

HEAVY METAL SPECIATION IN SEDIMENTS IN SAGULING LAKE WEST JAVA INDONESIA

Eka Wardhani^{1,2}, Suprihanto Notodarmojo³ and Dwina Roosmini⁴

¹Environmental Engineering Program ITB, Post-Graduate Academy, Bandung, Indonesia. ²Department of Environmental Engineering, Iteas Bandung, Indonesia.

^{3,4}Department of Environmental Engineering, ITB Bandung, Indonesia

* Corresponding Author, Received: 19 Aug. 2016, Revised: 27 Dec. 2016, Accepted: 30 Jan. 2017

ABSTRACT: The purpose of this study was to assess the chemical speciation of selected heavy metals (Cd, Cr, Cu, and Pb) in 12 surface sediments at Saguling Lake West Java Indonesia. A five-step sequential extraction technique was used to evaluate speciation heavy metals from Saguling Lake surface sediments. A risk assessment code (RAC) was applied to estimate the risk of heavy metals release in to the environment. The total mean value of heavy metals in surface sediment varied in the following descending order Cr>Cu>Cd>Pb. Based on the RAC value the sediments of Saguling Lake had been polluted by heavy metals, and they did pose medium ecological risk. The information on total metal concentrations in sediment was not sufficient for assessing the metal behavior in the environment, but metal speciation greatly determines the behaviors and toxicity of metals in the environment so it was more effective in estimating the environmental impact of contaminated sediments.

Keywords: Metals, Sediment, Speciation, Saguling

1. INTRODUCTION

Sediments are a significant storage compartment for metals that are released to the water column in rivers, lakes, and oceans. Because of their ability to sequester metals, sediments can describe water quality and record the effects of anthropogenic emissions [6].

It is well accepted that total metal content in sediments cannot predict the bioavailability and toxicity of that metal [4]. It is in fact the physicochemical forms of the metal that establish its possibility bioavailability and toxicity. Thus, the speciation and distribution study of metals in sediments has become one of the most important areas of environmental investigation [11],[16].

Metal speciation extremely determines the characters and toxicity of metals in the environment. Speciation indicates to the occurrence of a metal in a variant of chemical form. These forms may include free metal ions, metal complexes dissolved in solution and sorbed on solid surface, and metal species that have been co-precipitated in major metal solids or that occur in their own solid [10]. The speciation studies of metals in sediments not only conduct an showing of the current quality of the overlaying water but also provide important information on the transportation and fate of pollutants [5], [7], [14], [15].

Saguling lake was built on The Citarum River. The Citarum Watershed is home to the largest industrial area in West Java Province. Several economic activity are performed along Citarum

River, including mining and agriculture. Futhermore, large amounts of untreated wastewater containing heavy metals from industrial sources have contributed to increased pollution of the lakes. The quality of water in the Saguling lake has been monitored since 1990 by the state agency for environmental control, there are no reports about heavy metals in sediment of the lake. There is insufficient information for an assessment of heavy metals distribution in the lake [9].

The objective of this study was to evaluate performance of the heavy metal speciation in sediments from Saguling Lake West Java Provinces, and to use the calculated risk assessment code (RAC) to assess the potential ecological risk associated with the heavy metals present. This work will provide the direct evidence needed by local environmental authorities to allow them to design and implement the measures necessary to improve lake water quality.

2. MATERIAL AND METHOD

Surface sediment were collected in November 2015 at twelve sampling sites around Saguling lake. The sampling sites in Saguling lake presented in Table 1 and Figure 1. Surface sediment were collected using a Eickman Grab from the depth of 0-20 cm. The samples were packed by plastic spatula in plastic boxes and preserved at 4°C until theirs transfer to the laboratory. In the laboratory, samples were dried, crushed, grind and sieve to fraction <1.5 mm.

Table 1 The location of sampling sites in Saguling lake

No of the site	Latitude (N)	Longitude (E)	Location
1	06°56'29.8"	107°32'10.7"	Citarum River Nanjung section
2	06°54'58.9"	107°28'32.3"	Citarum River near Batujajar
3	06°53'13.5"	107°28'32.3"	Trash Boom Cihaur Village
4	06°53'13.4"	107°27'09.0"	Cimerang Village
5	06°53'13.0"	107°25'54.4"	Cihaur Estuary
6	06°56'07.6"	107°27'25.5"	Cipantik Estuary
7	06°57'14.6"	107°26'03.8"	Ciminyak Estuary
8	06°56'14.9"	107°24'50.8"	Cijere Estuary
9	06°56'00.4"	107°22'22.4"	Cijambu Estuary
10	06°54'54.4"	107°22'26.3"	intake structure
11	06°51'49.8"	107°20'57.0"	Trailrace
12	06°51'10.8"	107°20'58.0"	Bantar Caringin



Fig. 1 The location of sampling sites in Saguling Lake

2.1. Sequential extraction procedure of heavy metals

Sequential extraction was worked using a three stage modified procedure suggested by BCR plus the residual fraction [2]. The extraction steps took on in this study can be amply sum of as attends.

Step 1 (acid extractable/exchangeable fraction, F1): 40 mL of 0.11 M acetic acid was added to 1 g of sediment sample in a centrifuge tube and shaken for 16 h at room temperature. The concentrate was then separated from the solid residue by centrifugation and filtrate was separated by decantation as beforehand explained.

Step 2 (easily reducible fraction, F2): 40 mL of recently available hydroxyl ammonium chloride was added to the residue from step 1 in the centrifuge tube, and re-suspended by mechanical shaking for 16 h at room temperature. The separation of the extract collection of the supernatant, and cleansing of residues were the same as described in step 1.

Step 3 (oxidizable fraction, F3): The residue in step 2 was made twice with 10 mL of 8.8 M

hydrogen peroxide. First 10 mL of hydrogen peroxide was added to the residue 2 in the centrifuge tube. The digestion was allowed to proceed at room temperature for 1 h with occasional manual shaking, attended by digestion at $85\pm 2^\circ\text{C}$ for another 1 h. During the digestion, the centrifuge tube was freely protected to avoid significant loss of hydrogen peroxide. Next, the centrifuge tube was disclose and heating was sequented until the volume reduced to about 2-3 mL. An additional 10 mL of hydrogen peroxide was added to the tube, covered, and digested with cover at $85\pm 2^\circ\text{C}$ for another hour. Heating was continued as before until the volume reduced to 2-3 mL. Finally, 50 mL of 1 M ammonium acetate was added to the cold mixture and shaken for 16 h at room temperature. The separation of the extract, collection of the supernatant, and rinsing of residues were the same as described in step 1.

Step 4 (residual fraction, F4): The residue from step 3 was digested using a compound of aqua regia. An internal check was performed on the products of the sequential extraction by comparing the total quantity of metal extracted by variant reagents during the sequential extraction procedure with the results of the total digestion.

The content of heavy metals (Cd, Cr, Cu, and Pb) was determined by Inductively coupled plasma mass spectrometry (ICP-MS).

3. RESULT AND DISCUSSION

3.1. Environmental Setting

The Saguling lake region is 4.710 Ha the water storage capacity is 730,5 million m^3 . The surrounding area of Saguling Lake is hilly, while the river has many tributaries at this location. This makes the form of Saguling Lake very ragged or dendriform, with many extended bays. The lake area was previously densely populated by farmer resident with extensive agricultural lands. The catchment areas of the lake or the upper Citarum River basin are faced with high population tension. This is because more 50% of the population consists of farmers with a high annual growth rate (2.34% is the national average) [9].

Due to the high population density in the upper catchment of the lake, extensive agricultural land, soil erosion and the presence of industries, the lake water became polluted and eutrophic. The growth of aquatic weeds has been accelerated, with frequent blooms of *Microcystis* algae. The water is also contaminated by heavy metals, pesticides, etc. An extensive growth of water-hyacinth is maintained by fencing to reduce pollutant contents of water at inlets of the Citarum River [9]. Originally, the Saguling was planned for a single purpose lake to

generate electricity. Later, considering the environmental problems of the area, the Saguling was re-planned as a multipurpose lake such as raw water, fisheries, aquaculture, and tourism [9].

3.2. Physico-chemical characteristics of sediments

The physico-chemical characteristics of surface sediments were related with the speciation of heavy metals gives at Table 2. The pH is exactly influenced by many parameters, such as cation exchange capacity (CEC), clay content, redox conditions and others, being responsible for the solubility and mobility of metals and metalloids in soils and sediments [3]. The pH in sediments ranged from 6.1 to 7.0 and the average value is 6.4, explaining that the sediments were neutral and almost same value for all sampling location.

Table 1 Physico-chemical parameters of the Saguling lake surface sediments

No. of the site	pH	Sand	Silt	Clay
			%	
1	7.0	41.2	44.4	18.1
2	6.4	57.9	32.4	10.3
3	6.8	26.6	55.8	23.9
4	6.5	18.5	53.7	23.9
5	6.2	11.1	67.7	29.0
6	6.1	67.2	25.7	13.6
7	6.3	59.1	32.2	12.2
8	6.1	85.6	10.7	3.9
9	6.2	8.2	73.7	37.9
10	6.3	57.1	35.0	13.1
11	6.4	18.0	63.0	36.0
12	6.5	8.0	67.0	30.0

Sand content for the studied samples varies from 8.0-85.6% whereas silt and clay content varies from 10.7-73.7% and 3.9-37.8%, respectively. Sand, silt and clay value fluctuate from site 1 to 12. Site 8 had the highest value for sand, site 9 had the highest value for silt and site clay. Based on the analysis of the sediment type is silt-sand from site 1 and 2, site 7 and 10 are sand-silt, site 6 and 8 is sand, the last site 3,4,5,9,11, and 12 B is silt.

3.3. Total heavy metal concentrations

The concentrations of Cd, Cr, Cu, and Pb in surface sediment samples are shown in Table 3, Cd concentrations were greatest at site 2 at 29.2 mg/kg and lowest at site 11 at 12.9 mg/kg. The concentrations of Cr at site 8 is the highest with a value of 255.2 mg/kg, while lowest Cr concentration is at site 11 with a value of 93.4 mg/kg. The highest Cu concentration is at site 5 with a value of 96.3

mg/kg and the lowest Cu concentration is at site 11 with a value of 37.0 mg/kg. The concentration of Pb were highest at site 5 at 29.0 mg/kg and lowest at site 11 at 5.5 mg/kg. In summary the contents of Cd, Cr, and Cu were considerable higher than the standard level.

Table 3. Total heavy metals concentrations of the Saguling lake surface sediments

No. of the site	Total Concentration (mg/kg dry matter)			
	Cd	Cr	Cu	Pb
1	25.6	236.3	66.2	12.1
2	29.2	236.3	75.5	28.7
3	22.6	214.0	87.8	23.2
4	27.3	233.9	69.5	22.3
5	26.9	253.8	96.3	29.0
6	25.1	224.0	90.9	26.0
7	22.3	177.6	82.7	26.1
8	22.4	255.2	85.8	17.8
9	22.5	187.3	84.1	25.8
10	26.9	210.7	91.3	22.4
11	12.9	93.4	37.0	5.5
12	15.6	123.9	45.2	9.9
Mean	23.3	203.9	76.0	20.7
Standard Deviation	4.8	50.7	14.5	7.7
Sample Variance	23.4	2,568	209.6	59.8
Minimum	12.9	93.4	45.2	5.5
Maximum	29.3	255.2	96.3	29.0
ANZECC ISQG-Low ^a	1.5	80	65	50
Average shale ^b	0.3	90	45	20

a: [1] b: [13]

3.4. Heavy metal speciations

In a natural, aerobic freshwater aquatic system with typical Cd-S-CO₂ concentrations, Cd²⁺ is the predominant species below pH 8, CdCO₃⁰ is predominant from pH 8 to 10, and Cd(OH)₂⁰ is dominant above pH 10. The solubility of Cd is minimum at pH 9.5 [8].

F1 concentrations ranged between 0.0-8.5 mg/kg with an average of 0.46 mg/kg. The highest concentration is in site 1 located Saguling lake inlet in the Citarum River Nanjung section, while the lowest concentration is in the site 11 located Saguling lake outlet. F2 concentrations ranged between 3.6-8.9 mg/kg with an average of 3.1 mg/kg. The highest concentration is in site 9 while the lowest concentration is in the site 12. F3

concentrations ranged between 0.0-4.1 mg/kg with an average of 0.8 mg/kg. The highest concentration is in site 11 while the lowest concentration is in the site 1, 2, 4, 7, and 10. F4 concentrations ranged between 19.5-91.1 mg/kg with an average of 39.5 mg/kg. The highest concentration is in site 10 while the lowest concentration is in the site 7.

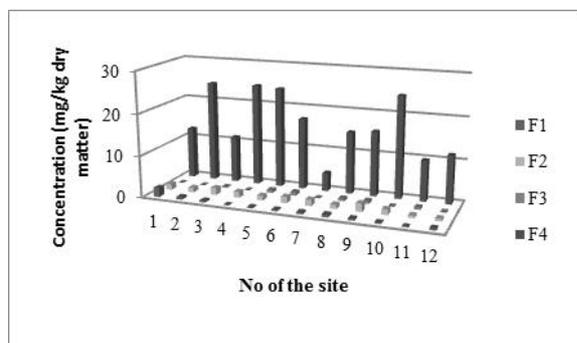


Fig. 2. Chemical speciation of Cd in twelve sediment samples from Saguling lake

Based on the average value of the concentration of the largest to the smallest fraction of the heavy metal Cd in Saguling lake is $F4 > F2 > F1 > F3$ so it can be concluded that only a small fraction of heavy metals Cd which are mobile.

The speciation of Cd is generally considered to be dominated by dissolved forms except in cases where the concentration of suspended particulate matter is high such as “muddy” rivers and reservoirs and near-bottom benthic boundary layers, and underlying bottom sediments in river sand lakes [20].

3.4.1. Chromium (Cr)

Cr, as well as Zn, are the most abundant of the “heavy metals” with a concentration of about 69 mg/kg in the lithosphere. Cr occurs in nature mainly in the mineral chromite. The metallurgy industry uses the highest quality chromite ore whilst the lower-grade ore is used for refractory bricks in melting furnaces. Major atmospheric emissions are from the Cr alloy and metal producing industries. Cr^{6+} is a potent carcinogen and Cr^{3+} is an essential trace element [19].

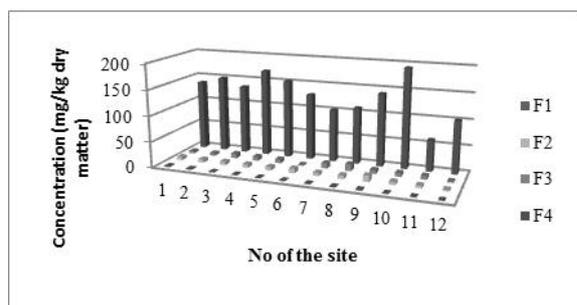


Fig. 3 Chemical speciation of Cr in twelve sediment samples from Saguling lake

The total content of Cr in Saguling lake surface sediment exceeds the standard base on Australian and New Zealand Environment and Conservation Council, 1997. Cr total concentration varied from 93.4-255.2 mg/kg. The minimum value of Cr is located in site 11 while the maximum value is located in site 8. The average value is 203.9 mg/kg, which is higher than the background value of world geochemical background value in average shale [13].

F1 concentrations ranged between 0.2-1.9 mg/kg with an average of 1.0 mg/kg. The highest concentration is in site 1 located Saguling lake inlet in the Citarum River Nanjung section, while the lowest concentration is in the site 12 located Saguling lake outlet. F2 concentrations ranged between 2.8-11.9 mg/kg with an average of 6.7 mg/kg. The highest concentration is in site 9 while the lowest concentration is in the site 12. F3 concentrations ranged between 2.5-13.44 mg/kg with an average of 7.1 mg/kg. The highest concentration is in site 8 while the lowest concentration is in the site 12. F4 concentrations ranged between 60.38-169.7 mg/kg with an average of 131.7 mg/kg. The highest concentration is in site 4 while the lowest concentration is in the site 11.

Based on the average value of the concentration of the largest to the smallest fraction of the heavy metal Cr in Saguling lake is $F4 > F3 > F2 > F1$ so it can be concluded that only a small fraction of heavy metals Cr which are mobile.

3.4.2. Copper (Cu)

F1 concentrations ranged between 4.5-12.3 mg/kg with an average of 8.6 mg/kg. The highest concentration is in site 9, while the lowest concentration is in the site 12 located Saguling lake outlet. F2 concentrations ranged between 1.6-5.4 mg/kg with an average of 3.1 mg/kg. The highest concentration is in site 7 while the lowest concentration is in the site 12. F3 concentrations ranged between 7.2-30.0 mg/kg with an average of 20.5 mg/kg. The highest concentration is in site 3 while the lowest concentration is in the site 6. F4 concentrations ranged between 1.2-54.8 mg/kg with an average of 22.1 mg/kg. The highest concentration is in site 10 while the lowest concentration is in the site 4. Based on the average value of the concentration of the largest to the smallest fraction of the heavy metal Cu in Saguling lake is $F4 > F3 > F1 > F2$ so it can be concluded that only a small fraction of heavy metals Cu which are mobile.

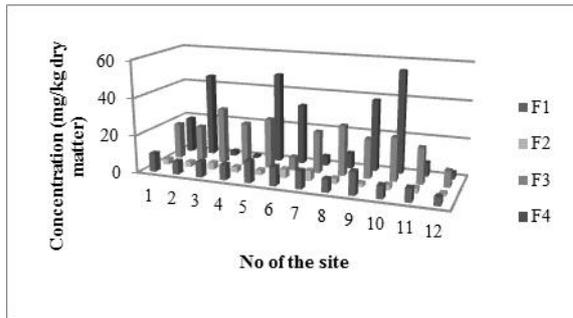


Fig. 4 Chemical speciation of Cr in twelve sediment samples from Saguling lake

3.4.3. Lead

F1 concentrations ranged between 0.0-1.5 mg/kg with an average of 0.1 mg/kg. The highest concentration is in site 1, while the concentration in other site are zero. F2 concentrations in all sampling point are zero. F3 concentrations almost zero in all sampling point except in site 6. F4 concentrations ranged between 3.4-23.3 mg/kg with an average of 12.3 mg/kg. The highest concentration is in site 5 while the lowest concentration is in the site 9.

Based on the average value of the concentration of the largest to the smallest fraction of the heavy metal Pb in Saguling lake is $F4 > F3 > F1 > F2$ so it can be concluded that only a small fraction of heavy metals Pb which are mobile.

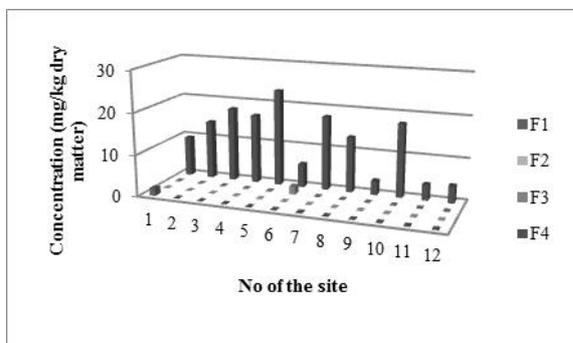


Fig. 5 Chemical peciation of Cr in twelve sediment samples from Saguling lake

The most important environmental sources for Pb are gasoline combustion (presently a minor source, but in the past 40 years a major contributor to Pb pollution), Cu-Zn-Pb smelting, battery factories, sewage sludge, coal combustion, and waste incineration [15].

3.4.4. Risk assessment code (RAC)

Metals are bound to different sediment fractions, with the binding strength determining their bioavailability and the risk associated with their presence in aquatic systems. The risk assessment code (RAC) was determined based on the percentage

of the total metal content that was found in the exchangeable and acid soluble fraction (F1). This fraction is considered to be the most unstable and reactive phase, which has greater potential for adverse effects on the aquatic environment compare to the other fractions [7]. When the percentage mobility is less than 1%, the sediment has no risk to the aquatic environment. Percentages of $1 < RAC < 10\%$ may reflect low risk, $11 < RAC < 30\%$ medium risk, and $31 < RAC < 50\%$ high risk. A RAC percentage above 50% poses a very high risk and it is considered dangerous because metals are easily able to enter the food chain [7]. As can be seen from Table 4, sediment had no or low risks associated with Cd and Cr, which had RAC value below 10% in all of the samples, indicating that these metals were only slightly mobile in the lake sediment. All of the samples had low or medium risks (RAC values below 30%) associated with Cu. Pb pose a medium risk to the environment at site 1. The results suggested that Cd, Cr, Cu, and Pb, were not easily released by the sediments into the water and therefore that heavy metals wouldnot be likely to enter the food chain in the Saguling lake ecosystem.

Table 4. Risk assessment code (RAC) for heavy metals in surface sediment from Saguling lake

No. of the site	Heavy Metals			
	Cd	Cr	Cu	Pb
1	Low	No	Medium	Medium
2	Low	No	Low	No
3	Low	No	Low	No
4	No	No	Medium	No
5	No	No	Medium	No
6	Low	No	Medium	No
7	Low	No	Medium	No
8	Low	No	Low	No
9	Low	No	Medium	No
10	No	No	Low	No
11	No	No	Medium	No
12	Low	No	Low	No

RAC value can be used as illustration that Saguling lake surface sediments have been contaminated by heavy metals and should be planned recovery efforts of the heavy metal pollution before causing an adverse impact on public health.

4. CONCLUSION

Based on result in the surface sediment of Saguling lake demonstrated the existence of

differences in the level of Cd, Cr, Cu, and Pb concentration. The possible main source of the metal contamination in the sediment are municipal and industrial waste water discharge, agriculture runoff, and atmospheric input. Based on calculations with the RAC value sediment had low to medium risks associated with Cd, Cr, Cu, and Pb which had RAC value below 30% in all of the samples. Based on the average value of the concentration of the largest to the smallest fraction of the heavy metal Cd in Saguling lake is F4> F2> F1> F3, Cr in Saguling lake is F4> F3> F2> F1, Cu in Saguling lake is F4> F3> F1> F2, Pb in Saguling lake is F4> F3> F1> F2 so it can be concluded that only a small fraction of heavy metals Cd, Cr, Cu, and Cd which are mobile.

5. REFERENCES

- [1] ANZECC (Australian and New Zealand Environment and Conservation Council) ANZECC Interim sediment quality guidelines report for the Environmental Research Institute of the Supervising Scientist, Sydney, Australia, 1997.
- [2] Bo Luji, Wang Dejian, Zhabg Gang, Wang Can. "Heavy metal speciation in sediments and the associated ecological risk in rural river in Southern Jiangsu Province, China". *Soil and Sediment Contamination*, Vol 24 2015, pp 90-102.
- [3] Camila V.A Santolin, Virginia S.T. Ciminelli, Clesia C. Nascentes, Claudia C. Windmoller; "Distribution and environmental impact evaluation of metals in sediments from the Doce River Basin, Brazil" *Environmental Earth Science*, 2015
- [4] Chakraborty Parthasarathi, babu Raghunadh P.V, Sarma V.V, "A study of lead and cadmium speciation in some estuarine and coastal sediments" *Chemical Geology* Vol. 294-295 2012 . pp 217-225
- [5] Cheng, Y., Hu, J., Luo, B., Xu, J.Z., "Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems". *Journal of Hazardous Materials* Vol 165 2009 pp 13-26.
- [6] Forstner U. Inorganic sediment chemistry and elemental speciation. In *Sediments: Chemistry and Toxicity on In Place Pollutants* (eds. R. Baudo, J. P. Giesy, and H. Mantau). Lewis, 1990 pp. 61-105
- [7] Gupta, A.K., Sinha, S., "Assessment of single extraction methods for the prediction of bioavailability of metals to *Brassica juncea* L. Czern. (var. Vaibhav) grown on tannery waste contaminated soil". *Journal of Hazardous Materials* 2007. Vol 149, 144-150.
- [8] Hem J. D "Chemistry and occurrence of cadmium and zinc in surface water and ground water". *Water Resour. Res.*8, . 1972 661-679.
- [9] anonim, Indonesia Power, *Water Monitoring Report*, 2014.
- [10] Kouassi, N.L.B., Yao. K.M., Trokourey A., Soro M.B., "Preliminary assessment of Cadmium mobility in surface sediment of a tropical estuary". *Bull. Chem. Soc. Ethiop*, Vol, 28 (2), 2014 pp 245-254"
- [11] Laing, G.D., De Vos, R., Vandecasteele, B., Lesage, E., Tack, F.M.G., Verloo, M.G., "Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary". *Estuarine, Coastal and Shelf Science* Vol 77, 2007 pp 589-602.
- [12] Li Y.-H., Burkhardt L., and Teraoka H. "Desorption and coagulation of trace elements during estuarine mixing". *Geochim. Cosmochim. Acta* Vol 48, 1984 pp 1879-1884
- [13] Turkerian, K.K and Wedepohl, K.H. "Distribution of the elements in soil mayor units of the earth's crust". *Bull. geol. Soc Am*, Vol 72, 1961 pp 175-192
- [14] Zhang, H., He, P., Shao, L.M., "Fate of heavy metals during municipal solid waste incineration in Shanghai". *Journal of Hazardous Materials* Vol 156, 2008 pp 365-373.
- [15] Zhao, X., Dong, D., Hua, X., Dong, S., "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, 2009 570-577.
- [16] Zhong, A.P., Guo, S.H., Li, F.M., Li, G.K., Jiang, X., "Impact of anions on the heavy metals release from marine sediments. *Journal of Environmental Sciences (China)*" Vol 18 2006, pp 1216-1220.