

Impact of Sewage Sludge Spreading on Heavy Metal Speciation in Ecosystem

M. N. Rashed* , M.E. Soltan, E.M.Fawzey, and M.A.El-Taher

Chemistry Department, Aswan Faculty of Science, South Valley University

81528 Aswan, Egypt.

mmrashed@hotmail.com

Abstract- Distribution, mobility and toxicity of heavy metals in the environment depend on the association form in the solid phase to which they are bound. Sequential extraction techniques used to obtain suitable information about heavy metals bounding form and eco- toxicity. In this work, the speciation of heavy metals (Cd, Co, Cu, and Pb), individual metal contamination factor (Cf) and mobility of metals from sewage sludge hills to surrounding ecosystem were conducted. An optimized two sequential extraction (Tessier and BCR) and single extraction procedures for sewage sludge were used. Sewage sludge samples were collected from sludge hills near a wastewater treatment plant at Kema region Aswan. The percentage of each metal as residual, oxidizable, reducible and exchangeable form was calculated. The results revealed that on the basis of heavy metals speciation, the individual contamination factor values of Cd and Co have the highest mobility (Cf: 27.38 and 36.36, respectively) and susceptibility to be released from the sludge, while Pb and Cu have the lowest mobility (Cf 2.25 and 1.39, respectively). This study provides valuable information on the mobility of metals in sludge and helps in predicting their behaviour to the ecosystem.

Keywords- Heavy metals; pollution; sewage sludge; contamination; metal speciation

I. INTRODUCTION

Sewage sludge is an unavoidable by-product of wastewater treatment plants and problematic in its disposal. The accumulation of sewage sludge from urban wastewater treatment is a growing environmental problem. However, this practice represents a potential threat to the environment because of the possible high heavy metal content. The main problem may be aggravated if the toxic metals are mobilized in the soil and be taken up by plants or transported in drainage waters or scattering to air cause air pollution [1- 4].

Metal accumulation in sludge poses an environmental problem concerning possible metal transfer from these sludge to ecosystem as well as their uptake by plants, thereby including them in the food chain. In order to estimate the reliable bioavailability of metals in the swage sludge, their capacity for mobilization and their potential toxicity it is desirable to determine the different chemical forms or ways of binding between heavy metals and the sludge sample [5 -6].

The distribution of metals in sewage sludge can provide researchers with evidence of the anthropogenic impact on ecosystems and, therefore, aid in assessing the risks associated with discharged human waste. The analysis of heavy metals is a very important task to assess the potential environmental and health risk associated with the sludge coming from waste water treatment plants. However, it is widely accepted that the determination of total elements does not give an accurate estimation of the potential environmental impact. So, it is necessary to apply sequential extraction techniques to obtain

suitable information about their bio availability or toxicity [7, 8].

Although the separation of various chemical forms of heavy metals is very difficult, the use of sequential extraction methods in this way provides an important approach. The application of sequential extraction procedures provides relevant environmental information on polluted samples. Therefore, several sequential extraction schemes have been developed to predict the metal distribution among different fractions, usually including exchangeable, associated to carbonates, associated to Fe–Mn oxides (or reducible), associated to organic matter and sulfides (or oxidizable) and residual [9-13].

The Community Bureau of Reference (BCR) in 1987 began a programme to harmonise the methodology used in the sequential extraction schemes used for determining metals in soils and sediments [14]. This procedure has been successfully applied to a variety of matrices, including lake, lagoon and marine sediments, sewage sludge, soil and industrially contaminated made-up ground [1, 2, 3, 15-20].

During recent decades, a great variety of extraction schemes, both simple and sequential have been developed. Sequential extraction is recognized as the best available method for gaining information on the origin, manner of occurrence, bioavailability, mobilization and transport of heavy metals and also, therefore, for sewage sludge [21].

The main objective of this work was to compare, in treated sewage sludge samples, the results the extracted heavy metals Cd, Co, Cu and Pb obtained using the conventional Tessier and BCR sequential extraction methods with those achieved from single extractions, employing similar operating conditions to the corresponding Tessier and BCR individual steps. Also the objective was to evaluate the studied metals toxicity through calculating the metal contamination factor (cf).

II. METHODOLOGY

A. Sample Collections

Sewage sludge samples were collected in polyethylene containers from wastewater treatment plant located in Kema region Aswan. The samples were dried at 110 °C in an oven until a constant weight was achieved, after which one part of the sample was ground using an agate mortar. Then, the sample was sieved and the sludge with a particle size < 70 µm was separated. The sieved sample was kept in polyethylene bags until sequential extraction or digestion for total analysis.

B. Reagents and Glassware

Extraction solutions (listed in the protocol of the Tessier and BCR schemes) were prepared from analytical-reagent grade reagents (BDH, UK). Standard solutions of Cd, Co, Cu, and Pb were prepared by dilution of metal certified standard solutions (1000 ppm) for atomic absorption spectrometry (BDH, UK). The hydroxyl ammonium chloride was prepared prior to use. Dilute nitric acid and ammonia solutions were used for pH adjustments. All glassware and plastic materials used were previously treated for 24 h in 2M nitric acid and rinsed with double distilled water and then with ultra pure water. 50ml of acid washed polyethylene centrifuge tubes was used for extraction, while 50 ml polyethylene vessels

C. Instrumentation

Metal determination in the extracts was carried out by means of a Perkin-Elmer Model 2380 double-beam atomic absorption spectrometer. Hollow cathode lamp for each metal was used as radiation source. Resonance lines employed were 324.8, 357.9, 230.0, 217.0 and 213.9 nm for Cu, Co, Pb and Cd, respectively. Lamp intensity and band pass width were used according to the manufacturer's recommendations. WIROWKA Laboratoryjna type WE-1, nr-6933 centrifuge; speeds range 0–6000 rpm, timer 0–60 min (Mechanika Phecyzyjna, Poland) used for centrifugation.

D. Swage Sludge Analysis

The chemical parameters (C, O, Mg, Al, Si, S, P, Ca and Fe) in the sewage sludge samples are presented in Table I.

TABLE I CHEMICAL ANALYSIS OF SEWAGE SAMPLE

Element	C	O	Mg	Al	Si	S	P	Ca	Fe
Concentration (%)	64	6.3	0.63	2.4	8.36	2.44	1.62	9.81	4.4

TABLE II HEAVY METAL CONCENTRATIONS IN CERTIFIED STANDARD REFERENCE MATERIAL

Metal	Unit	Certified Concentration	Measured	Recovery %
Cd	mg/kg	0.148±0.21	0.150±0.26	98
Co	mg/kg	0.9±0.007	0.8±0.010	1.12
Cu	mg/kg	10.01±0.34	10.06±0.44	99.5
Pb	mg/kg	2.008±0.039	2.010±0.41	99.9

E. Quality Control and Analysis

The quality control of the experiments was performed with the analysis of the certified reference materials (SRM1646a Estuarine sediment) obtained from the National Institute of Standards and Technology. The analyses of the sequential extractions procedure were being replicated three times. A blank was also run at the same time. All glassware and plastic containers were previously soaked in suprapure nitric acid (Merck) overnight, and rinsed with deionized water. The results and the certified values are presented in Table II. A good agreement was observed between the obtained and the certified values for the metals analyzed (Cd, Co, Cu and Pb).

F. Sequential Extraction

Sequential extraction involves the treatment of a sewage sludge material with a series of chemical reagents with increasing dissolution and displacement power, in order to extract metals according to the chemical activity and property of their binding to the solid. Depending upon the reagents chosen, the method can assess the level of water-soluble and exchangeable metals, as well as metals contained in easily reducible or oxidizable compounds. Thus, the Tessier and BCR sequential extraction methods were applied in this paper. Sequential extraction was performed using five-stage Tessier method and three-stage procedure recommended by BCR.

1). Tessier Scheme

Step 1. (F1) Exchangeable/acid soluble fraction

One gram of sludge was agitated at room temperature for 1 h with 8 ml of 1 mol/l MgCl₂ at pH7.

Step 2. (F2) Associated to carbonates fraction

The solid residue from step 1 was agitated with 8 ml of 1 mol/l sodium acetate/acetic acid buffer at pH 4.5 for 15 h at room temperature.

Step 3. (F3) Associated to Fe–Mn oxides (or reducible)

The solid residue from step 2 was extracted with 20 ml of 0.04 mol/l hydroxylamine hydrochloride in 25% (v/v) acetic acid at 96±5 °C in a water bath for 5 h 30 min.

Step 4. (F4) Associated to organic matter (or oxidizable)

The residue from step three was extracted with 3 ml of 0.02 mol/l nitric acid and 5 ml of 30% (v/v) hydrogen peroxide. The mixture was heated to 85±5 °C in a water bath for 2 h. A second aliquot of 3ml of 30% H₂O₂ was then added and the mixture was heated at the same temperature for 3 h. After cooling, 5 ml of 3.2 mol/l ammonium acetate in 20% (v/v) nitric acid were added. Then, the sample was diluted to 20 ml and agitated continuously for 30 min.

Step 5. (F4) Residual fraction

The final solid residue was digested with a mixture of hydrofluoric and perchloric acids in Teflon beakers. A 0.2 g of sample was first digested with a solution of concentrated HClO₄ (2 ml) and HF (10 ml) and evaporated to near dryness; subsequently a second addition of HClO₄ (1 ml) and HF (10 ml) was made and again the mixture was evaporated to near dryness. Finally HClO₄ (1 ml) was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in concentrated nitric acid and diluted to 25 ml.

2). BCR Scheme

The BCR three-step sequential extraction procedure described by Ure et al. [14] was followed.

Step 1. (F1) Exchangeable/acid soluble fraction

40 ml of acetic acid (0.11 mol/l) was added to 1 g sludge in a 100 ml centrifuge tube with stopper and extracted by shaking for 16 h at 22±5 °C (overnight). No delay should occur between the addition of the extractant solution and the beginning of the shaking. The extractant was separated from the solid residue by centrifugation at 3000 rpm for 20 min and supernatant liquid was decanted into a polyethylene container and analysed immediately. The residue was washed by adding 20 ml distilled water, shaking for 15 min on the end-over-end

shaker and was centrifuged for 20 min at 3000 rpm. The supernatant was decanted and discarded.

Step 2. (F2)Reducible fraction

40ml of a freshly prepared of hydroxylamine hydrochloride(0.1 mol/l) was added to the residue from step 1 in the centrifuge tube, resuspended by manual shaking, and then extracted by mechanical shaking for 16 h at 22 ± 5 °C(overnight). No delay should occur between the addition of the extractant solution and the beginning of the shaking. The extractant was separated from the solid residue by centrifugation and decantation as in step 1. The extract was retained in a polyethylene container, as before, for analysis. The residue was washed by adding 20 ml distilled water, shaking for 15 min on the end-over-end shaker and centrifuging for 20 min at 3000 rpm. The supernatant was decanted and discarded

Step 3. (F3)Oxidizable fraction

10 ml of hydrogen peroxide (8.8 mol/l)was added carefully to the residue in centrifuge tube and was digested at room temperature for 1 h with occasional manual shaking. The digestion was continued for 1 h at 85 ± 2 °C, with occasional manual shaking for the first 1/2 h in a water bath and then the volume was reduced to less than 3 ml by further heating of the uncovered tube. A further aliquot of 10 ml of hydrogen peroxide was added. The vessel was covered again and heated to 85 ± 2 °C and was digested for 1 h, with occasional manual shaking for the first 1/2 h . The cover was removed and reduced the volume of liquid to about 1 ml. 50 ml of ammonium acetate (1.0 mol/l) was added to the cool moist residue and was shaken for 16 h at 22 ± 5 °C(overnight). The extract was separated from the solid residue by centrifugation and decantation as in step 1.

Step 4. (F4)Residual fraction

The residue was digested with HF/HNO₃/HClO₄.

3).Single Extractions

Single extractions were carried out by employing a separate aliquot of sample (2 g) for each individual reagent. Centrifugation and storage of extracts was performed as in the sequential extraction schemes. However, in this case, the solid residue was also rejected. The main advantage of this proposed procedure is that all fractions can be simultaneously extracted and, consequently, it supplies faster results than the sequential methods. In contrast, a larger sample amount is needed, which does not pose an additional problem when environmental samples are being studied. With the exception of the first fraction of the two methods, the metal content corresponding to each individual fraction was calculated by subtracting the results obtained in two consecutive stages. In all cases, metal recovery was calculated as the following ratio: [metal content using single extraction/metal / content using sequential extraction] X 100

III. RESULTS AND DISCUSSION

The accuracy of the method was checked by recovery studies. The results of this study provide important information on the potential of the heavy metals to the environment ecosystem. The average concentration of heavy metals in samples by Tessier and BCR methods were presented in Tables III and IV.

A. Application of Sequential Extraction Scheme

1).Heavy Metal Distribution in Sewage Sludge by Tessier Sequential and Single Extraction Scheme

Extractable Pb, Cd ,Co and Cu concentrations in sewage applying both conventional Tessier method and single extraction are shown in Table III and Figure 1 and distributed in different fractions as follows (the percentage of metal regards to the total metals):-

Exchangeable fraction (F1):

From Fig.1 Cd was the predominant metal in this fraction in both sequential extraction (32%) and single (16%) extraction. Pb, Co and Cu extracted in low percentage (5.6, 3.4 and 2.6 % , respectively). This results was in agreement with low Pb in this fraction by Albores et al.[5] and Alonso et al [22]. Sequential extraction reveals higher metal extraction than single procedure.

Carbonate Fraction (F2)

Small amount of all metals were extracted in this fraction. On comparison of sequential and single extraction; single extraction possesses lower values of Cd and Co (0.8 and 3.7%, respectively) than in sequential extraction (3.2 and 5.8%, respectively) (Fig.1).

Fe-Mn fraction (F3)

For most of the metals, this fraction comprised a much larger proportion of the whole sample than in the other fractions. Pb and Co were mainly associated with this fraction (25.8 and 15.6% for sequential extraction, respectively, and 27.4 and 66.1% for single extraction, respectively). Single extraction reveals higher metal extraction for Pb, Cd, Co and Cu (27.4, 24, 66.1 and 5.2%, respectively) than sequential procedure (25.8, 8, 15.6 and 3.6, respectively) (Fig.1).

Organic Matter fraction (F4)

In this fraction Cu was mainly associated with oxidizable fraction (39.6 and 42.6% in sequential and single extraction, respectively) (Fig.1). Copper is predominantly associated with the organic matter fraction. Results obtained in this study are agreed with that obtained by Ashwoth and Alloway [23].

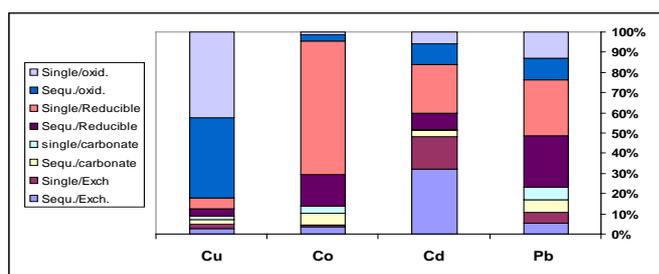


Fig.1. Partitioning patterns corresponding to the Tessier methods in sewage sludge sample

2).Heavy Metal Distribution in Sewage Sludge with the BCR and Single Extraction Scheme

Extractable Pb, Cd ,Co and Cu concentrations in sewage applying both conventional BCR method and single extraction are shown in Table IV and Fig.2 and distributed in different fractions as follows (the percentage of metal regards to the total metals):-

For overall procedures using a conventional BCR method, all metals (Pb, Cd, Co, and Cu) were quantified in all fractions.

TABLE III
RESULTS OBTAINED FOR SLUDGE SAMPLES (EXPRESSED IN $\mu\text{g/g}$) USING BOTH THE CONVENTIONAL TESSIER METHOD AND SINGLE EXTRACTIONS

Metals	Exchangeable fraction			Associated to carbonates fraction			Associated to Fe-Mn fraction		
	Seque.	Single	% Recovery	Seque.	Single	% Recovery	Seque.	Single	% Recovery
Pb	0.86	0.78	91	0.947	0.96	102	3.98	4.23	106
Cd	0.04	0.02	50	0.004	0.001	25	0.01	0.03	300
Co	0.175	0.05	28.5	0.30	0.192	64	0.814	3.44	423
Cu	3.58	3.51	98	2.596	2.85	110	5.07	7.24	143
Pb	Associated to organic matter fraction			Residue			Sum of 4 steps and residue		
Cd	Seque	Single	% Recovery.	Seque	Single	% Recovery.	Seque	Single	% Recovery.
Co	1.65	2.01	121	5.78	0.89	649	13.2	8.9	149
Cu	0.013	0.007	54	0.013	0.005	260	0.1	0.1	127
	0.152	0.081	53	0.15	0.61	25	1.6	4.4	36
	55.3	59.4	107	11.74	12.7	92	78.3	85.7	91

TABLE IV

RESULTS OBTAINED FOR SLUDGE SAMPLES (EXPRESSED IN $\mu\text{g/g}$) USING BOTH THE CONVENTIONAL BCR METHOD AND SINGLE EXTRACTIONS

Metals	Acid-soluble fraction			Reducible fraction			Oxidizable fraction		
	Seque.	Single	% Recovery	Seque.	Single	% Recovery	Seque.	Single	% Recovery
Pb	2.32	2.33	100	2.8	1.2	42	8.41	6.53	78
Cd	0.11	0.72	654	0.17	0.89	523	0.12	0.13	108
	0.38	2.39	628	0.25	0.04	160	0.713	0.143	20
Co	2.1	2.34	111	6.81	5.74	84	55.2	51.3	92
Cu									
Pb	Residue			Sum of 3 steps and residue					
Cd	Seque.	Single	% Recovery	Seque.	Single	% Recovery	Seque.	Single	% Recovery
Co	6.01	6.81	88	19.5	16.9	115			
Cu	0.011	0.09	12	0.41	1.79	23			
	0.16	0.25	64	1.5	3.18	47			
	11.43	13.94	82	75.5	53.3	142			

Acid-soluble fraction (F1)

From Fig.2 the acid – soluble fraction single extraction procedure displayed the higher detectable Pb, Cd ,Co and Cu contents than using sequential procedure .Cd and Cu were leached in small amount when using sequential extraction. Single extraction showed higher proportion extraction of Cd and Co (33.6 and 61%, respectively) than sequential extraction (5.1 and 9.7%, respectively). Pb and Cu extracted in both sequential and single procedures in small amounts.

Reducible fraction (F2)

Cadmium (Cd) was the most extracted metal in this fraction (41.6%) in the single procedure (Fig.2). Similar result was found by Albores et al. [5] in heavy metals fractionation of sewage sludge with different stabilization degrees. These could be related to the medium in reducing conditions in single procedure.

Oxidizable fraction (F3)

This fraction provides high extraction efficiency for all metals except Cd which reveal the lowest extraction (5.6 for sequential and 6.1 for single procedures). Sequential extraction displayed the higher detectable Pb, Cd , Co and Cu contents (35.7, 5.6, 18.2 and 44.7%, respectively) than using single procedure (27.7, 6.1, 3.7 and 41.5%, respectively) (Fig.2). Yuan et al. [18] reported high percentages of Cu (74.15%) in the oxidizable fraction of sewage sludge.

The European Community Bureau of Reference (BCR) proposed the three-step modified sequential extraction scheme, focusing on the reproducibility of the extraction and the selectivity of the extract- ants. Most of the reagents used in the BCR method are acid-stabilized or adjusted to pH 1.5- 2.0, thus also minimizing readsorption. It has been adopted for the certification of the extractable metal amounts in reference soil and sediment material and sewage sludge-amended soil reference material [24].

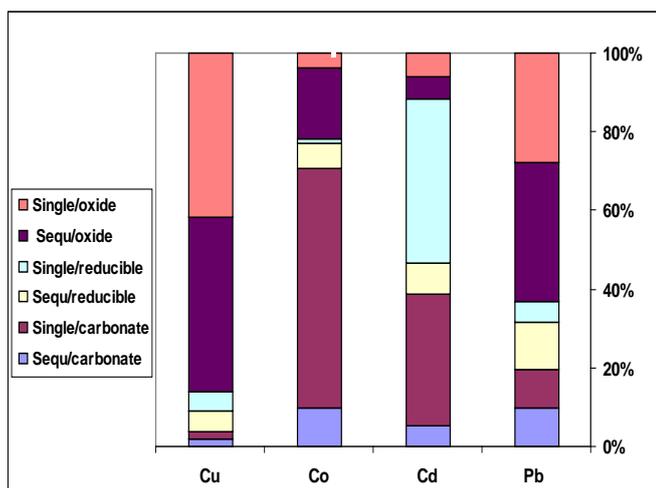


Fig.2. Partitioning patterns corresponding to BCR methods in sewage sludge simple

B. Comparison of Heavy Metal Extractions by Tessier and Bcr Sequential and Single Methods

The distribution of the metallic fractions differs according to extraction scheme used (Tables III and IV).Over all, the higher value of copper (Cu) presented in organic fraction for

both sequential and single extraction (55.3 and 59.4 μg , respectively) by Tessier method, and 55.2 and 51.3 μg , respectively by BCR methods in the oxidisable fraction (Tables III and IV). The recovery of Cu % in organic fraction by Tessier method is higher (107%) than in the oxidisable fraction in BCR method (92%). This high Cu level may be attributed to the preference of Cu for organic matter which is supported by the high stability constant of copper complexes, and also with the fact that binding phase of Cu was organic and sulfide fraction in the sludge [2, 21-23]. Cu–organic matter complexes were generally considered relatively stable and the evaluation of the bioavailability of metals to environment is essential to predict changes in metal behavior in response to environment conditions. Swage sludge is rich in Fe oxide and Cu in oxidizable fraction can be mobilized and available in this oxidizing conditions. So, the Cu in all sludge samples had a high potential eco-toxicity and bioavailability to the ecosystem [25].

The high proportion of Pb was observed in Fe-Mn fraction at Tessier method (3.98 and 4.23 μg for sequential and single extraction, respectively), and this agree with Fuentes et al.[2] and Kazi, [26] finding. In the BCR method, Pb was distributed between the oxidizable fraction and the residual fraction. Recovery of Pb% in the Fe-Mn fraction by Tessier is higher (106%) than in oxidizable fraction (78%) by BCR method.

In BCR method a relatively high concentration of Cd was obtained in reducible fraction (0.17 μg and 0.89 μg for sequential and single extraction, respectively) and acid-soluble fraction (0.11 and 0.72 μg for sequential and single extractions). In Tessier method Cd was distributed between the exchangeable fraction and Fe-Mn fraction. Recovery of Cd % in the reducible fraction (523%) in BCR method was much higher than in the exchangable (50%) and Fe-Mn fractions (300%) by Tessier method. In general highly metal extraction were found in soluble fraction in weak acids for Cd, in bound to Fe-Mn oxide fraction for Cu in oxidizable fraction for Pb. Sanchez-Martin [17] reported the same finding. Co is predominant in Fe-Mn fraction (0.81 and 3.44 μg for sequential and single extraction, respectively) in Tessier method. In BCR method Co represented the high extraction (0.713 and 0.143 μg) for sequential and single extraction, respectively) with lower Co recovery (20%) than in Tiessier method (423%).

In Conclusion in the Tessier and BCR methods Pb, Cd and Co contents leached from both compared extraction procedures was nearly equivalent (Table V).Only Cu extracted by single in the Tessier method and in sequential extraction by BCR method show different trend in comparing metal extraction by Tessier and BCR methods.

C. Contamination Factor of Heavy Metals (Cf)

It is an important aspect that indicates degree of risk of heavy metals to environment in relation with its retention time. A high contamination factor of heavy metal shows low retention time and high risk to the environment. The individual contamination factor (Cf) of heavy metals was used to estimate the relative retention time of heavy metals retained in the sludge. It is determined by dividing the sum of concentration of each heavy metal in the mobile phase (non-residue phase) by its concentration in the residue phase. The global contamination factor (Cf) is equal to the sum of individual factor [27].

TABLE V TOTAL METAL EXTRACTED FROM SEWAGE SLUDGE SAMPLE BY THE CONVENTIONAL TISSER/BCR METHODS AND SINGLE EXTRACTIONS

Metals	Tessier methods (µg/g)			BCR methods (µg/g)		
	Single ^a	Seque ^a	R%	Single ^a	Seque	R%
Pb	13.5	10.1	134	7.4	7.98	93
Cd	0.40	1.7	24	0.1	0.06	116
Co	1.34	2.93	48	1.4	3.76	38
Cu	64.1	39.3	16	66.	73	91

R%. Recovery percentage

a Sum of metals extracted in the four stages of the BCR method (expressed in µg/g).

b Sum of metals extracted in the three stages of the Tessier method (expressed in µg/g).

c Recovery is calculated using the following ratio: [total metal content extracted by the sequential procedure/total metal content extracted using single extraction method] x 100.

TABLE VI HEAVY METAL CONTAMINATION FACTOR (Cf) IN EACH FRACTION OF SLUDGE BY TISSER AND BCR METHODS

Metal	Pb	Cd	Co	Cu
Tisser Fractions				
Exchangeable.	0.15	3.08	1.17	0.30
Carbonate.	0.16	0.31	2.00	0.22
Oxidizable	0.17	0.08	1.28	0.24
Org.Matter	0.73	2.31	22.93	0.62
Total	1.21	5.77	27.38	1.39
BCR Fractions				
Soluble	0.39	10.00	2.38	0.18
Reducible	0.47	15.45	1.56	0.60
Oxidizable	1.40	10.91	4.46	4.83
Total	2.25	36.36	8.39	5.61

Fig.3. Contamination Factors of each metal at different mobile phase by Tessier method

Table VI, Figure 3 and Figure 4 show estimated contamination factor (Cf) of each metal in the sludge in both Tessier and BCR procedures. The calculated factors in both methods show highest ability of Co (Cf 27.38) and Cd (Cf 36.36) to be released from the sludge piles , whereas Pb (Cf 2.25) and Cu (Cf 1.39) have the lowest. The residual concentration of heavy metal is considered non-mobile fraction and is an important part influencing the mobility nature of the heavy metal. The combined effect of Cd in high concentration and with high mobility potential shows the increased possible risk of these metals to the environment

Heavy metals that are distributed in acid soluble/exchangeable fraction and reducible fraction are readily to be absorbed in plants or in water system causing pollution. So, these fractions should be identified as direct effect fraction. The oxidizable fraction in this oxidizing condition is easily mobilized and transformed into acid soluble/exchangeable fraction or

reducible fraction , potential of that eco-toxicity should not be ignored. So, the oxidizable fraction can be identified as potential effect fraction. The heavy metal bound to residual fraction is often considered “unreactive”, and not affected by environment changes, is identified as stable fraction [28].

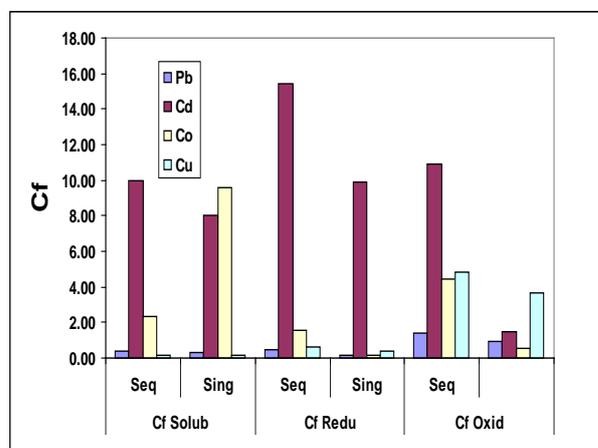
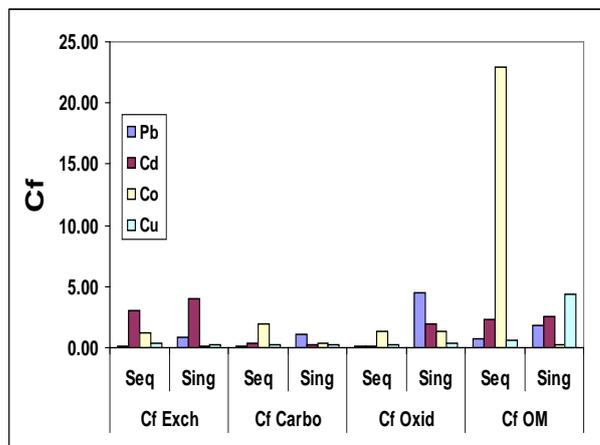


Fig.4. Contamination Factors of each metal at different mobile phase by BCR method

Metals bound to reducible and organic fractions are presumed to be more bioavailable and thus more harmful to biota [29]. Trace elements in unpolluted soils or sediments are mainly bound to silicates. In environmental studies the determination of the different ways of binding gives more information on trace metal mobility, as well as on their availability or toxicity, in comparison with the total element content [30].

D. Mobility Potential of Heavy Metals

The mobility and immobility and thus toxicity of heavy metals in sewage sludge depend largely on their type of binding forms. Table VII compare the mobility potential of heavy metals in different forms. It was noticed from Tables 7 and 8 that Cd and Co has the highest ability and susceptibility to be released from the sludge by the simple ion exchanged mechanism, while Pb and Cu have the lowest mobility. It is seen that the chloride content in the leachate can bind with Cd and enhances its mobility in the solid waste [31]. The presence of acid soluble portion of Pb indicates its sensitivity to the acidic condition and tendency to leach easily. Under varied reduction conditions, the release of Cd, Co, Pb and Cu from the solid waste sludge is expected. This is in contrast with Cu which precipitates with sulfide, absorbed on the organic matter, and appears to be stable under the anaerobic condition.

TABLE VII MOBILITY OF HEAVY METALS IN SEWAGE SLUDGE WITH TESSIER AND BCR PROCEDURES

procedures Steps	Condition	Metal mobility
Tessier 1 2 3 4 5	Exchangeable fraction	Cd>Co>Cu>Pb
	Carbonate fraction	Co > Cd >Cu>Pb
	Fe-Mn fraction	Co > Cu >Pb >Cd
	Organic matter fraction	Co > Cd > Pb > Cu
	Residual fraction	Co > Cd >Cu>Pb
BCR 1 2 3 4	Acid-soluble fraction	Cd>Co> Pb > Cu
	Reducible fraction	Co > Cd >Cu>Pb
	Oxidizable fraction	Cd > Cu > Co > Pb
	Residual fraction	Co > Cd >Cu>Pb

IV. CONCLUSIONS

The analysis of heavy metals is a very important task to assess the potential environmental and health risk associated with the sludge coming from wastewater treatment plants. In this study the application of sequential extraction methods to sewage sludge samples provides relevant information about possible toxicity of heavy metals when they are discharged into the environment. The calculated factors in both methods show highest ability of Co (27.38) and Cd (36.36) to be released from the sludge piles, whereas Pb (2.25) and Cu (1.39) have the lowest. The long treatment time required in these procedures could be shortened by replacing the sequential treatment by single extractions. Also this study provides valuable information on the mobility of metals in sludge and helps in predicting their behavior to the ecosystem.

REFERENCES

- [1] A Fuentes., L. Mercedes, S. Jose, S. Antonio, A. Ma Isabel, Juan F. Ortuno, Victor F. Meseguer, Simple and sequential extractions of heavy metals from different sewage sludges *Chemosphere*, 54 ,1039–1047,2004.
- [2] A. Fuentes., M. Lloréns, J. Slez, A. Soler, M.I. Aguilar, J.F. Ortuno, V.F. Meseguer, Comparative study of six different sludge by sequential speciation of heavy metals, *Bioresour. Technol.* 99,517–525, 2008.
- [3] E. A. Alvarez -, M. Callejon Mochon_ J.C. Jimenez Sanchez, M. Ternero Rodriguez, Heavy metal extractable forms in sludge from wastewater treatment plants) / *Chemosphere* 47,765–775,2002.
- [4] R. Zuñuere, A. Olivares, P.Chamorro, C. Nerón, A. Callizo, Speciation of metals in sewage sludge for agricultural uses. *Analyst* 123, 255–259, 1998..
- [5] Ibores. Fernandez, B. Perez Cid, E. Fernandez Gomez and E. Falque Lopez. Comparison between sequential extraction procedures and single extractions for metal partitioning in sewage sludge samples. *Analyst*, 125, 1353–1357,2000.
- [6] alter, F. Martı́nez, V. Cala, Heavy metal speciation and phytotoxic effects of three representative sewage sludges for agricultural uses. *Environ. Pollut.* 139, 507–514, 2006.
- [7] C.W .Jin, S.J. Zheng, Y.F. He, G.D. Zhou, Z.X. Zhou, Lead contamination in tea garden soils and factors affecting its bioavailability. *Chemosphere* 59, 1151– 1159, 2005.
- [8] S. Tandy, J.P. Healey, M.A. Nason, J.C.Williamson, D.L. Jones, Heavy metal fractionation during the co-composting of biosolids, deinking paper fibre and green waste. *Bioresour. Technol.* 100(2009) 4220–4226, 2009.
- [9] K.Muhammad, I. Jamalia, G.Tasneem Kazia,, B.A. Muhammad, I.A. Hassan, J.Nusrat, K.A.Ghulam,Q.S. Abdul, A.B. Jameel, Speciation of heavy metals in untreated sewage sludge by using microwave assisted sequential extraction procedure. *Journal of Hazardous Materials* 163 1157–1164, 2009
- [10] Y.A.O. Zhigang, Comparison between BCR sequential extraction and geoaccumulation method to evaluate metal mobility in sediments of Dongting Lake, Central China. *Chinese Journal of Oceanology and Limnology* 26 (1), 14–22, 2008.
- [11] M. Pueyo, J. Mateu, A. Rigol, M. Vidal, J.F. Lopez-Sanchez, G. Rauret., Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. *Environmental Pollution* 152, 330–341, 2008.
- [12] U. Forstner, W. Salomons, Trace metal analyses on polluted sediments. Part I: Evaluation of environmental impact. *Environ. Technol. Lett.* 1, 506–517, 1980.
- [13] Tessier, P.G.C.Campbell, M. Bisson, M., Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 51, 844–851, 1979.
- [14] A.M. Ure, P.H. Quevauviller, H. Muntau, B. Griepink, 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.* 51,135–151, 1993.
- [15] Dell'Anno, F. Beolchini, M. Gabellini, L. Rocchetti, A. Pusceddu, R. Danovaro, Bioremediation of petroleum hydrocarbons in anoxic marine sediments: consequences on the speciation of heavy metals. *Mar. Pollut. Bull.* 58 ,1808–1814, 2009.
- [16] L. Rodríguez, E. Ruiz, J. Alonso-Azcárate, J.Rincon, Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. *J. Environ. Manage.* 90, 1106–1116, 2009.
- [17] M.J. Sánchez-Martín, M. García-Delgado, L.F. Lorenzo, M.S. Rodríguez-Cruz, M. Arienzo, Heavy metals in sewage sludge amended soils determined by sequential extractions as a function of incubation time of soils), *Geoderma* 142, 262–273, 2007.
- [18] X. Yuan, H. Huajun, G. Zeng, Hui Li, J. Wang, C. Zhou, Huina Zhu, X. Pei, Z. Liu, Zh. Liu, Total concentrations and chemical speciation of heavy metals in liquefaction residues of sewage sludge. *Bioresource Technology* 102, 4104–4110, 2011.
- [19] J. Scancar, R. Milacic, M. Strazar, O. Burica, Total metal concentrations and partitioning of Cd, Cr, Cu, Fe, Ni and Zn in sewage sludge. *Sci. Total Environ.* 250, 9–19, 2000.
- [20] M. Sprynskyy, P. Kosobucki, Kowalkowski, B. Buszewski, Influence of clinoptilolite rock on chemical speciation of selected heavy metals in sewage sludge. *J. Hazard. Mater.* 49, 310–316, 2007.
- [21] M.R. Lasheen, N.S. Ammar, Assessment of metals speciation in sewage sludge and stabilized sludge from different Wastewater Treatment Plants, Greater Cairo, Egypt. *Journal of Hazardous Materials* 164, 740–749, 2009.
- [22] E. Alonso, I. Aparicio, J.L. Santos, P. Villar, A. Santos, Sequential extraction of metals from mixed and digested sludge from aerobic WWTPs sited in the south of Spain. *Waste Management* 29, 418–424, 2009.
- [23] D.J. Ashworth, B.J. Alloway, Soil mobility of sewage sludge-derived dissolved organic matter, copper, nickel and zinc. *Environmental Pollution* 127, 137–144, 2004.
- [24] G. Rauret, J.F. Lopez-Sanchez, A. Sahuquillo, E. Barahona, M. Lachina, A.M. Ure, C.M. Davidson, A. Gomez, J. Luck, J. Becon, M. Yli-Halla, H. Muntau, P.H. Quevauviller, Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil references material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content. *J. Environ. Monit.* 2, 228–233, 2000.
- [25] V. Illera, I.Walter, P. Souza, V. Cala, Short-term effects of biosolid and municipal solid waste applications on heavy metals distribution in a degraded soil under a semi-arid environment, *Sci. Total Environ.* 255, 29–44, 2000.
- [26] T.G. Kazi, M.K. Jamali, A. Siddiqui, G.H. Kazi, M.B. Arain, H.I. Afridi, An ultrasonic assisted extraction method to release heavy metals from untreated sewage sludge samples. *Chemosphere* 63, 411–420, 2006
- [27] K. Nemati, N.K. Abu Bakar, M.R. Abas, Investigation of heavy metals mobility in shrimp aquaculture sludge—comparison of two sequential extraction procedures. *Microchem. J.* 91, 227–231, 2009.
- [28] M. Chen, X. Li, Q. Yang, G. Zeng, Y. Zhang, De-Liao, J. Liu, J. Hu, L. Guo., Total concentrations and speciation of heavy metals in municipal

- sludge from Changsha, Zhuzhou and Xiangtan in middle-south region of China *Journal of Hazardous Materials* 160, 324–329, 2008.
- [29] ICRL, Guidance on the assessment and redevelopment of contaminated land, Guidance Note 59/83, ICRL, Department of Environment, London, 1987.
- [30] J. Usero, M. Gammero, J. Morillo, I. Garcia, Comparative study of three sequential extraction procedures for metals in marine sediments, *Environ. Int.* 24, 487–496, 1998.
- [31] J. Sahuquillo, J.F. Lopez-Sanchez, R. Rubio, G. Ruret, R.P. Thomas, C.M. Davidson, A.M. Ure, Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure, *Anal. Chim. Acta.* 382, 317, 1999.