

Characterization Changes of Heavy Metals Contents and Fractions in Sewage Sludge from Sirt Wastewater Treatment Plant, Libya

R. M. R. Hedia

Soil and Water Sciences Department, Faculty of Agriculture, Alexandria University, Alexandria, Egypt.

MONITORING changes of the main chemical properties of sewage sludge from Sirt Wastewater Treatment Plant, Libya was investigated. Ten random sewage sludge samples were monthly collected for a time span of one year. Average year values of TDS, pH, organic matter and C/N recorded 1428.91 mg kg⁻¹, 6.90, 76.3% and 7.97, respectively. Total N, P and K contents were in the normal range (5.63, 1.41 and 0.019%, respectively). The total concentrations of Fe, Zn and Mn recorded high levels (2768, 1142 and 169 mg kg⁻¹, respectively). Low and more fluctuated total concentrations of Cu, Pb and Ni were recorded (107, 45 and 35 mg kg⁻¹, respectively). In general, the total concentrations of heavy metals were found to be far below the US-EPA ceiling limits except Cd and As which had concentrations at or very close to their ceiling limits. The BCR sequential extraction scheme was applied to investigate the fractionation of heavy metals in the sludge. More than 50% of total As, Pb, Fe, Mn and P were found in the fourth residual stable fraction while the other heavy metals were mostly released in the first three more mobile fractions (soluble-exchangeable, reduceable and oxidizable) of the applied fractionation scheme. Special cautions should be considered when using this sludge safely in agriculture concerning the calculation of the loadings of heavy metals and their mobility in soils.

Keywords : Heavy metals, Sewage sludge, Sirt wastewater treatment plant, Libya .

Due to the yearly increasing amounts of sewage sludge as well as the simplicity of its use, a lot of attention has been paid to its application in agriculture. Sewage sludge is characterized by an abundance of organic matter and several nutrients (Lasheen and Ammar, 2009, Garcia-Delgado *et al.*, 2007, Jakubus and Czekala, 2001 and Hani, 1991). Advantageous effects on the physical and chemical soil properties should be taken into account when applying sewage sludge to agricultural soils, including the increase in bioavailability of phosphorus, cation exchange capacity and supplying the soil with exchangeable ions (Attenborough *et al.*, 1995 and Cavallaro *et al.*, 1993).

Unfortunately, sewage sludge potentially carries pollutants, since many wastewater treatment plants receive discharges not only from residential areas but also from industrial ones (Iwegbue *et al.*, 2007, Dai *et al.*, 2007, Bright and

Healey, 2003 and Berti & Jacobs, 1998). The pollutants such as heavy metals are transferable and are not biodegradable, and at some levels, they become toxic and tend to accumulate along the food chain, where man is the last sink (Dudka and Miller, 1999 and Amir *et al.*, 2005). Therefore, sewage sludge undergoes a strict process of verification in terms of total heavy metal content. On the other hand, total metal contents are not the best indicators of their bioavailability and do not determine the character of bonds in which they occur (Hooda and Alloway, 1994). Thus, it is possible to establish the degree of their solubility and mobility in the environment only by taking into account various physical and chemical forms created by these elements. In this way, it is also possible to determine their availability for plants. Several authors (Jamali *et al.*, 2009, Wang *et al.*, 2006, Amir *et al.*, 2005, Fuentes *et al.*, 2004 and Merrington *et al.*, 2003) have investigated the distributions of total and chemical fractions of heavy metal elements in sludge at different process stage.

The mobility of heavy metal combinations in sludge in terms of the rate of their release and potential negative effect on soil and plants can be assessed using the sequential extraction procedures (Lin *et al.*, 2007 and Fuentes *et al.*, 2004). These methods facilitate the determination of the percentage of water-soluble, exchangeable and easily soluble forms in the total metal content in sludge. On the basis of such information, the amount of a given element is established as it may be either a potential source of the nutrient for plants, or a threat for both plants and the whole environment (Bright and Healey, 2003). Therefore, the aims of this study were to characterize the sewage sludge produced from Sirt Wastewater Treatment Plant, Libya and to investigate the total content of some heavy metals and their chemical fractions and forms in this sludge and monitor their changes along a one year time period.

Material And Methods

The Sirt Wastewater Treatment Plant, located in the north-western part of the city was launched in 1995 with an area of 45 ha, for a secondary treatment of sewage water of Sirt city,. With almost seventy thousands of total population and according to the latest records of the year 2009/2010, the plant treats and discharges about 7.67×10^5 m³/yr of sewage water (Abufayed and Elkebir, 2010 and SWTPR, 2010). Solids separated from the primary and secondary precipitation processes are combined to form the raw sludge produced by this plant. This raw sludge is being stored in heaps on a 17 ha yard area.

Sludge sampling

Sludge samples were taken from each recent heaps and from various places in the heap, using an 8 cm i.d. auger. Sampling process was carried out monthly started in November, 2009 till October, 2010. Samples were generally not taken from the outer layer of the heap, as the material tended to be very dry in those places. After 10 individual samples were taken from the heap, they were all mixed together and one representative sample was compiled for analysis. The

collected material was prepared by air-drying and ground to pass through 0.5 mm stainless steel sieve.

Characterization of the sewage sludge

The sludge samples were analyzed for the main basic physicochemical properties using standard procedures described by Black (1965) and Page *et al.* (1982) as follows:

The concentration of TDS (mg/kg dry matter): 1:5 sludge : water extract was used to measure total dissolved solids (TDS) by an electrical conductivity meter (Jenway, Model 4520). The *pH* was measured by a pH-meter (Jenway, Model 3520) with a glass electrode in 1:2.5 extract of 1.0 M KCl.

Organic matter (OM, %): Sludge samples were ignited at 550°C for 8 hr, weight loss representing the loss of organic material. The amount of *Organic carbon (OC, %)*, was determined by wet dichromate oxidation with sulphuric acid of Walkley-Black. The amount of *Total Nitrogen (TN, %)* was determined using Kjeldhal method.

Total heavy metal content (mg/kg dry matter) was determined following HF digestion. The mixture was evaporated to dryness and the residue was dissolved in 2.0M HNO₃. All reagents used for analysis were pure.

Total metals content, 0.2 g of powdered dry samples were digested using 8 ml HNO₃ and 2 ml HClO₄ in a 25 ml Teflon vials for 6 hr at room temperature. 1 ml of HF acid was then added, mixed and heated until near dryness. The cooled residues were dissolved in 5ml 5% HNO₃ and suitable DDW volumes were added up to 25 ml in total. Total Phosphorus (*TP, %*) in the extract was determined by using the ammonium molybdate -ascorbic acid method described by Murphy and Riley (1962), and the Jenway, Model 6310 spectrophotometer was used.

All analyses were carried out in triplicate and the average values were calculated.

Fractionation of metals in sludge using BCR Scheme

The sequential extraction analysis of metals in sludge was performed according to four-step sequential extraction procedure described by Ure *et al.* (1993) and applied by many authors (Fuentes *et al.*, 2004, Scancar *et al.*, 2000 and Rauret *et al.*, 1999). An around-year composited sludge sample was used in this part by taking 5 g air-dried monthly sludge samples which were kept frozen till the end of the year. These samples were finally thoroughly and carefully mixed to form a representative sample on which fractionation experiment was conducted. The conducted extraction procedure was as follows:

Step (1) *Water-soluble and Exchangeable/acid fraction (S1):* 0.5 g of powdered sludge sample was well homogenized with 20 ml 0.11M acetic acid in a 50 ml centrifugal PE-tube. The tubes were shaken at 200 rpm for 16 hr at room

temperature. The suspension was centrifuged at 4000 rpm for 25 min and the extract was transferred into a PE-tube for keeping at -4°C . The residue was rinsed with 16 ml of double-distilled water (DDW) by shaking for 15 min at 200 rpm and the liquid supernatant was removed after centrifuging.

- Step (2) *Reducible fraction (S2)*: the residue from the step (1) was extracted with 20 ml 0.1M $\text{NH}_2\text{-OH-HCL}$ (pH 2) for 16 h in the PE-tube, which was shaken at 200 rpm for 16 h at room temperature. The extract was transferred into a PE-tube for keeping at -4°C after centrifuging at 4000 rpm for 25 min. The residue was rinsed with 16 ml of DDW by shaking for 15 min at 200 rpm and the liquid supernatant was removed after centrifuging.
- Step (3) *Oxidizable fraction (S3)*: residue from step (2) was oxidized with 8 ml H_2O_2 (30%) for 4 hr. Another 8 ml of H_2O_2 was added and digestion was allowed to proceed to near dryness at 85°C by heating the uncovered tube in a water bath. 40 ml 0.1 M NH_4OAc (adjusted to pH 2 with nitric acid) was added to the cooled residue, which was then shaken for 16 hr at room temperature. The extract was transferred into a PE-tube for keeping at -4°C after centrifuging. The residue was rinsed with 16 ml of DDW by shaking for 15 min at 200 rpm and the liquid supernatant was removed after centrifuging.
- Step (4) *Residual fraction (S4)*: the metal content in residual fraction was extracted by 16 ml of concentrate HF acid.

The percent of heavy metal fractions to the total content of sludge of each corresponding metal was calculated. Total contents as well as amounts of heavy metals and nutrients in sequential extractions were measured by AAS Flame Photometry (Thermo Scientific, Model iCE 3500). Ca, Mg and K elements were determined using Flame Photometer (Corning, Model FP 410). Analyses were carried out in triplicate.

Results and Discussion

Chemical properties and nutrients content

Monthly measured values of some chemical properties and composition of the studied sewage sludge are presented in Table 1 and the descriptive statistics of these values are presented in Table 2. The TDS values ranged from 1261.57 to 1766.40 mg kg^{-1} with an average of 1428.71 ± 138.13 around the year (Table 2). It can be noticed that TDS values reached their highest values during July and August (Table 1). This may be due to the highest temperature and the lowest domestic water consumption in the city during summer vacation. The average TDS measured values of Sirt sludge can be considered of low values if compared with those of other sludge materials (Elsokkary and Abdel Salam, 1998, El-Sayed, 1998 and El-Shebiny & Khalifa, 2001). Measured pH values ranged from 6.71 to 7.07 with an annual average of 6.90 ± 0.11 (Table 3). The highest pH values were observed in May through August (Table 1). These measured pH values can be considered within the normal range of such materials reported by many authors. Total organic carbon (OC, %) and total nitrogen (TN, %) contents ranged from 37.21 to 49.64 % and from 4.65% to 6.41 %, respectively.

respectively with averages of $44.68 \pm 3.28\%$ and $5.63 \pm 0.55\%$, respectively (Table 3). It was found that OC recorded the lowest levels in June through August period (Table 1). The C/N ratios were also calculated and were found to range from 6.87 to 8.76 with an average 7.97 ± 0.65 around the year (Table 3). The lowest C/N ratio was observed in August (Table 1), presumably as a result of high air temperature and the consequent nitrogen volatilization from the sludge heaps. Organic matter content recorded a range from 73.14 to 79.98% with an average of $76.30 \pm 2.30\%$ around the year (Table 3). These C/N and OM values were found to fall within the normal range of sewage sludge material investigated by many authors (Elsokkary and Abdel Salam, 1998, El-Sayed, 1998, Harrison *et al.*, 1999 and El-Shebiny & Khalifa, 2001).

Total phosphorus and total potassium contents of the sludge ranged from 1.29 to 1.53% and from 169.86 to 20.51 mg kg⁻¹ with averages of $1.41 \pm 0.07\%$ and 185.91 ± 9.57 mg kg⁻¹, respectively (Table 3). These results were also found to be consistent with many other investigations on the nutrients contents of sewage sludge from Egypt (El-Shebiny and Khalifa, 2001, Harrison *et al.*, 1999, Elsokkary and Abdel Salam, 1998 and El-Sayed, 1998) or sludge samples from eight states in USA (Kelley *et al.*, 1984). Comparison between the tested Sirt sludge and the analyses of other sludge materials revealed that N, P and K contents of Sirt sludge can be considered as moderate. Total calcium (TCa, %) and magnesium (TMg, %) contents recorded ranges of 1.06 - 2.08 % and 0.15 - 0.20% with averages of $1.78 \pm 0.17\%$ and $0.17 \pm 0.02\%$, respectively (Table 3).

Total concentration of heavy metals

Results of the total concentration of heavy metals in the tested Sirt sludge are presented in Table 2 and depicted in Fig. 1 and their descriptive statistics are presented in Table (3). The total concentrations of Fe, Zn and Mn recorded the highest levels among the measured elements (Fig. 1). Ranges of total concentrations of these elements were from 2591.38 to 3055.41, from 985.69 to 1270.87 and from 23.70 to 203.14 mg kg⁻¹, respectively, with averages of 2767.87 ± 150.48 , 1141.57 ± 105.09 and 168.50 ± 27.57 mg kg⁻¹, respectively. A peak of total concentration Fe (3055.41 mg kg⁻¹) was observed in May while neither Mn nor Zn had certain trends. Comparison of the measured total concentration of Zn in the sludge with the US-EPA ceiling limits (Table 3) showed that this sludge has very low content of total Zn. Lower and more fluctuated total concentrations of Cu, Pb and Ni were observed (Fig. 1) ranging from 90.29 to 24.09, from 37.77 to 59.03 and 23.95 to 41.05 mg kg⁻¹, respectively with averages of 106.73 ± 11.49 , 45.29 ± 6.57 and 34.71 ± 5.31 mg kg⁻¹, respectively. Examination of the total concentrations of these elements showed that they are far below the US-EPA ceiling limits (1500, 300 and 420 mg kg⁻¹, respectively). Total concentrations of Cr, Cd and As ranged from 48.54 to 61.69, 36.22 to 44.05 and 29.98 to 39.86 mg kg⁻¹, respectively and their averages recorded 54.09 ± 4.36 , 38.75 ± 2.42 and 32.93 ± 3.01 mg kg⁻¹, respectively (Table 3). Peaks of total concentration of 61.69 and 39.86 mg kg⁻¹ were observed for Cr and As, respectively in August and 44.05 mg kg⁻¹ for Cd in July (Table 2). Cr concentration was found to be far below the US-EPA limits (100 mg kg⁻¹) while Cd and As concentrations were at or very close to their ceiling limits (39 and 41 mg kg⁻¹, respectively).

TABLE 1 . Measured pH, EC, OM and total concentrations of some selected elements in Sirt sewage sludge .

Criteria	Months											
	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May.	Jun.	Jul.	Aug.	Sep.	Oct.
TDS, mg/kg	1261.6	1324.0	1342.5	1351.7	1380.4	1415.2	1496.1	1486.8	1568.0	1766.4	1440.0	1312.0
pH	6.71	6.81	6.89	6.87	6.91	6.90	7.03	7.06	7.07	6.83	6.88	6.85
OM, %	77.85	79.98	78.21	75.61	73.20	73.14	76.37	79.15	73.15	75.94	76.95	76.04
OC, %	43.20	47.38	45.68	47.05	44.98	46.27	49.64	37.21	42.25	42.08	43.51	46.87
TN, %	5.11	5.46	6.24	5.89	6.41	5.28	6.00	4.65	5.52	6.12	4.98	5.94
C/N	8.45	8.68	7.32	7.99	7.02	8.76	8.28	8.00	7.66	6.87	8.74	7.89
TP, %	1.50	1.35	1.47	1.40	1.36	1.53	1.49	1.39	1.29	1.41	1.38	1.35
TCa, %	1.61	1.67	1.73	2.08	1.69	1.87	2.04	1.98	1.63	1.82	1.60	1.64
TMg, %	0.152	0.157	0.163	0.195	0.159	0.176	0.192	0.186	0.154	0.171	0.150	0.154
TK (mg/kg)	197.59	178.11	193.39	184.68	179.03	201.51	196.93	183.69	169.82	185.89	182.41	177.90

TABLE 2 . Total concentrations of some selected heavy metals in Sirt sewage sludge.

Elements	Months											
	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May.	Jun.	Jul.	Aug.	Sep.	Oct.
	----- mg kg ⁻¹ -----											
As	30.01	30.51	31.62	29.98	30.75	32.37	33.61	33.06	37.55	39.86	32.94	32.88
Cd	39.11	39.04	37.53	36.22	36.41	39.51	36.97	37.14	44.05	42.67	38.54	37.81
Cr	48.54	49.11	51.12	50.64	51.03	53.14	52.36	56.34	58.34	61.69	57.69	59.14
Pb	40.53	59.03	47.75	45.37	38.44	45.04	50.59	51.72	38.48	40.07	37.77	48.66
Ni	29.34	34.30	38.31	35.72	40.23	27.08	36.55	41.05	37.32	23.95	34.46	38.25
Cu	113.54	120.97	118.83	124.09	97.07	97.92	96.35	114.65	95.78	90.29	102.36	108.96
Fe	2797.96	2648.12	2734.46	2591.38	2737.55	2976.63	3055.41	2948.94	2687.60	2692.27	2597.61	2746.51
Mn	130.29	173.35	202.83	197.49	151.46	203.14	165.18	177.76	123.70	188.20	137.95	170.70
Zn	1057.83	1150.09	1238.64	1163.79	1113.93	1249.73	998.37	1260.64	1187.11	1270.87	1021.84	985.96

TABLE 3. Descriptive statistics of the measured parameters of Sirt sewage sludge.

Criteria	Minim	Maxim	Mean	SD	US-EPA Ceiling Limits*
TDS, mg/kg	1261.57	1766.40	1428.71	138.13	-
pH	6.71	7.07	6.90	0.11	-
OM, %	73.14	79.98	76.30	2.30	-
TOC, %	37.21	49.64	44.68	3.28	-
TN, %	4.65	6.41	5.63	0.55	-
C/N	6.87	8.76	7.97	0.65	-
TP, %	1.29	1.53	1.41	0.07	-
Ca, %	1.60	2.08	1.78	0.17	-
Mg, %	0.15	0.20	0.17	0.02	-
K (mg/kg)	169.82	201.51	185.91	9.57	-
	----- mg kg ⁻¹ -----				
As	29.98	39.86	32.93	3.01	41
Cd	36.22	44.05	38.75	2.42	39
Cr	48.54	61.69	54.09	4.36	100
Pb	37.77	59.03	45.29	6.57	300
Ni	23.95	41.05	34.71	5.31	420
Cu	90.29	124.09	106.73	11.49	1500
Fe	2591.38	3055.41	2767.87	150.48	-
Mn	123.70	203.14	168.50	27.67	-
Zn	985.96	1270.87	1141.57	105.09	2800

* US-EPA (1993)

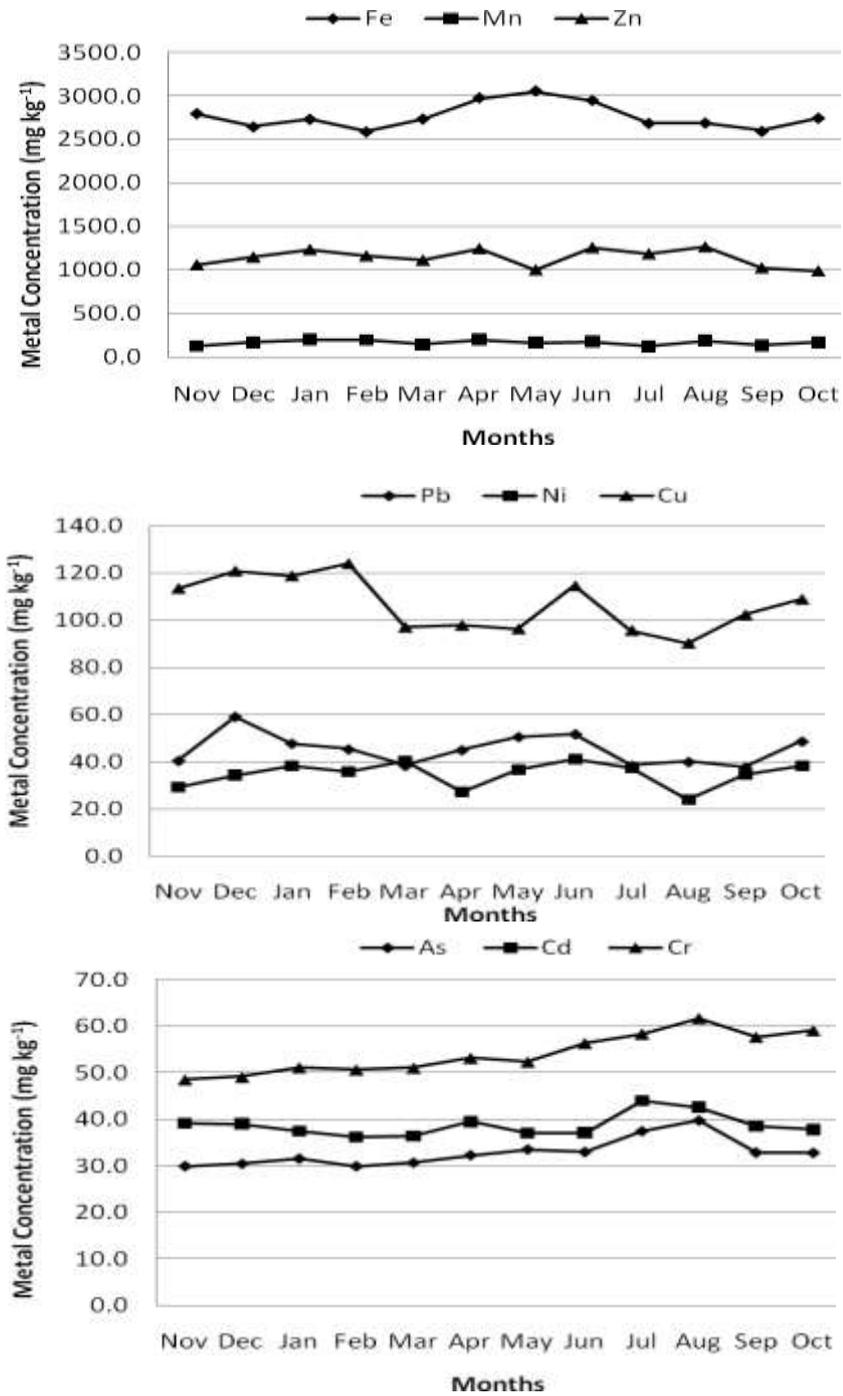


Fig. 1. Total concentration of some heavy metals of monthly collected Sirt sewage sludge samples from sirt wastewater treatment plant.

Egypt. J. Soil Sci. 54, No. 3 (2014)

Fractionation of heavy metals and plant nutrients in sewage sludge

The partitioning of the studied metals were determined (mean of five subsamples) and are presented in Fig. 2. The relative standard deviation of parallel determinations in each particular step was found to be better than $\pm 6\%$ for all metals analyzed. This indicates that the sample was homogeneous (Scancar *et al.*, 2000). For all metals; concentrations determined in a particular extraction step were higher than their corresponding detection limits. Concentrations of each metal in steps 1-4 were summed and compared to its total concentration. The mass balance of metals analyzed agreed within $\pm 4\%$ for Cd, Pb, Ni, Cu, Fe, Mn and Zn and $\pm 6\%$ for As, Cr and P. These data can be taken as an indication for the precision of the analytical work.

From the obtained data shown in Fig. 2, it is evident that the concentrations of water-soluble and exchangeable fraction (S1) are very low for As, Cr, Pb, Cu, Fe, Mn and P. (0.4 - 1.7%), moderate for Cd (11.7%) and high for Zn and Ni (45.8 and 48.0%, respectively). Although the total concentrations of these metals are below the ceiling limits of US-EPA (Table 2), this fraction is considered of high mobility and bioavailability. Therefore, this sludge can be safely used in agriculture but special caution is to be taken to calculate the loadings of these heavy metals of moderate and high mobility and bioavailability (LIU and SUN, 2013, Garcia-Delgado *et al.*, 2007 and Harrison *et al.*, 1999). It can be further seen from Fig. 2 that 53.1% of the total Cd was released in the second sparingly soluble fraction (S2, bound to Fe and Mn oxides and hydroxides). The portions of the other heavy metals released in this fraction were below 40% and was 11% for P. The third fraction (S3, oxidizable fraction) ranged from 54.1 to 61.8% for Cu and Cr; from 10.2 to 34.6% for Zn, Ni, Cd and P, from 1.1 to 5.1% for Fe, Mn, As and Pb. More than 50% proportion of As, Pb, Fe, Mn and P were found in the fourth residual fraction (S4: 53.2 - 59.29%). However, other heavy metals were mostly released in the first three fractions of the applied fractionation scheme. The same results were obtained by other authors for the fractionation of these heavy metals in different sewage sludge materials (LIU and SUN, 2013, Jamali *et al.*, 2009, Wang *et al.*, 2006, Amir *et al.*, 2005, Fuentes *et al.*, 2004, Merrington *et al.*, 2003 and Scancar *et al.*, 2000).

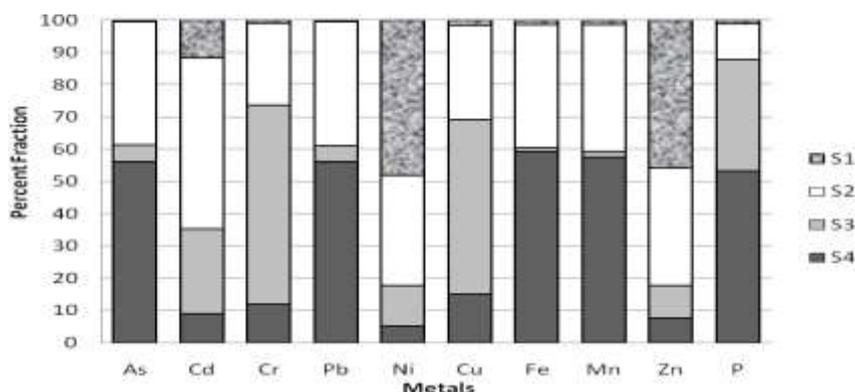


Fig. 2. Percent fraction distribution of some heavy metals and plant nutrients in Sirt sewage sludge: S1= Exchangeable; S2= Reducible; S3= Oxidizable; S4= Residual Fraction .

Egypt. J. Soil Sci. **54**, No. 3 (2014)

Conclusion

Sewage sludge from Sirt Wastewater Treatment Plant was analyzed for some chemical properties, nutrients contents and heavy metals total concentration and fractionation for a time span of one year. The TDS of the sludge was low and its reaction was slightly acidic. The organic matter, organic carbon, total nitrogen, total phosphorus and total potassium contents and C/N ratio were found within the ranges reported in the literature. Fluctuations in the values of these parameters along the year were observed. TDS values increased during the summer period. The total concentrations of Fe, Zn and Mn recorded the highest levels among the measured elements. Lower and more fluctuated total concentrations of Cu, Pb and Ni were observed. In general, the total concentrations of the analyzed heavy metals were found to be far below the US-EPA ceiling limits except Cd and As which had concentrations at or very close to their ceiling limits. The BCR scheme was applied to investigate the fractionation of these heavy metals in the sludge. More than 50% proportion of As, Pb, Fe, Mn and P were found in the fourth residual stable form while the other heavy metals were mostly released in the first three fractions of the fractionation scheme. Concerning heavy metals contents and their fractions, this sludge can be safely used in agriculture with special caution to the calculation the loadings of heavy metals and their relative mobility in the amended soil. Further investigations should be carried out to assess the environmental risks due to possible organic pollutants and pathogens.

References

- Abufayed, A.A. and Elkebir, A.A. (2010)** Water supply and sanitation in Libya: Gap analysis, national needs and UNDP interventions strategic entry points identification. Water Governance Program for Arab States, Tripoli
- Amir, S., Hafidi, M., Merlina, G. and Revel, J.C. (2005)** Sequential extraction of heavy metals during composting of sewage sludge. *Chemosphere* **59**: 801-810.
- Attenborough, G.M., Smith, S.R. and Minski, M.J. (1995)** The fate and environmental activity of heavy metals in sewage sludge applied to soil. In: *"International Conference Heavy Metals in the Environment"*, R., Wilken, U. Forstner and A., Knochel (Ed.), September – Hamburg.
- Berti, W.R. and Jacobs, L.W. (1998)** Distribution of trace elements in soil from repeated sewage sludge application. *J. Environ. Qual.* **2**: 1280-1286.
- Black, C.A. (1965)** " *Methods of Soil Analysis Parts 1 and 2* ", Am. Soc. Agron. No. 9, Madison, Wisconsin, USA .
- Bright, D.A. and Healey, N. (2003)** Contaminant risk from biosolids land application: contemporary organic contaminant levels in digested sewage sludge from five treatment plants in greater Vancouver. *British Columbia. Environ. Pollut.* **126**: 39-49.
- Cavallaro, N., Padilla, N. and Villarrubia, J. (1993)** Sewage sludge effects on chemical properties of acid soils. *Soil Sci.* **156** (2): 63-71.

- Dai, J.Y., Xu, M.Q., Chen, J.P., Yang, X.P. and Ke, Z.S. (2007)** PCDD/F, PAH and heavy metals in the sewage sludge from six wastewater treatment plants in Beijing, China. *Chemosphere* **66**: 353-361.
- Dudka, S. and Miller, W.P. (1999)** Accumulation of potentially toxic elements in plants and their transfer to human food chain. *J. Environ. Sci. Health B.* **34**: 681-708.
- El-Sayed, S.A.M. (1998)** Use of sewage sludge and farmyard manure as N-fertilizer in New Valley Governorate. *Egypt. j. Soil Sci.* **38**:1-19.
- El-Shebiny, G.M. and Khalifa, K.I. (2001)** Heavy metals content in maize plants as affected by sewage sludge fertilization. *Alex. Sci. Exch.* **22**: 33-42.
- Elsokkary, I.H. and Abdel Salam, A.A. (1998)** Bioavailability and DTPA-extractability of soil heavy metals from successive sewage sludge treated calcareous soil. *Alex. J. Agric. Res.* **43**: 349-365.
- Fuentes, A., Llorens, M., Saez, J., Soler, A., Aguilar, M. I., Ortuno, J. F. and Meseguer, V. F. (2004)** Simple and sequential extractions of heavy metals from different sewage sludges. *Chemosphere* **54**: 1039–1047.
- García-Delgado, M., Rodríguez-Cruz, M.S., Lorenzo, L.F., Arienzo, M. and Sánchez-Martín, M.J. (2007)** Seasonal and time variability of heavy metal content and of its chemical forms in sewage sludges from different wastewater treatment plants. *Sci. Total Environ.* **382**: 82–92.
- Hani, H. (1991)** Heavy metals in sewage sludge and town waste compost. In: "*Metals and Their Compounds in the Environment Occurrence, Analysis and Biological Relevance*", E. Merian (Ed.), pp. 357-367, Weinheim-New York-Basel-Cambridge.
- Harrison, E. Z., McBride, M.B. and Bouldin, D.R. (1999)** Land application of sewage sludge: an appraisal of the US regulations. *Int. J. Environ. Pollut.* **11**: 1-32.
- Hooda, P.S. and Alloway, B.J. (1994)** Changes in operational fractions of trace metals in two soils during two-years of reaction time following sewage sludge treatment. *Intern. J. Environ. Anal. Chem.* **57**: 289-297.
- Iwegbue, C.M.A., Emuh, F.N., Isirimah, N.O. and Egun, A.C. (2007)** Fractionation, characterization and speciation of heavy metals in composts and compost-amended soils. *African J. Biotech.* **6**: 67-78.
- Jakubus, M. and Czekala, J. (2001)** Heavy metal speciation in sewage sludge. *Polish J. Environ.* **10**: 245-250.
- Jamali, M.K., Kazi, T.G., Arain, M.B., Afridi, H.I., Jalbani, N., Kandhro, G.A., Shah, A.Q. and Baig, J.A. (2009)** Speciation of heavy metals in untreated sewage sludge by using microwave assisted sequential extraction procedure. *J. Hazard. Mater.* **163**: 1157–1164.
- Kelley, W. D., Martens, D.C., Reneau, R.B. and Simpson, Jr.T.W. (1984)** Agricultural Use of Sewage Sludge: A Literature Review. *Bulletin* 143, p. 46, Dept. Agron., Virginia Polytech. Inst. and State Univ.
- Egypt. J. Soil Sci.* **54**, No. 3 (2014)

- Lasheen, M.R. and Ammar, N.S. (2009)** Assessment of metals speciation in sewage sludge and stabilized sludge from different wastewater treatment plants, Great Cairo, Egypt. *J. Hazard. Mater.* **164**:740-749.
- Lin, Y., Ma, L., Li, Y. and Zheng, L. (2007)** Evolution of heavy speciation during the aerobic composting process of sewage sludge. *Chemosphere* **67**: 1025-1032.
- LIU, J. and SUN, S. (2013)** Total concentrations and different fractions of heavy metals in sewage sludge from Guangzhou, China. *Trans. Nonferrous Met. Soc. China* **23**: 2397–2407.
- Merrington, G., Oliver, I., Smernik, R.J. and McLaughlin, M.J. (2003)** The influence of sewage sludge properties on sludge-borne metal availability. *Adv. Environ. Res.* **8**: 21–36.
- Page, A.L., Miller, R.H. and Keeney, D.R. (1982)** "Methods of Soil Analysis", Part II, 2nd ed., Agron. Monogr. 9 Madison, Wisconsin, USA.
- Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure A.M. and Quevauviller, P.H. (1999)** Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monit.* **1**: 57-61.
- Scancar, J., Milacic, R., Trazar, M. and Burica, O. (2000)** Total metal concentrations and partitioning of Cd, Cr, Cu, Fe, Ni and Zn in ssewage sludge. *Sci. Total Environ.* **250**: 9-119.
- SWTPR (2010)** Sirt Wastewater Treatment Plant Records. Sirt, Libya.
- Ure, A.M., Quevauviller, P.H., Muntau H. and Griepink, B. (1993)** Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of European Communities. *Int. J. Environ. Anal. Chem.* **5**: 135-151.
- US-EPA (1993)** Standards for the use or disposal of sewage sludge; Final Rules. 40 CFR Part 257.
- Wang, C., Li, X.C., Wang, P.F., Zou, L.M. and Ma, H.T. (2006)** Total contents and extractable fraction of metals in sludges from urban wastewater treatment plants of China. *Pedosphere* **16**: 756-761.

(Received 27/10/2013;
accepted 29/ 9/ 2014)

دراسة خصائص التغيرات في المحتوى الكلي والصور الكيميائية للعناصر الثقيلة للحماة المنتجة من محطة معالجة مياه الصرف الصحي بمدينة سرت - ليبيا

رمزي مرسى رزق هدية

قسم علوم الأراضي والمياه - كلية الزراعة - جامعة الإسكندرية - الإسكندرية - مصر .

تمت في هذه الدراسة بحث الخصائص الكيميائية الأساسية والتركيزات الكلية للعناصر الثقيلة وتتبع تغيراتها وكذلك تقدير الصور الكيميائية لهذه العناصر في الحماة التي تنتج من محطة معالجة مياه الصرف الصحي بمدينة سرت - ليبيا. حيث تم تجميع عدد عشرة عينات من أماكن تخزين الحماة بالمحطة شهريا ولمدة عام كامل. وقد تم تجهيز العينات بالطرق المتعارف عليها تمهيدا لتحليلها. وأوضحت نتائج التحليل أن متوسط قيم المواد الصلبة الكلية الذائبة TDS ، ودرجة التفاعل pH ، ومحتوى المادة العضوية OM وكذلك نسبة الكربون:النيتروجين C/N سجلت 1428,91مجم/كجم ، 6,90 ، 76,3% ، 7,97 ، على التوالي. كما وجد أن محتوى هذه الحماة من عناصر النيتروجين N والفسفور P والبوتاسيوم K في المدى الطبيعي لهذا النوع من المواد حيث سجلت 5,63% ، 1,41% ، 1,019% على التوالي. وقد سجلت التركيزات الكلية للعناصر الثقيلة Fe ، Zn ، Mn في هذه الحماة هي الأعلى بالنسبة لباقي العناصر المقاسة حيث سجلت 2768 ، 1142 ، 169 مجم/كجم على التوالي. ووجدت مستويات أقل وتغيرات شهرية أكبر في التركيز الكلي لعناصر Cu ، Pb ، Ni والتي سجلت 107 ، 45 ، 35 مجم/كجم على التوالي. وعموما فقد وجد أن التركيزات الكلية للعناصر الثقيلة التي تم تقديرها في هذه الحماة أقل بكثير من الحدود المسموح بها لاستخدام الحماة في الزراعة والتي وضعتها هيئة حماية البيئة الأمريكية US-EPA عام 1993، ما عدا عنصري As ، Cd والتي سجلت تركيزات تقترب أو عند الحدود المسموح بها. كما تم استخدام نظام BCR للإستخلاص المتتابع Sequential Extraction لتقدير الصور الكيميائية Chemical Fractions للعناصر والتي تتواجد عليها في الحماة. وقد دلت النتائج المتحصل عليها أن أكثر من 50% من التركيز الكلي لعناصر As ، Pb ، Fe ، Mn ، P وجدت في الصور المتبقية الرابعة في نظام الإستخلاص والتي تعتبر الأعلى ثباتا ، بينما باقي العناصر Cu ، Cr ، Ni ، Cd تواجدها في الصور الكيميائية الثلاثة الأولى والأسهل في الانطلاق أو التحرر (الصورة الذائبة القابلة للتبادل ، الصورة القابلة للاختزال ، الصورة القابلة للاكسدة). وعليه فإن الاستخدام الامن لهذه الحماة في الزراعة يجب وأن يؤخذ بوجه الحذر من ناحية حساب الحمل التراكمي من العناصر الثقيلة وحركتها في التربة على المدى الطويل .