or remediation. Furthermore, to estimate the metal pollution index *MPI* and enrichment factor *EF* for each element of interest.

The accuracy of the analyses was checked by simultaneous analysis of the following standard reference materials: 2709 (NIST, Soil, San Joaquin), 2710 (NIST, Montana Soil, Highly Elevated Trace Element Contents), 2711 (NIST, Soil, Moderately Elevated Trace Elements Contents), 433 (IAEA, Marine Sediment), 1633b (NIST, Constituent Elements in Coal Fly Ash), 1632c (NIST, Trace elements in coal). Saldanha Bay where collected from rafts of mariculture farms, *ie* these samples represent farmed mussels while the former two ones are naturally grown molluscs.

Statistical methods

Both of descriptive and multivariate statistic data analyses such as Cluster, Factor as well as Principal Component Analysis [10] were used for data processing from the current

research. ArcGIS technique was used for mapping and studying the thematic distribution of some elements and getting the kriging interpolations of the radio-contaminant contents. The calculations were done by means of OriginLabTM, StatSoftTM, MSTM Excel and PAST 3.

Results and discussion

Contents of contaminants in soil

From the determined 36 elements in 20 soil samples six elements were chosen as potentially hazardous. Their concentrations are given in Table 2.

Table 2

Heavy metal contents in soils

ID	Coordinates		Contents of contaminants [mg/kg]					
	Latitude	Longitude	As	Ba	Co	Cr	Ni	Zn
w-01	30.4624	30.82437	8.6±0.9	369±18	22.7±0.4	138±7	55±4	96±3
w-02	30.45459	30.82677	6.9±0.7	242±12	12.6±0.2	69±3	30±2	54±2
w-03	30.44808	30.82918	10.0±1.0	483±24	30.7±0.6	200±10	71±5	87±3
w-04	30.44127	30.83021	10.2±1.0	497±25	30.0±0.6	184±9	69±5	114±3
w-05	30.43505	30.83021	17.1±1.7	358±18	22.1±0.4	124±6	50±4	95±3
w-06	30.43032	30.83021	61.3±6.1	241±12	14.2±0.3	98±5	30±2	60±2
w-07	30.42528	30.83124	9.0±0.9	484±24	26.5±0.5	178±9	57±4	97±3
w-08	30.41907	30.83089	6.5±0.7	412±20	25.6±0.5	173±9	57±4	109±3
w-09	30.41374	30.82986	5.8±0.6	281±14	15.4±0.3	104±5	34±2	61±2
w-10	30.40781	30.82918	8.1±0.8	327±16	21.7±0.4	129±6	50±4	90±3
w-11	30.40308	30.82815	8.3±0.8	432±22	25.3±0.5	145±7	51±4	95±3
w-12	30.39804	30.82746	10.1±1.0	469±23	28.6±0.6	179±5	64±5	115±3
w-13	30.39242	30.82815	5.10±0.5	280±14	14.2±0.3	98±5	38±3	48±2
w-14	30.38916	30.82883	4.9±0.5	286±14	13.8±0.3	114±6	30±2	58±2
w-15	30.38679	30.82986	5.28±0.53	200±10	10.6±0.2	67±3	26±2	48±2
w-16	30.38413	30.83055	8.5±0.8	449±22	26.0±0.5	157±8	57±4	95±3
w-17	30.38294	30.83021	6.7±0.7	373±19	22.1±0.4	129±6	46±3	81±3
w-18	30.37998	30.83124	6.4±0.6	227±11	10.4±0.2	54±3	26±2	49±2
w-19	30.37587	30.83055	5.8±0.6	297±15	11.0±0.2	99±5	30±2	73±3
w-20	30.37317	30.83021	8.0±0.8	415±21	24.8±0.5	156±8	51±3	80±3

Arsenic (As) is the twentieth most abundant element in the Earth's crust. An ubiquitous element known for its toxicity to biota naturally occurs in several oxidation states between -III and +V. Total As contents in the soil solid phase range between 0.1 and 55 mg/kg uncontaminated soils but may be as high as several percent in soils contaminated by mining, smelter and other industrial activities. Estimates of the global average content of As in soils are in the range of about 5-7.5 mg/kg with a common range between 0.1 and 55 mg/kg. This is supported by data from major regions (continents) of the world. Larger arsenic contents found at regional or local scale can generally be attributed to geogenic anomalies (bedrock) or anthropogenic activities [11]. The average content of As in the studied samples was found to be 10.6 with standard error of 2.7 mg/kg with a minimum value of 4.9 to maximum one of 61.3 mg/kg. The obtained data was 7 times higher compared with those published worldwide for Upper Continental Crust UCC [12] and two times higher than published by Vinogradov [13]. From Table 3, it can be seen that content of As is less than the intervention level [14].

Barium (Ba) is a common element in the Earth's crust and is naturally present in higher contents than most other trace elements. Industrial uses of **Ba** are wide and variable including: oil and gas drilling muds. Barium is not very mobile in most soils although plants may take up Ba easily from acid soils, but there are few reports of toxic contents of **Ba** in plants. **Ba** is a common element with a mean content in the Earth's crust of 425 mg/kg and range from 550 to 668 mg/kg in the upper continental crust [12]. It is 14th in order of abundance in the Earth's crust and occurs at higher contents than most other trace elements [15]. The content of Ba in the current studied samples ranged from 200 to 497 mg/kg with an average of 356 mg/kg with SE of 21.4 mg/kg. The obtained data seems to be less than the obtained one by Turekian et al [16] (580 mg/kg) and UCC [12] for sediments (580 mg/kg). But it is worth to point out that the obtained results of Ba near to the value of further test requirements needed class B so it is a good argument to continue studying this location and follow the increment dynamics of the **Ba** content.

Cobalt (Co) in sedimentary rocks the contents of **Co** are highly variable, but as a rule they are highest in fine-grained sediments *eg*, shales, and lowest in coarse-grained sediments *eg*, sandstones. The variations in contents of **Co** in metamorphic rocks are as great as those in the parent rocks and so the variations are as great as those found in igneous and sedimentary rocks. The total content of **Co** in soil is ranging from 1-40 mg/kg [17] comparing with the obtained results which ranges from 10.4 to 30.7 mg/kg with an average value of 20.4 mg/kg. The obtained content of **Co** is within the range which was found by Levinson [17] and more than the values of background (19 mg/kg) by Turekian et al [16] and UCC (17 mg/kg) by Condie [12] and three times higher (8 mg/kg) than found by Vinogradov 1959 [13]. The content of Co is less than the obtained value (26 mg/kg) by Gromet 1984 [18].

Chromium (Cr) Chromium is used on a large industrial scale including metallurgy, electroplating, production of paints and pigments, tannery, wood preservation, chromium chemical production, and pulp and paper production. Chromium is largely used to form stainless steel. Wastes from **Cr** industries (*eg* sludge, fly ash, slag, etc.) have been employed as a fill material at numerous locations [19] at which leaching and seepage of **Cr(VI)** from the soils into the groundwater is a considerable health hazard to the man. World Health Organization WHO established a limit for the content of **Cr** in the drinking water to be not to exceed 50 $\mu\text{g}/\text{dm}^3$. The obtained results range from 53.9 to 200 mg/kg with an average of 129 mg/kg. The content of Cr in the studied samples \approx 1.5 times higher than the background value of 90 mg/kg reported in [16] and \approx 2 times higher than the published worldwide for UCC (69 mg/kg) [12], but on the other hand is less than the content of **Cr** (200 mg/kg) reported in [13]. The obtained results of **Cr** are quite close to the content of the same element (125 mg/kg) in the sediment obtained in [18].

Nickel (Ni) is an element naturally present in all rock types and present in the pedosphere in a range from trace amounts to relatively high contents, as compared to other trace elements. Nickel is an important element for high demand in the industrial field. The variation of the world mine production of nickel over the last 40 years [20-22]. On the other hand, the toxicity and carcinogenicity of high doses of Ni are well documented and depend mainly on its potential to damage proteins and nucleic acids [23]. The obtained results show that the content of **Ni** ranges from 25.7 to 71 mg/kg with an average of 46 mg/kg. The content of **Ni** was compared with the content of the same element and it is less than the published worldwide (68, 55 and 58 mg/kg) by [16, 12, 18], respectively. But it is higher

than that published (40 mg/kg) by [13]. Higher content of nickel (53 mg/kg) was found in Kavadarci region - Republic of Macedonia for topsoil [24].

Zinc (Zn) is naturally present in all soils in typical background contents 10-100 mg/kg. Human activities have enriched to soils with Zn through atmospheric depositions, fertilization and sewage sludge application [11]. Zinc is a micronutrient for all biota. Elevated Zn contents can cause toxic effects to plants, soil dwelling organisms and microorganisms and these ecotoxicological effects precede effects on humans. The obtained results show that the content of Zn in the studied samples ranges from 48.2 to 115 mg/kg with an average value of 81 mg/kg. The results were compared with those of worldwide published ones by [12, 18, 13] 67, 2.7, 50 mg/kg, respectively but less than the background (95 mg/kg) reported in [16].

Table 3

The average value and standard deviation (SD) (in [mg/kg]) of all 6 elements in studied samples compared with Background (BKG) [16], Upper Continental Crust (UCC) [12], North American Shale Composite (NASC) [18] and Vinogradov (Vng.) [13]

Metals	Soil [mg/kg]			BKG Turekian [16]	UCC [12]	NASC [18]	Vng. [13]	Present work	Relative difference [%]
	A	B	C						
As	20	30	50	13	1.60	ND	5.00	10.6 ±2.7 (4.9-61.3)	78.8
Ba	200	400	2,000	580	570.00	636.00	500.00	356 ±21 (200-497)	82.2
Co	20	50	300	19	17.00	26.00	8.00	20.4 ±1.5 (10.4-30.7)	93.0
Cr	100	250	800	90	69.00	125.00	200.00	129.8 ±9.4 (53.9-200.0)	83.9
Ni	50	100	500	68	55.00	58.00	40.00	46.1 ±3.3 (25.7-71.0)	90.8
Zn	200	500	3,000	95	67.00	2.70	50.00	80.4 ±4.9 (48.2-115.0)	97.3

A - reference value, B - test requirements, C - intervention value, Relative difference = (ref value - current value)/ref value

Statistical analysis

The contents of the studied elements was normalized to the content of the Upper Continental Crust UCC and the statistical descriptive of the elements were plotted in Figure 2. From Figure 2, it is obviously that after normalization the average value of **As** is the highest value and **Ba** is the lowest one.

The content of **As** was compared with the content from some countries according to their national regulations for cleanup action, further investigations or intervention is required. Table 4 shows the contents of **As** in soil and sediments in some countries based on guidelines done by national regulatory bodies.

The comparison of **As** - content revealed that the obtained data of the present work is higher than that regulated for Thailand with almost 2.5 times and 2 times for South Korea. While it was less than done for others from different countries. From the point of view of ecotoxicology it is highly recommended to follow up the dynamics of arising the **As**-content due to the release from the neighbored industrial city.

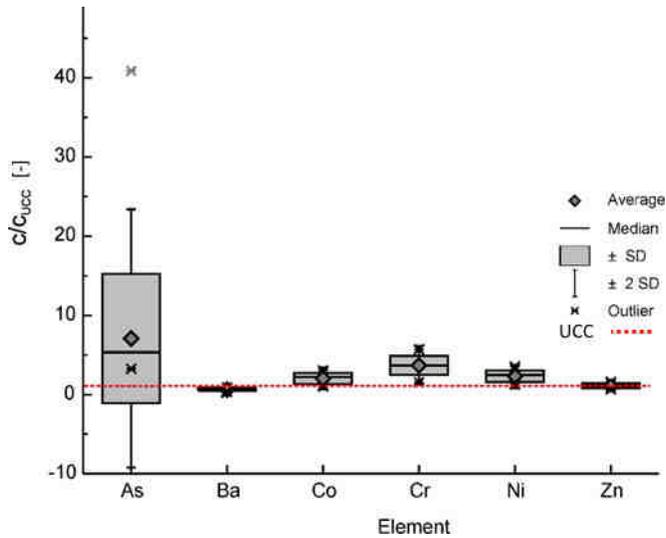


Fig. 2. Statistical descriptive of contents normalized to C_{UCC}

Comparison of As contents in soil with some countries

Table 4

Country	Content of As [mg/kg]	Reference
Australia	20	[25]
Italy	20	[26]
Japan	15	[27]
South Korea	6	[28]
Thailand	3.9	[29]
USA	22	[30]
Present work	10.6	Current

Correlation matrix

Table 5, reflects the correlation coefficient matrix, listing the Pearson's product moment correlation coefficient. A very significant correlation was found between the current results and Vinogradov's ones ($r = 0.991$) [13]. This means that the obtained data for the studied metals is in good agreement with the obtained one by Vinogradov [13].

Table 5
The correlation coefficients between Background (BKG) [16], Upper Continental Crust (UCC) [12], North American Shale Composite (NASC) [18] and Vinogradov (Vng.) [13] and the present results

	BKG	UCC	NASC	Vng.
UCC	0.999			
NASC	0.984	0.988		
Vng.	0.956	0.953	0.974	
Present results	0.977	0.972	0.972	0.991

On the other hand, the correlation coefficients between the studied heavy metal elements was constructed as in table 6 and it is obviously that there is significant correlation between Ni and Co ($r = 0.980$); Co and Ba ($r = 0.963$); Cr and Ba ($r = 0.961$) and Ni and

Ba ($r = 0.947$). It is important to point out here that the negative correlation between As and other elements exists.

Table 6

Correlation coefficients between studied heavy metal elements ($n = 20$)

	As	Ba	Co	Cr	Ni
Ba	-0.167				
Co	-0.083	0.963			
Cr	-0.078	0.961	0.957		
Ni	-0.130	0.947	0.980	0.946	
Zn	-0.074	0.881	0.893	0.862	0.890

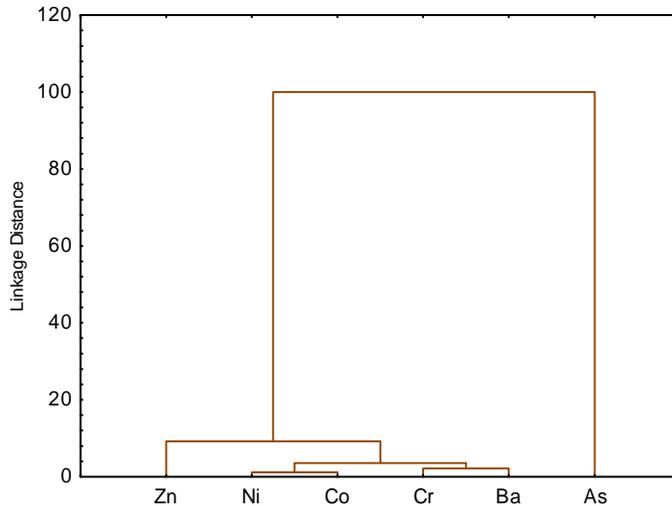
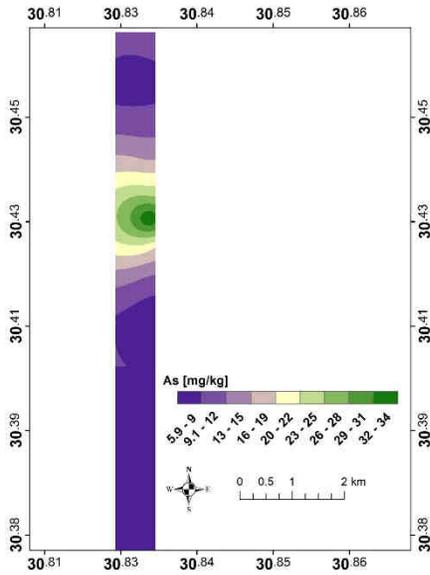


Fig. 3. Hierarchical clustering ($r =$ Pearson correlation coefficient) including 6 soil elements

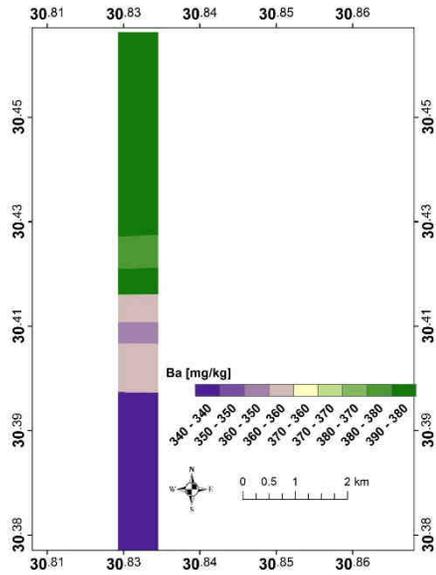
Using the Pearson's correlation coefficient the hierarchical clustering of the soil heavy metals in Figure 3 were plotted. The high correlations between soil heavy metals may reflect that these heavy metals had similar pollution level and similar pollution sources [31]. The elements, Ba, Cr, Zn, Ni, Co are grouped together, indicating that the lithogenic sources of these heavy metals are closely related in the soil of the studied area, which was consistent with the research reported by Romić and Romić [32], Sun et al [33] and Li et al [31]. However, Arsenic (As) is not grouped with the other elements because the anthropogenic activities are the main source of As in the environment and this can explain the high content of As due to the influence of the industries of ceramics in Sadat City on the environment of El Tawfikia canal.

The spatial distribution of the soil heavy metals was interpolated as shown in Figure 4. It is clearly that the heavy metals in soil were distributed upwards in the direction of the Mediterranean Sea and this may be explained with the direction of current of water in the canal and the wind direction.

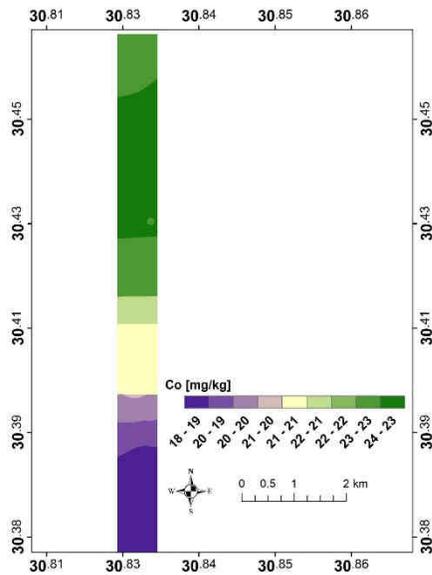
a)



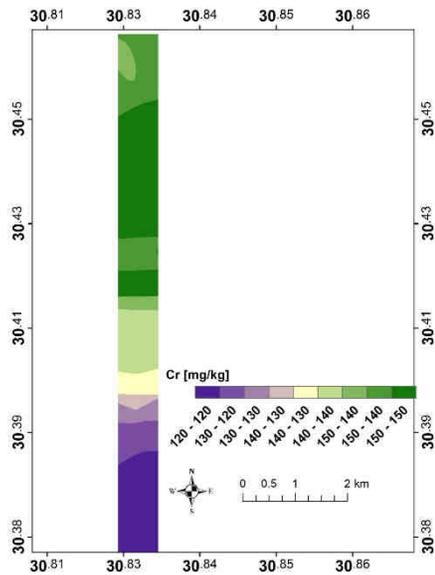
b)



c)



d)



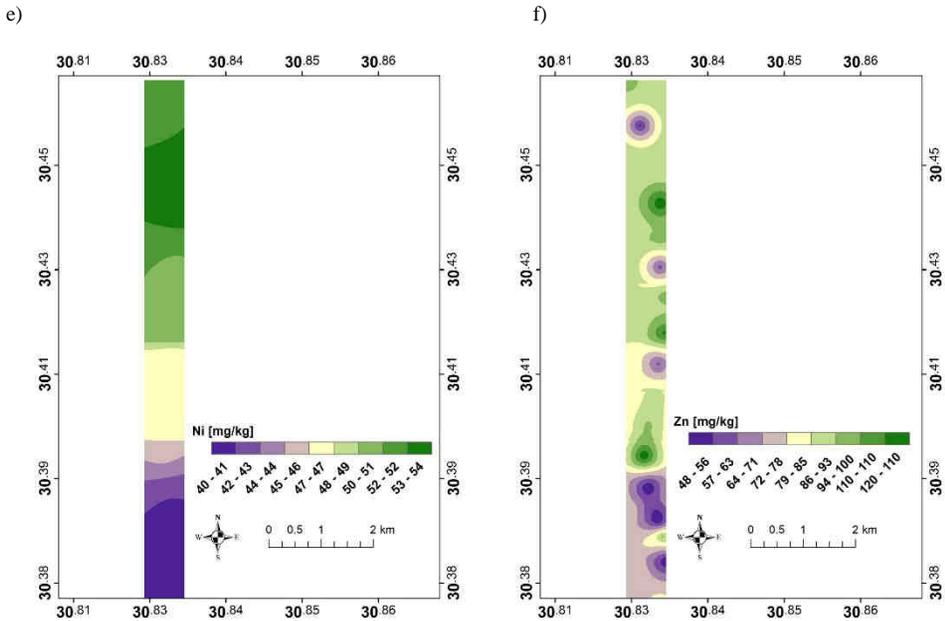


Fig. 4. The spatial distribution of heavy metals: a) As, b) Ba, c) Co, d) Cr, e) Ni and f) Zn

Assessment of contamination parameters from heavy metals

Metal Pollution Index *MPI*

The overall metal contents at the sites investigated in this study were compared, using the metal pollution index (*MPI*) calculated according to Usero et al [34, 35] with the formula (1):

$$MPI = (As \cdot Ba \cdot Co \cdot Cr \cdot Ni \cdot Zn)^{1/6} \quad (1)$$

The obtained results for *MPI* are plotted in Figure 5. It is well known that the higher value of the *MPI*, the higher degree of pollution with the metal in the studied samples. From the current work, *MPI* ranged between 31.4 to 77.8 with an average of 55.5 with standard deviation of 15.2 and standard error of 3.4. *MPI* is considered high in some locations such as w-03, w-04, w-07 and w-12 and this can be explained by the contamination from the industrial areas of Sadat City.

Similar work was done by El Nemer [36] on sediments from Lake Burullus (*MPI* = 162.5) and comparing with those done it was found that in the current work the *MPI* is less than calculated by [36]. The *MPI* was calculated for the studied elements from different work and *MPI* for Upper Continental Crust UCC content of the 6 elements as shown in Table 7.

The obtained *MPI* for different work which was carried out in Egypt compared with the present work was plotted as shown in Figure 6. It is clear that the *MPI* from the present work is higher than those of UCC done in [2, 12] and almost near to the results done in [37]. It could be explained by existence of the studied area in the west of Nile Delta near to

Sadat City. *MPI* has a significance value from the work done in [36] which is higher three times than the *MPI* in the present work because of Lake of Burullus is a closed aquatic system and the disposal rate of waste from industry and sewage is high.

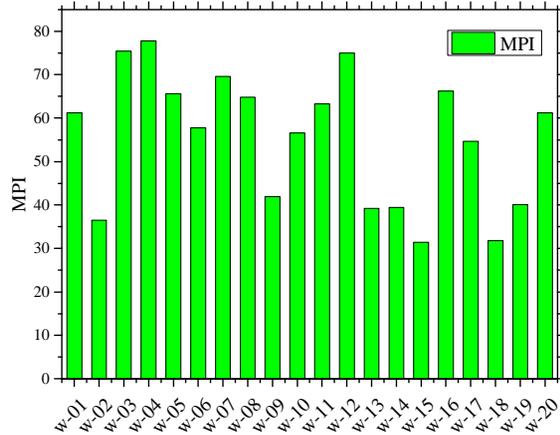


Fig. 5. *MPI* value in different locations of the soil samples

Table 7

MPI of the studied contaminants from different work

Country	<i>MPI</i>	Reference
Egypt (Lake Burullus)	162.51	[36]
Egypt (Nile Delta)	45.47	[2]
UCC*	49.72	[37]
UCC**	39.75	[12]
Present work	55.50	Current

*Composition of the Upper Continental Crust by [37], **Upper Continental Crust by [12]

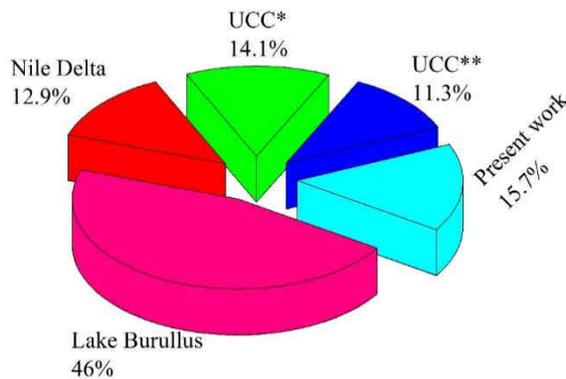


Fig. 6. *MPI* pie chart of present work compared with [2, 12, 36, 37]

Enrichment Factor

Enrichment Factor (EF) can be easily used to differentiate between elemental contents from anthropogenic source and those from natural origin. EF values between 0.5 and 1.5 indicate the metal is entirely from crustal materials or natural origin, while $EF > 1.5$ suggests that the sources are more likely to be anthropogenic [38]. Using the equation (2) the EF was calculated and it is given in Table 8 [39]:

$$EF = (C_x/C_{Fe})_{Sample} / (C_x/C_{Fe})_{reference} \quad (2)$$

where $(C_x/C_{Fe})_{Sample}$ is ratio of the content of the element in the sample and the content of Fe in the sample while $(C_x/C_{Fe})_{reference}$ is the ratio of the same element the Continental Shale and the content of Fe in the Continental. The world average elemental contents reported by Turekian and Wedepohl [16] in the earth's crust were used as reference in this study because the regional geochemical background values for these elements are not available.

As follows from Table 8, Ba has the lowest enrichment factor EF and As has the highest one, while Co, Cr, Ni, and Zn are of minor enrichment.

Table 8

Levels of metal pollution suggested by Chen et al [40]

EF Value	Enrichment level [40]	Enrichment of metals in the samples of present study
$EF < 1$	no enrichment	Ba
$1 < EF < 3$	minor enrichment	Co, Cr, Ni, Zn
$3 < EF < 5$	moderate enrichment	
$5 < EF < 10$	moderate to strong enrichment	As
$10 < EF < 25$	strong enrichment	
$25 < EF < 50$	very strong enrichment	
$EF > 50$	extremely strong enrichment	

Conclusion

The contents of 6 elements As, Ba, Co, Cr, Ni, and Zn in 20 samples collected along El Manashi Tawfikia canal - Sadat City were determined. The plotted spatial distribution of heavy metals in soil showed a noticeable increase of their content upwards the direction of the Mediterranean Sea. MPI parameter was calculated to study the overall content of heavy metals which ranged from 32 to 78 with an average value of 55 ± 15 , and it is less than that calculated by El Nemer [36] for the sediments from Lake Burullus ($MPI = 162.5$). It was shown that As moderately enriched in the study area: $5 < EF < 10$.

Acknowledgments

The authors express their gratitude to Mr. Ahmed Zahw (Faculty of Science, Menoufia University) for collection of samples for this study. The authors also acknowledge the grant # 405 for 2012-2014 of the Academy of Scientific Research and Technology of Egypt and Joint Institute for Nuclear Research, Dubna, Russia (ASRT-JINR).

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