



Chemical Speciation of some selected Heavy Metals in Soil from the Obajana Industrial Zone Kogi State, Nigeria

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To cite this article:

Okorie, E. and Fatai K.F.
Chemical Speciation of some
selected Heavy Metals in Soil
from the Obajana Industrial
Zone Kogi State, Nigeria.
*International Journal of
Research and
Technopreneurial
Innovations*, 2025; 2(1): 85-92

Keywords:

Industrial discharge,
Heavy metal,
Soil,
FAAS,
Pollution,
Speciation.

ABSTRACT

The speciation of selected heavy metals (Pb, Cd, Cu and Ni) from soil found at Obajana industrial site was carried out with FAAS detection. The results of this speciation showed that Pb concentration ranged from 0-3.228 $\mu\text{g/g}$ for soil sample from Operating Office and 0-0.05 $\mu\text{g/g}$ (Cd), 0-0.511 $\mu\text{g/g}$ (Cu) and 0-0.431 $\mu\text{g/g}$ (Ni). The total values of the Pb, Cd, Cu and Ni at the Operating Office are 4.031 $\mu\text{g/g}$, 0.057 $\mu\text{g/g}$, 0.964 $\mu\text{g/g}$ and 0.431 $\mu\text{g/g}$ respectively. The metals in soil samples from the Power Point with the exception of Ni did not show any presence in the exchangeable phase. However Ni was detected at the exchangeable phase with a concentration of 0.021 $\mu\text{g/g}$. The total metal concentrations at the Power Point site are 3.597 $\mu\text{g/g}$ (Pb), 0.338 $\mu\text{g/g}$ (Cd), 0.806 $\mu\text{g/g}$ (Cu) and 1.052 $\mu\text{g/g}$ (Ni). The total heavy metal contents at Line 3A are 0.868 $\mu\text{g/g}$ (Pb), 0.064 $\mu\text{g/g}$ (Cd), 1.245 $\mu\text{g/g}$ (Cu) and Ni was not detected in any of the fractions. The soil sample Close To The River showed a Pb concentration of 0.224 ± 0.001 $\mu\text{g/g}$ with a total concentration value of 1.467 $\mu\text{g/g}$. For the soil from Workshop, the observed concentrations are 4.632 $\mu\text{g/g}$ (Pb), 0.385 $\mu\text{g/g}$ (Cd) and 1.17 $\mu\text{g/g}$ (Cu), while Ni was not detected. The result showed that all the heavy elements are all below EPA sediment quality guidelines except for Cd at soil sample from the Workshop which is a bit higher than the recommended EPA value, suggesting the soil from the Workshop is polluted and unfit for agricultural purpose. The enrichment factor analysis result show that Pb, Cd and Cu in samples are extremely severe in enrichment of their site. However, Cd in Operating Office occurred as no enrichment factor, while Ni was observed as no enrichment in all the samples. The risk index factor analysis showed that Cd in samples from the Power Point and Workshop are of high risk index while Pb occur as low risk index.

1. INTRODUCTION

The total metal content in soil and samples cannot be used to ascertain the toxicity and bioavailability of metals to plants and humans [1]. The important factor that determines the

bioavailability and toxicity of metals is the physicochemical forms of their occurrence. Thus, the speciation study of metals in sediments has become widely as one of the most important areas of environmental investigation [2]. Metal

speciation usually gives information on the behaviour and toxicity of metals in the environment. Speciation shows how metals occur in various chemical forms in the environment. These various forms may include free metal ions, metal complexes dissolved in solution and sorbed on the solid surface, and metal species that have been co-precipitated in major metal solids or that occur in their own solid [3]. The speciation studies of metals in sediments provide important information on the transportation and fate of pollutants [4].

Previous reports have shown that metals have great ecological significance due to their toxicity and ability to accumulate in both sediment and biota [5]. These elements are not biodegradable and can easily accumulate in the sediments when introduced into an aquatic environment thus becoming a potential source of pollutants when environmental conditions change [6]. Therefore, sediments are important sinks for metals and subsequently play an important role in the assessment of metal contamination [7]. Many metals such as Ni, Zn and Mn are essential for organism at an appropriate concentration while other metals like Pb and Cd are extremely toxic to living organisms and human health even at a low concentration [8].

Metals have in recent times received important attention due to the environmental pollution caused by their toxicity, abundance, non-biodegradable characteristic, persistence and accumulation [9]. In aquatic environments, trace elements frequently affect aquatic eco systems impacting animals, plants and benthic communities. Trace element has been proved to cause ecological problems while accumulating in the food chain, creating risks for humans and inland organisms [10]. Sediments in the aquatic

ecosystem can act as a sink of pollutants by accumulating a considerable amount of metal, while a minor fraction remains in the water phase [11]. Metal are partitioned into several chemical forms, where some are more labile during physical and chemical fluctuations. Variations of the aquatic system are caused by natural and anthropogenic activities like mining, dredging and use of engines, or under environmental changes such as fluctuation of salinity, pH, redox potential and ionic strength [12]. This study is aimed at assessing the level of metal pollution in soil around Obajana industrial site.

2. MATERIALS AND METHOD

2.1 *Materials and reagents*

Volumetric flask, pH meter, Beaker, Measuring cylinder, Conical flask, Filter paper, Heating mantle, Weighing balance, Spatula, glass rod, Acetic acid, Hydroxylamine hydrochloride, Nitric acid, Hydrogen peroxide, Sulphuric acid and distilled water. Flame Atomic Absorption Spectrometer (FAAS) (Buck Scientific Model AVG 210 UK).

2.2 *Sample Preparation and method*

Five soil samples were randomly collected from different points in Obajana industrial site in Kogi state. The sampled points are Operating Office, Power Point, Line 3A, Close to the River and Workshop. The analytical procedure involves the use of Bureau Community of Reference (BCR) sequential chemical extraction procedure for the partitioning of particulate heavy metals (Pb, Cd, Cu, Ni). Modified sequential extraction technique (Table 1) was used to analyze content of chemical speciation of heavy metal in soil [13].

Table 1: Modified BCR Sequential Extraction Procedure: (1g dry weight mass sample).

Fraction	Compound Extraction	Extraction Reagent	Extraction Method
Fraction 1, Acid soluble	Exchangeable and bound to carbonates	20 ml of 0.11 mol/L HOAc	Shaking at 22± 5°C for 16 h
Fraction 2, Reducible	Bound to Fe/Mn oxides	20 ml of 0.5 mol/L NH ₂ OH.HCl (adjusted to pH 1.5 with HNO ₃).	Shaking at 22± 5°C for 16 h
Fraction 3, Oxidizable	Bound to organic matter and sulphides	5 ml of 8.8 mol/L H ₂ O ₂ (adjusted to pH with HNO ₃).	Digesting at room temperature for 1 h with occasional manual shaking, then cover the tube and heat at 85±2°C for 1 h, and then remove the cover and reduce the volume to a few milliliters. Cover the tube and heat at 85±2°C for 1 h, and then remove the cover and reduce the volume to dryness/ Shaking at 22± 5°C for 16 hr
Fraction 4, Residual	Metals within lithogenic minerals	Aqua regia	

The residue of each step was rinsed with 20 ml distilled water and filtered into pre-cleaned 100 ml volumetric flasks. The supernatant liquid of each fractions after filtration were stored for metal determination which are analyzed using flame atomic absorption spectrometer (FAAS).

3. RESULTS AND DISCUSSION

The Results of the chemical speciation of heavy metals in soil from the Obajana Industrial

Sites are presented in Tables 2-6. Table 7 is the Comparison of heavy metal concentrations with EPA Sediment Quality Guideline (SQG) while Table 8 is the Enrichment Factor (EF) analysis of soil samples from different point at Obajana industrial site. Table 9 is the Potential Ecological Risk index (RI) and level of Risk while Table 10 is the Potential Ecological Risk Index (RI) analysis of soil samples from different point at Obajana industrial site.

Table 2: Result of Speciation of Soil Sample at Obajana Industrial Site from Operating Office (µg/g)

Fractions	Parameters (µg/g)			
	Pb	Cd	Cu	Ni
Exchangeable	0.285± 0.002	0.003± 0.002	0.097± 0.0	ND
Bound to Carbonate	3.228± 0.001	ND	0.511±0.0	ND
Organic Matter	ND	ND	0.214±0.0	ND
Residual	0.0518± 0.001	0.054± 0.001	0.142± 0.001	0.431± 0.001
Total	4.031	0.057	0.964	0.431
E.P.A Valve	16	0.38	36	30

Table 3: Result of Speciation of Soil Sample at Obajana Industrial Site from Power Point (µg/g)

Fractions	Parameters (µg/g)			
	Pb	Cd	Cu	Ni
Exchangeable	ND	ND	ND	0.021±0.001
Bound to Carbonate	2.746± 0.001	0.021± 0.0	0.617± 0.0	0.27± 0.001
Organic Matter	ND	0.199± 0.0	ND	ND
Residual	0.851± 0.001	0.118± 0.0	0.189± 0.001	0.761± 0.001
Total	3.597	0.338	0.806	1.052
E.P.A Value	16	0.38	36	30

Table 4: Result of Speciation of Soil Sample at Obajana Industrial Site from Line 3A (µg/g)

Fractions	Parameters (µg/g)			
	Pb	Cd	Cu	Ni
Exchangeable	ND	ND	0.133± 0.001	ND
Bound to carbonate	0.548± 0.0	ND	0.39± 0.0	ND
Organic Matter	ND	ND	0.664± 0.0	ND
Residual	0.32± 0.001	0.064± 0.001	0.058± 0.009	ND
Total	0.868	0.064	1.245	ND
E.P.A Value	16	0.38	36	30

Table 5: Result of Speciation of Soil Sample at Obajana Industrial Site from Close to The River (µg/g)

Fractions	Parameters (µg/g)			
	Pb	Cd	Cu	Ni
Exchangeable	0.224± 0.001	ND	0.023± 0.0	ND
Bound to Carbonate	0.724± 0.0	0.125± 0.0	0.162±0.001	ND
Organic Matter	0.032± 0.0	ND	0.449± 0.0	ND
Residual	0.487± 0.0	0.105± 0.0	0.177± 0.0	ND
Total	1.467	0.23	0.811	ND
E.P.A Valve	16	0.38	36	30

Table 6: Result of Speciation of Soil Sample at Obajana Industrial Site from Workshop (µg/g)

Fractions	Parameters (µg/g)			
	Pb	Cd	Cu	Ni
Exchangeable	0.211± 0.001	ND	ND	ND
Bound to Carbonate	3.684± 0.0	ND	0.499± 0.0	ND
Organic Matter	0.018± 0.0	ND	0.11± 0.0	ND
Residual	0.719± 0.001	0.385± 0.0	0.561± 0.0	ND
Total	4.632	0.385	1.17	ND
E.P.A Value	16	0.38	36	30

Table 7: Comparison of heavy metal concentrations with EPA Sediment Quality Guideline (SQG) (µg/g)

Metal	Non-polluted	Moderately polluted	Heavily polluted	Present Study, µg/g				
				Operating office	Power point	Line3A	Close to the River	Workshop
Pb	< 40	40-60	> 60	0.285-3.228	0.851-2.746	0.320-0.548	0.032-0.724	0.018-3.684
Cd			> 6	0.003-0.054	0.021-0.199	0.000-0.064	0.105-0.125	0.000-0.385
Cu	< 25	25-50	>50	0.097-0.511	0.189-0.617	0.058-0.664	0.162-0.449	0.110-0.561
Ni	< 20	20-50	>50	0.000-0.431	0.021-0.761	ND	ND	ND

Table 2 shows the speciation of Pb, Cd, Cu and Ni in soil found at Operating Office of Obajana industrial site. The observed Pb concentration ranged from 0-3.228 µg/g, with a total Pb concentration of 4.031 µg/g . Cd was not detected in bound to carbonate and organic matter fractions, however a concentration of 0.003±0.002 µg/g and 0.54±0.001 µg/g was observed in exchangeable and residual fractions respectively. The observed Cu concentration

ranged from 0.097-0.511 µg/g. Ni was not detected in the first three fractions. Ni concentration of 0.431±0.001 µg/g was detected in the residual fraction. The total concentration for Cd, Cu and Ni are 0.057 µg/g, 0.964 µg/g and 0.431 µg/g respectively.

For Table 3 which is a speciation of soil from Power point at Obajana industrial site, the observed Pb concentration ranged from 0- 2.746 µg/g with a total Pb concentration of 3.597 µg/g.

Cd ranged from 0-199 $\mu\text{g/g}$ with total Cd concentration of 0.338 $\mu\text{g/g}$. Cu was not detected in the exchangeable and bound to organic matter fraction, but a Cu concentration of 0.617 $\mu\text{g/g}$ and 0.189 ± 0.001 $\mu\text{g/g}$ was detected in bound to carbonate and residual fractions respectively. The total Cu concentration is 0.806 $\mu\text{g/g}$. The concentration of Ni ranged from 0-0.761 $\mu\text{g/g}$ with a total Ni concentration of 1.052 $\mu\text{g/g}$.

The speciation of soil sample obtained in Line 3A as indicated on Table 4, showed that Pb was not observed in the exchangeable and organic matter phases while a concentration of 0.546 $\mu\text{g/g}$ and 0.320 ± 0.001 $\mu\text{g/g}$ was observed in bound to carbonate and residual phases respectively. The total Pb concentration is 0.868 $\mu\text{g/g}$. Cd was only observed at residual fraction with a total concentration of 0.064 $\mu\text{g/g}$. The observed Cu concentration ranged from 0.058-0.664 $\mu\text{g/g}$, with a total Cu concentration of 1.254 $\mu\text{g/g}$. Ni was not detected in any of these fractions.

For soil samples Close to the River (Table 5), the speciation indicates a Pb concentration with a range of 0.032-0.724 $\mu\text{g/g}$, while Cd ranged from 0-0.125 $\mu\text{g/g}$. The observed Cu concentration ranged from 0.023-0.449 $\mu\text{g/g}$, while Ni was not detected in any of the fractions. The total metal concentrations of Pb, Cd and Cu are 1.467 $\mu\text{g/g}$, 0.2 $\mu\text{g/g}$ and 0.811 $\mu\text{g/g}$ respectively.

The concentration of the heavy metals from soil sample from the Workshop as shown on Table 6, had a Pb concentration with a range of 0.018-3.684 $\mu\text{g/g}$ and total Pb concentration of 4.632 $\mu\text{g/g}$. Cd was only detected in the residual phase with concentration 0.385 $\mu\text{g/g}$. Cu concentration ranged from 0.110-0.561 $\mu\text{g/g}$ while Ni was not detected in soil samples from the workshop.

3.1 Enrichment Factor

Assessment of heavy metal pollution in marine sediments requires knowledge of pre-industrial metal concentrations to act as a reference against which measured values can be compared [14]. So in order to better understand the sediment quality in the Bay, levels of metal pollution were evaluated by different techniques for environmental assessment. One of them is Enrichment Factor (EF) which is a powerful tool to distinguish between anthropogenic and

naturally occurring sources of heavy metals. EF technique is used in the area of atmospheric aerosols, sediments, soil and solid wastes to determine the degree of modification in the composition [15].

The EF of metal is defined as follows using Ni as a reference element

$$EF = \frac{(C_x/C_{Ni})_{sample}}{(C_x/C_{Ni})_{background}}$$

where $(C_x/C_{Ni})_{sample}$ is the ratio of the metal and Ni concentration of the sample and $(C_x/C_{Ni})_{background}$ is the ratio of metal and Ni concentration of background. The background concentration of Pb, Cd, Cu and Ni in the average shale obtained from Turekian and Wedopohl [16] are used in this study.

Birch [17] divided contamination into different categories based on EF values. $EF < 1$ demonstrates the “no enrichment”, $EF < 3$ is “minor enrichment”, $EF = 3-5$ is “moderate enrichment”, $EF = 5-10$ is “moderately severe enrichment”, $EF = 10-15$ is “severe enrichment”, $EF = 25-50$ is a very severe enrichment” and $EF > 50$ is “extremely severe enrichment”.

Table 8: Enrichment factor analysis of soil samples from different point at Obajana industrial site

Samples	Pb	Cd	Cu	Ni
Operating Office	129.9	0.120	131.6	000.7
Power Point	53.42	53.18	54.71	0.019
Line 3A	125.9	129.5	131.3	000.7
Close to the River	130.9	130.0	134.3	000.7
Workshop	129.5	129.8	129.3	000.7

3.2 Potential Ecological Risk Index (RI)

The contaminated soil with heavy metal can enter the human body through several pathways and various exposure approaches [18]. Elevated levels of toxic heavy metals in agricultural soil can influence food chain; hence lead to increase in the exposure of several dangerous diseases, such as cancer, leukemia and kidney or liver damage [19]. Therefore, the assessment of potential ecological risk (RI) is necessary, which developed by Hakanson [20], represents the toxicity of heavy metals and their

risks levels to the environment. RI value is calculated by the following equation as proposed by Hakanson, [20].

$$RI = \sum_{i=1}^n \frac{(Ti \cdot Ci)}{Bi}$$

Where T_i is toxicity factor of heavy metals; the T_i values for the metals under investigation are: Cd=30, Pb=5, Ni=5, Cu=5, C_i is measured concentration of heavy metal (i), and B_i is background concentration of heavy metal (i).

Table 9: Potential Ecological Risk index (RI) and level of Risk (Hakanson [20])

RI Value	Risk level
$RI \leq 50$	Low risk
$50 < RI \leq 100$	Moderate risk
$100 < RI \leq 150$	High risk
$150 < RI \leq 200$	Very high risk
$200 < RI$	Extreme risk

Table 10: Potential Ecological Risk Index (RI) analysis of soil samples from different point at Obajana industrial site

Samples	Pb	Cd	Cu	Ni
Operating Office	1.362	17.1	0.15	0.043
Power Point	1.215	101.4	0.161	0.175
Line 3A	0.293	19.2	0.249	0.1
Close to the River	0.496	69.0	0.481	0.1
Workshop	1.565	115.3	0.234	0.1

The observed Pb concentration occurred more in bound to carbonate fraction for all the samples under investigation. This may be ascribed to its natural presence in the soil. It is interesting to note that the soil samples at Line 3A and Close To The River (Tables 4 and 5) have close Pb concentration values, while the Pb concentration observed in Tables 2, 3 and 6 in their bound to carbonate fraction also have very close values. These may be attributed to various locations where flue gases from the cement industrial machine quarry are deposited on this site thereby elevating the concentration of Pb in this area. Another factor may be the formation of oxide and carbonate which may be incorporated in the cement ore. These results agree with the works of [8]. In comparison with the EPA guidelines (Table 7) all the observed Pb concentration are lower than EPA SQG of 16 $\mu\text{g/g}$ [21]. Consequently, the exchangeable and bound to carbonate fraction of the Pb may be available for bioaccumulation in plant and humans.

Cadmium concentration are generally low and may be ascribed to its natural presence in the soil. However, the total Cd concentrations are below the permissible limit by EPA for samples at Operating Office, Power Point, Line 3A and Close

to the River. However, the total Cd concentration was above permissible limit by EPA in the soil sample from Workshop (Table 5). The Workshop in the Obajana industrial site hosts a lot of soil activities and it is not surprising that Cd can attain such elevation at residual fraction. Cu concentrations observed are all below EPA permissible limit and therefore do not hold any significant risk to the environment. Consequently, Ni was mostly not detected and therefore does not pose any threat to both plant and animal.

From the results of the enrichment factor analysis (Table 8), Pb Cd and Cu in samples are extremely severe in enrichment of their sites. However, Cd in Operating Office occurred as no enrichment factor, while Ni was observed as no enrichment factor in all samples. Results of the potential ecological risk index analysis (Table 10) showed that Cd in samples Power Point and Workshop are high in risk index (Table 9) while it is moderate in Close To The River and low in Line 3A and Operating Office. The other heavy metals (Pb, Cu and Ni) are all of low risk index. From the EPA Sediment Quality Guidelines [21] as presented in Table 7, all heavy metals under study are <40 and therefore non-polluted.

4. CONCLUSION

With the exception of Ni which may bioaccumulate with time on the ecological matrix, all the other metal examined do not pose any significant danger to the environment. The observed Cu concentration on the exchangeable and bound to carbonate phase was attributed to the influence of the ores used in cement manufacture at the industrial site. Flue gases from quarry contribute significantly to the presence of these heavy metals in the soil.

COMPETING INTERESTS

There are no competing interests in this work.

AUTHORS CONTRIBUTION

The authors did not receive any funding for this work. The sponsorship of this research was borne by the authors.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the Federal Polytechnic Idah Kogi State Nigeria for granting them access to their laboratory.

Reference

- [1] Chakraborty, P., Babu, R.P.V. and Sarma, V.V. (2012). A study of lead and Cadmium speciation in some estuarine and coastal sediments. *Chemical Geology*, **294-295**: 217-225. DOI: 10.1016/J.CHEMGEO.2011.11.026
- [2] Zhang, H., He, P. and Shao, L.M. (2008). Fate of heavy metals during municipal soil waste incineration in Shanghai. *Journal of Hazardous Materials*, **156**: 365-373. DOI: 10.1016/j.jhazmat.2007.12.025
- [3] Kang, X., Song, J., Yuan, H., Duan, L., Li, X., Li, N., Liang, X. and Qu, B. (2017). Speciation of heavy metals in different grain sizes of jiaozhou Bay sediments: bioavailability, ecological risk assessment and source analysis on a centennial timescale. *Ecotoxicology and Environmental Safety*, **143**: 296-306. DOI: 10.1016/j.ecoenv.2017.05.036
- [4] Zhao, X., Dong, D., Hua, X. and Dong, S. (2009). Investigation of the transport and fate of Pb, Cd, Cr(VI) and As (V) in soil zones derived from moderately contaminated farmland in Northeast, China. *Journal of Hazardous Materials*, **170**: 570-577. DOI: 10.1016/j.jhazmat.2009.05.026
- [5] Ho, S.T., Tsai, L.J. and Yu, K.C. (2003). Correlations among aqua-regia extractable heavy Metals in vertical river sediments. Diffuse pollution Conference, Dublin, 1, 12-18.
- [6] Nowrouzi, M., Pourkhabbaz, A. and Rezaei, M. (2012). Bioaccumulation and distribution of metals in sediments and *Avicenna marina* tissues in the Hara Biosphere Reserve, Iran. *Bull. Environ. Contam. Toxicol.*, **89**: 799-804. DOI: 10.1007/s00128-012-0751-3
- [7] Gangaiya, P., Tabudravu, J., South, R. and Sotheeswaran, S. (2001). Heavy metals Contamination of the Lami coastal environment. *The South Pacific journal of National and Applied Sciences*, **19**(1): 24-29. DOI: 10.1071/SP01005
- [8] Islam, M.S., Ahmed, M.K., Raknuzzaman, M., Habibullah-Al-Mamun, M. and Masunaga, S. (2015). Metal speciation and their bioaccumulation in fish species of three urban rivers in Bangladesh. *Arch. Environ. Contam. Toxicol.*, **68**: 92-106. DOI: 10.1007/s00244-014-0079-6
- [9] Bastami, K.D., Neyestani, M.R., Esmailzadeh, M., Haghparast, S., Alavi, C., Fathi, S., Nourbakhsh, S., Shirzadi, E.A. and Parhizgar, R. (2017). Geochemical speciation, Bioavailability and source identification of selected metals in surface sediments of the Southern Caspian Sea. *Mar. Pollut. Bull.* **114**: 1014-1023. DOI: 10.1016/j.marpolbul.2016.11.025
- [10] Thinh, N.V., Osanai, Y., Adachi, T., Thai, P.K., Nakano, N., Ozaki, A., Kuwahara, Y., Kato, R., Makio, M. and Kurosawa, K. (2018). Chemical speciation and bioavailability concentration of arsenic and heavy metals in sediment and soil cores in estuarine ecosystem, Vietnam.

- Microchemical Journal*, **139**: 268-277. DOI: 10.1016/j.microc.2018.03.005
- [11] Kamaruzzaman, Y. and Ong, M.C. (2009). Geochemical proxy of some chemical elements in sediments of kemaman river estuary, Terengganu, Malaysia. *Sains Malaysiana*, **38**(5): 631-636.
- [12] Fathollahzadeh, H., Kaczala, F., Bhatnagar, A. and Hogland, W. (2014). Speciation of metals in Contaminated sediments from Oskashamn harbor, Oskashamn, Sweden. *Environ. Sci. Pollut. Res. Int.* **21**: 2455-2464. DOI: 10.1007/s11356-013-2173-0.
- [13] Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A. and Quevauviller, P. (1999). Improvement of the BCF three step sequential Extraction procedure prior to the certification of New sediment and soil reference material. *Journal of Environmental Monitoring*, **1**(1): 57-61. DOI:10.1039/a807854h
- [14] Abraham, G.M.S and, Parker, R.J. (2008). Assessment of heavy metal enrichment factors and degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environmental Monitoring and Assessment*, **136**: 227-238. DOI: 10.1007/s10661-007-9678.
- [15] Pekey, H. (2006). The distribution and sources of heavy metals in iznit Bag surface sediments affected by a polluted stream. *Marine Pollution Bulletin*, **52**: 1197-1208. DOI: 10.1016/j. Marpolbul. (2006).02.012
- [16] Turekian, K.K. and Wedepohl, D.H. (1961). Distribution of the elements in some major units of the earths crust. *Bulletin Geological Society of America*, **72**:175-192. DOI: 10.1130/0016-7606(1961)72[175:DOTE]2.0.CO;2
- [17] Birch, G., ed. C.D.a. Woodroffe, F. (2003). Coastal GIS 2003, Wollongong University Papers in Center of Maritime Policy, 14, Australia, Edition edn.
- [18] Bade, R., Oh, S., Shin, W.S. and Hwang I. (2013). Human health risk assessment of soils contaminated with metal (loid)s by using DGT uptake: A case study of a former Korean metal refinery site. *Human and Ecological Risk Assessment*, **19**(3): 767-77. DOI: 10.1080/10807039.2012.708276
- [19] Khan, M.N., Wasim, A.A., Sarwar, A. and Rasheed, M.F. (2011). Assessment of heavy metal toxicants in the roadside soil along the N-5, National Highway, Pakistan. *Environ Monit Assess.* **182**(1-4): 587-95. DOI: 10.1007/s10661-011-1899-8
- [20] Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research*, **14**(8): 975-1001. DOI: 10.1016/0043-1354(80)90143-8
- [21] U.S. Environmental Protection Agency (1977). (U.S EPA). *Guidance for the pollutional classification of Great Lake Harbour Sediments, RegionV, Chicago, Illinois.*