

Evaluation of Status of Heavy Metals Pollution of Sediments in Qua-Iboe River Estuary and Associated Creeks, South-Eastern Nigeria

Ikama E. Uwah¹, Solomon F. Dan², Rebecca A. Etiuma¹ & Unyime E. Umoh¹

¹ Department of Pure & Applied Chemistry, University of Calabar, Calabar, Nigeria

² Department of Marine Biology, Faculty of ocean Science and Technology, Akwa Ibom State University Ikot Akpaden, Nigeria

Correspondence: Ikama E. Uwah, Department of Pure & Applied Chemistry, University of Calabar, Calabar, Nigeria. Tel: 234-803-736-2413. E-mail: ikamauwah@yahoo.co.uk

Received: June 17, 2013 Accepted: August 21, 2013 Online Published: September 26, 2013

doi:10.5539/ep.v2n4p110

URL: <http://dx.doi.org/10.5539/ep.v2n4p110>

Abstract

Sixteen bottom sediment samples collected from Qua-Iboe River estuary and associated creeks were analyzed for Cd, Cr, Cu, Fe, Pb, Zn, Ni, pH, Organic carbon (orgC), and grain size in order to assess the current pollution status in sediment of the study area. Concentration data were processed using Pearson correlation analysis. Sediment pollution assessment was carried out using Enrichment factor, Geo-accumulation index and Modified degree of contamination. The calculated enrichment factor showed that the sediment was enriched with Cd, Zn, Cu and Pb. The results of geo-accumulation index (I_{geo}) indicated that sediments are unpolluted with Fe, moderately polluted with Cr, Cu, Pb, strongly polluted with Cd and extremely polluted with Ni. This was attributed mainly to oil contaminating wastes and metal scraps. The results of the modified degree of contamination (mC_d) revealed that the sediment of Qua Iboe estuary and associated creeks fall between $8 \leq mC_d \leq 16$ indicating very high degree of contamination.

Keywords: heavy metals, enrichment factor, geo-accumulation index, sediment quality

1. Introduction

The pollution of aquatic environment (especially estuaries) by heavy metals has been a source of serious concern to government regulatory agencies, environmentalist and the public at large (Manahan, 1991). This is particularly important because estuaries are rich in nutrient and as a result mothers varieties of fishery resources. Heavy metals play important roles in our society as most of them are vital raw materials in most industries. As trace elements, some heavy metals (e.g. Cu, Se, and Zn etc.) are essential in the maintenance of some metabolic activities in human bodies. However, at certain concentrations they become toxic. They are natural components of the earth's crust with large variations in concentration. They cannot be degraded nor destroyed due to their persistence in the environment. Their distribution in aquatic environment has been evidenced in human health effects and aquatic life disruptions due to long term exposure and bioaccumulation (Dahilia, Apodaca, Emerson, Tui, & Allyn, 2003). Marine sediments are the ultimate sinks of pollutants in the marine environment and it constitutes an important medium for scientific research. Like soils in the terrestrial environment, marine sediments in the aquatic ecosystem are the sources of substrate nutrients and become the basis of support to living aquatic organisms (Abdullah, Sidi, & Aris, 2007). The enrichment of metal in a sink is shown mainly by an increase in their concentrations in the bottom sediment. Their occurrence in the environment results primarily from anthropogenic activities. Also, natural processes, such as weathering of rocks and volcanic activities play a significant role in the enrichment of heavy metals in water bodies (Forstner & Wittmann, 1981; Forstner & Wittmann, 1983; Nriagu, 1989).

Heavy metals accumulate in sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds (Maher & Aislabie, 1992; Leivouri, 1998; Ankley et al., 1992). Several processes enhance the association of heavy metals with solid phase such as direct adsorption by fine-grained inorganic particles of clays, adsorption of hydrous ferric and manganic oxides which may in turn be associated with clays, adsorption on natural organic substances, which may also be associated with inorganic particles and direct precipitation as new solid phases (Gibbs, 1973). The dissolution and adsorption processes are influenced by several physicochemical parameters such as: pH, dissolve

oxygen, salinity, redox potential, organic and inorganic carbon contents, and the presence in water phase of some anions and cations that can bind or co-precipitate the water-dissolved or suspended pollutants (Di Toro et al., 1991; Calmano, Hong, & Forstner, 1993; Wen & Allen, 1999).

2. Study Area

The Qua Iboe River estuary (Figure 1) lies within latitude $4^{\circ}30'$ to $4^{\circ}45'$ N and longitude $7^{\circ}30'$ to $8^{\circ}00'$ E on the south eastern Nigeria coastline. It is a mesotidal estuary having tidal amplitude of 1m and 3m at neap and spring phases respectively. The river originating from Umuahia hills traverses mainly sedimentary terrains of cretaceous to recent ages and develops into extensive meanders before emptying into the Atlantic Ocean. Creeks and channels islands are common throughout the length of the estuary while sand bars occur at the mouth as a result of interplay between the long shore drift which runs approximately in a west-east direction (parallel to the shoreline) and the river current.

Whereas the area has some coastal plain sands which are not older than the quaternary age, the Creeks have younger alluvial covers. Sediments are brought into the estuary by long shore drift, tide flow, waves and river transport. Coarse to medium-grained sand occurs mostly in the mouth of the estuary and middle of the main channels where the tidal currents are strong but most parts of the banks and Creeks, where they are weak are characterized by fine sand, silt and clay. The latter has a high affinity for pollutants such as hydrocarbon and heavy metals.

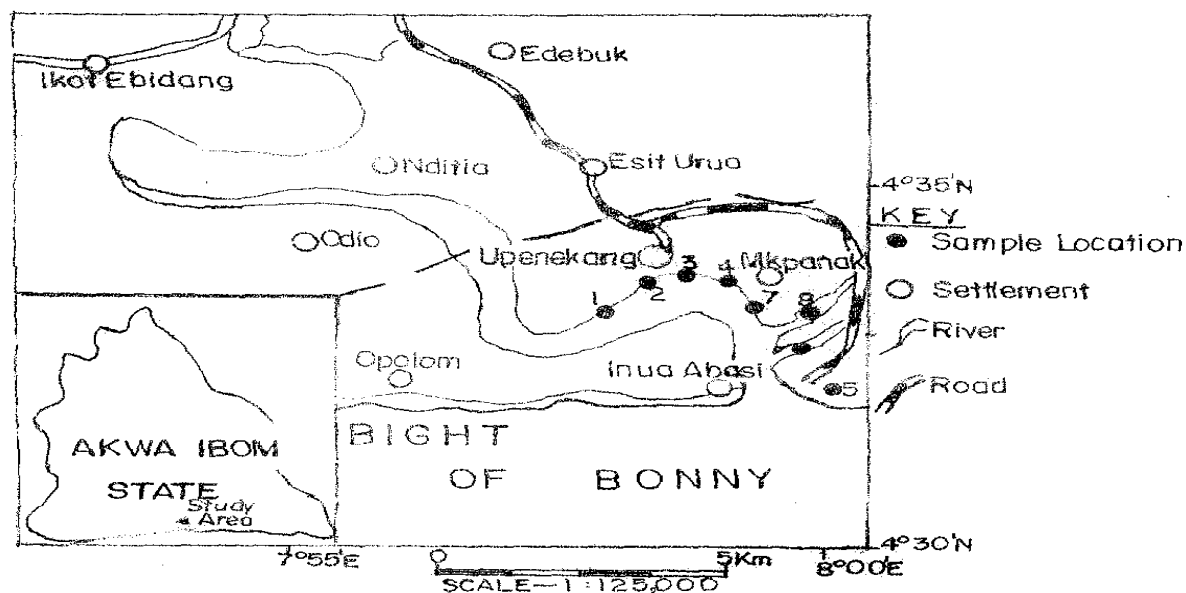


Figure 1. Map of the study area

The climate of the area is characterized by a long wet season usually lasting from April to November and a short spell of dry weather from December to March. The main occupation of the inhabitants include small scale fish farming, boat construction, transportation along the river, oil exploration, sand excavation for commercial purposes as well as timber logging of mangrove vegetation as fuel wood (Ekwere, Akpan, & Ntekim, 1992).

3. Materials and Methods

3.1 Sampling and Grain Size Analysis

A total of sixteen sediment samples were collected from the study area from eight stations using a Van Veen grab sampler. The samples for heavy metals analysis were placed in polyethylene bags while samples for organic carbon determination were placed in aluminum foil. The samples were immediately placed in an ice box as soon as retrieved and then taken to the laboratory. The sediment samples were oven dried to a constant weight at 60°C for 24 h and were further disaggregated in an agate mortar and sieved to $63\ \mu\text{m}$ sizes. The $63\ \mu\text{m}$ mesh was chosen in order to normalize the result by a chemical factor. Grain size analysis was done using the sieve analysis procedure with the aid of a sieve shaker machine. The different laboratory test sieve ranged from; 2 mm

→ 1mm → 0.50mm → 0.11mm → 0.050 mm → Pan (clay). 100 grams of each sample was placed on the arranged laboratory test sieve, and inserted into the sieve shaker machine for 10 minutes. After this duration, particles that passed through were retained on the standard set of sieves of various sizes and were measured for the weight percentage of particles. The procedure was repeated for each sample and the grain size % was calculated using the formula as given by Wikipedia (2013) and modified as given below:

$$\text{Grain Size} = \frac{\text{Sieve weight}}{\text{Total weight}} \times 100 \quad (1)$$

3.2 Sample Digestion and Analysis of Metal Ions

1 g of sediment sample was digested with a solution of concentrated HClO_4 (2 ml) and HF (10 ml) to near dryness. Subsequently, a second addition of HClO_4 (1 ml) and HF (10 ml) were made and the mixture was evaporated to near dryness. Finally, HClO_4 (1ml) was added and the sample was evaporated until white fumes appeared. The residue was dissolved in concentrated HCl and diluted to 25 ml prior for heavy metals analysis using Atomic Absorption Spectroscopy (Model: SpetrAA B65). The total organic carbon content was evaluated using the Walkey and Black titration method (Walkey & Black, 1934). The sediment pH was determined using JENWAY 370 pH meter. A buffer solution with pH 7.0 was added to a beaker and the pH electrode was then inserted, the pH meter was calibrated to a pH of 7.0. 20 g of each sample was placed in a beaker; 50ml of distilled water was added to each sample and stirred for 30 minutes before inserting the probe into the system. Also, 50 ml of filtered water samples were placed in beakers after which the pH probe was inserted and the values were then read off from the electronic meter attached to the probe and data obtained recorded (Bascomb, 1994).

4. Results and Discussion

The total organic carbon (orgC) in sediments of Qua Iboe River estuary and associated creeks ranged from 0.05% to 1.36%, with an average of 0.38% during the dry season and 0.08% and 1.03% with an average of 0.28% during the wet season (Table 1). The higher values observed during dry season may be as a result of high anthropogenic activity during this season. Also, co-precipitation with carbonate minerals is another important source of organic carbon (Fortsner & Wittmann, 1983; Alloway, 1990). pH values ranged from 6.71 to 9.69 with an average of 7.82 during dry season and 5.99 to 7.67 with an average of 6.59 during wet season. The higher concentrations of Cd, Cr, Cu, Fe, Ni, Pb, Zn, and Hg during this season were attributed to lower pH levels in the sediments. The lower pH values may have been from run-off from bush land areas which particularly introduces tannic acid (tannins) which are found naturally in leaves which also account for a tea-like colour of the seas (Barnes, Meyer, & Freeman, 1998).

Table 1. Descriptive statistics

Variable	Dry Season				Wet Season			
	Mean	StDev	Min	Max	Mean	StDev	Min	Max
<i>pH</i>	7.82	0.85	6.71	9.65	6.59	0.61	5.99	7.65
<i>orgC</i>	0.38	0.41	0.05	1.36	0.28	0.31	0.08	1.03
<i>Sand</i>	43.6	17.39	18.62	75.32	43.6	17.39	18.62	75.32
<i>Silt</i>	33.58	8.37	20.42	49.68	33.58	8.37	20.46	49.68
<i>Clay</i>	24.07	14.72	4.22	45.24	24.07	14.72	4.22	45.24
<i>Cd</i>	0.08	0.04	0.02	0.16	0.21	0.36	0.04	1.1
<i>Cr</i>	0.1	0.04	0.01	0.13	0.06	0.04	0.03	0.14
<i>Cu</i>	0.09	0.03	0.01	0.13	0.07	0.03	0.03	0.13
<i>Fe</i>	42.2	1.9	39.54	44.63	28.53	1.14	26.05	29.4
<i>Pb</i>	0.08	0.03	0.03	0.13	0.07	0.03	0.03	0.12
<i>Zn</i>	7.51	0.29	7.06	7.85	6.44	0.34	5.86	6.9
<i>Ni</i>	12.51	0.49	11.43	13.03	10.86	1.07	9.2	11.95
<i>Hg</i>	0.0005	0.0005	0.00	0.001	0.000125	0.00035	0	0.001

The descriptive statistics of pH, orgC (%), sand (%), silt (%), clay (%) and heavy metals content (mg/g) in sediment of Qua-Iboe estuary and associated creeks during wet and dry seasons.

The percentage of sand fraction ranged from 18.62% to 75.32% with an average of 43.06%, while silt fraction ranged from 20.42% to 49.68% with an average of 33.08% and the percentage fraction of clay ranged from 4.22% to 45.28% with an average of 24.07%.

From the data presented on Table 1, it is observed that both physical and chemical parameters vary between seasons (wet and dry), and these may be as a result of differences in anthropogenic inputs due to intense seasonal variations, influence of tides and salt water intrusion (Asuquo, 1998; Ekwere et al., 1992). However, mean concentrations of Cd (0.08 ± 0.004 mg/g d-wt), Cr (0.1 ± 0.04 mg/g d-wt), Cu (0.09 ± 0.003 mg/g d-wt), Fe (42.2 ± 1.9 mg/g d-wt), Pb (0.08 ± 0.003 mg/g d-wt), Zn (7.51 ± 0.29 mg/g d-wt), Ni (12.51 ± 0.49 mg/g d-wt) obtained during dry season were higher than the mean concentrations of Cd (0.21 ± 0.03 mg/g d-wt), Cr (0.06 ± 0.004 mg/g d-wt), Cu (0.07 ± 0.003 mg/g d-wt), Fe (28.53 ± 1.14 mg/g d-wt), Pb (0.07 ± 0.003 mg/g d-wt), Zn (6.44 ± 0.34 mg/g d-wt) and Ni (10.86 ± 1.07 mg/g d-wt) obtained during the wet season. Apparently, the mean values of Cd and Zn were higher than marine sediment quality standards (MSQS) of 5.1 and 410 ppm respectively. The lower concentrations of these metals in sediment during wet season may be attributed to the lower pH levels dissolving these metals into the water column.

The analyses of the data using Pearson's correlation matrix among the levels of orgC, pH, Sand, Silt, Clay, Cd, Cr, Cu, Fe, Pb, Zn, Ni, and Hg in sediment samples during wet and dry seasons are presented in Tables 2 (a & b). During wet season, strong positive correlations were observed between Cd and Clay ($r = 0.87$), Pb ($r = 0.65$), Zn ($r = 0.91$), Hg ($r = 0.61$), Fe ($r = 0.76$), Cu with Clay ($r = 0.80$), Fe with Clay ($r = 0.88$), Cu ($r = 0.82$), Pb with Clay ($r = 0.72$), Fe ($r = 0.64$), Zn with Clay ($r = 0.81$), Fe ($r = 0.83$), Pb ($r = 0.55$), Ni with pH ($r = 0.65$), Hg with Zn ($r = 0.56$).

Table 2. Pearson's correlation matrix

(a)

	pH	orgC	Sand	Silt	Clay	Cd	Cu	Fe	Pb	Zn	Ni
orgC	-0.315										
Sand	0.547b	-0.028									
Silt	-0.105	0.037c	-0.650								
Clay	-0.683	-0.038	-0.822	0.135c							
Cd	-0.856	-0.053	-0.731	0.238c	0.865a						
Cu	-0.515	0.218c	-0.698	0.105c	0.797a	0.496b					
Fe	-0.631	-0.181	-0.863	0.332c	0.879a	0.756a	0.824a				
Pb	-0.335	-0.144	-0.867	0.559b	0.718a	0.646a	0.392c	0.643a			
Zn	-0.776	-0.324	-0.632	0.096c	0.806a	0.906a	0.481b	0.828a	0.551b		
Ni	0.654a	0.305c	0.382c	0.126c	-0.734	-0.839	-0.393	-0.597	-0.313	-0.827	
Hg	-0.908	0.482b	-0.239	-0.166	0.467b	0.611a	0.429b	0.390c	0.042b	0.558b	-0.511

(b)

	pH	orgC	Sand	Silt	Clay	Cd	Cr	Cu	Fe	Pb	Zn	Ni
orgC	-0.227											
Sand	-0.350	-0.079										
Silt	-0.081	0.663a	-0.650									
Clay	0.420b	-0.310	-0.822	0.135c								
Cd	-0.534	0.036c	0.138c	0.057c	-0.242							
Cr	-0.145	-0.257	0.022c	-0.416	0.446b	-0.221						
Cu	0.553b	-0.033	-0.848	0.349c	0.789a	-0.351	-0.049					
Fe	0.223c	-0.033	-0.810	0.543b	0.716a	-0.379	0.222c	0.532b				
Pb	0.237c	-0.210	-0.739	0.401b	0.682a	-0.447	0.148c	0.671a	0.766a			
Zn	0.206c	-0.179	-0.820	0.326c	0.913a	-0.223	0.497b	0.634a	0.830a	0.809a		
Ni	-0.241	0.165c	0.655a	-0.040	-0.902	0.236c	-0.627	-0.706	-0.500	-0.610	-0.856	
Hg	-0.164	-0.107	-0.041	-0.266	0.440b	-0.190	0.980a	-0.061	0.282c	0.157c	0.157c	-0.626

Pearson's correlation matrix of pH, Organic carbon, Silt, Clay and heavy metals in sediment of Qua-Iboe River estuary and associated creeks during wet (a) and dry (b) seasons.

a * significant at $p < 0.01$.

b * significant at $p < 0.05$.

c * not significant.

During dry season, low positive correlations were observed between Cd and orgC ($r = 0.04$), Sand ($r = 0.14$), Silt ($r = 0.06$), Ni ($r = 0.24$), Cr with ($r = 0.02$), Clay ($r = 0.45$), Fe ($r = 0.22$), Pb ($r = 0.15$), strong positive correlation with Zn ($r = 0.50$), Hg ($r = 0.98$), Strong significant correlations between Cu and pH ($r = 0.55$), Clay ($r = 0.79$), Fe ($r = 0.53$), Pb ($r = 0.67$) and Zn ($r = 0.63$) were observed.

There was positive correlation between Fe and pH ($r = 0.22$), Hg ($r = 0.28$) but strong positive correlations with Silt ($r = 0.54$), Clay ($r = 0.72$), Pb ($r = 0.77$) and Zn ($r = 0.83$), strong positive correlations between Pb and Clay ($r = 0.68$), Zn ($r = 0.81$), Zn with Clay ($r = 0.91$) and Hg ($r = 0.54$), Ni with Sand ($r = 0.66$). Significant correlation among the variables indicates that there are linear relationships between the parameters. It is well established that organic matter content is an important controlling factor in the abundance of heavy metals (Rubio, Nombela, & Vilas, 2000). The poor correlation between Cd, Cr, Cu, Fe, Zn, Pb, Ni, Hg, and organic carbon, sand, silt fractions indicates that organic carbon and silicates are not the main geochemical carriers of the metal in

sediments of the study area (Chatterjee et al., 2006).

Apparent difference of the anthropogenic inputs of heavy metals from the geogenic sources is important in evaluating the extents of heavy metal pollution. Enrichment factor (EF), Geo-accumulation index (Igeo), Modified degree of contamination (mC_d) was used to assess and interpret the pollution status of the estuary in different stations. Several kinds of refractory metals such as Al, Fe, Mg, Ti, Sc, Li and Cs have been used to normalize the grain size effect for heavy metal concentrations in sediments (Habes & Nigem, 2006; Baptista Neto, Smith, & McAllister, 2000; Schiff & Weisberge, 1999). In this study iron was used as a conservative tracer to differentiate natural from anthropogenic components. Although Fe and the heavy metals in the sediments showed discrepancies depending on the type of elements, significant correlations from Pearson correlation analysis were observed. Heavy metal concentrations were normalized to Fe to account for differences in grain size and mineralogy and then normalized by background values from the study carried out by Ekwere et al. (1992) who studied the geochemistry of sediments in Qua-Iboe estuary and associated creeks, to assess the anthropogenic input of metals in the study area. The advantage of using enrichment factor (EF) analysis is that it is possible to establish a contamination guideline. This technique has been well applied in several studies to assess metal contamination in marine sediments (Khaled, El-Neme, & El-Sikkaily, 2006; Acevedo-Figueroa, Jimenez, & Rodriguez-Sierra, 2006; Ghrefat & Yusuf, 2006; Barakat, Baghdadi, Rais, & Nadem, 2012; Mashiatullah, Chaudhary, Ahmed, Javel, & Ghaffar, 2013).

Enrichment factor is a convenient measure of geochemical trends and is used for comparison between areas. It is applied widely in sediment geochemical studies (Abraham, 1998; Soto-Jimenez & Pacz-Osuna, 2001; Kamau 2002; Qu, Chen, Yang, & Lu, 1993; Kehing, Pinto, Moreira, & Malm, 2003; Barakat et al., 2012).

According to Ergin, Saydam, Basturk, Erdem, and Yoruk (1991), the metal enrichment factor (EF) is defined by the equation below:

$$EF = \frac{\frac{M}{Fe} \text{ Sample}}{\frac{M}{Fe} \text{ Background}} \quad (2)$$

$\frac{M}{Fe} \text{ Sample}$ is the ratio of metal and Fe concentration of the sample, and $\frac{M}{Fe} \text{ Background}$ is the ratio of the metal and Fe concentration of the background value.

The formula below was applied to the studied heavy metals in the study to assess the anthropogenic and lithogenic contributions:

$$[M]_{\text{Lithogenic}} = [Fe]_{\text{Sample}} \times \left(\frac{M}{Fe} \right)_{\text{Lithogenic}} \quad (3)$$

where $\left(\frac{M}{Fe} \right)_{\text{Lithogenic}}$ corresponds to the average background ratio. The anthropogenic heavy metals can be

estimated by the formula shown below:

$$[M]_{\text{Anthropogenic}} = [M]_{\text{Total}} - [M]_{\text{Lithogenic}} \quad (4)$$

Birch (2003) divided contamination into different categories based on EF values. $EF < 1$ demonstrates “no enrichment”, $1 < EF < 3$ is “minor enrichment”, $EF = 3-5$ is “moderate enrichment”, $EF = 5-10$ is “moderately severe enrichment”, $EF = 10-25$ is “severe enrichment”, $EF = 25-50$ is “very severe enrichment” and $EF > 50$ is “extremely severe enrichment”. The enrichment of heavy metals in sediments of Qua Iboe River estuary and associated creeks is shown in Table 3.

The factor obtained for the studied area revealed that there were extreme enrichment of cadmium in all the stations during dry and wet seasons, severe enrichment of zinc, minor to moderate enrichment of lead, minor enrichment of copper, minor enrichment of nickel, no enrichment of chromium, mercury and iron. This is similar to work reported by Joseph (2002) in sediments of Port-Reitz creek, Mombasa; Rezaee, Saion, Yab, Abdi, and Riyahi (2010) in sediments cores from South China Sea; Habes and Nigem (2006), in bottom sediments of Wadi

Al-Arab Dam, Jordan.

Table 3. The result of enrichment factor (EF)

Stations	WET SEASON								DRY SEASON							
	Cd	Cr	Cu	Fe	Pb	Zn	Ni	Hg	Cd	Cr	Cu	Fe	Pb	Zn	Ni	Hg
Ikotlwang	56	0.6	4.2	1	1	11.5	1.1	5.1	32.1	0.5	6.2	1	7.3	15.3	1.2	0
Iwoachang	47.3	0.5	3.8	1	3.7	11.4	1.1	0	45.4	0.4	4.4	1	4.3	14.3	1.1	0
Ukpenekang	39.5	0.55	2.9	1	3.6	11.3	1.1	0	65	0.3	3.6	1	4.4	14.6	1.5	0
Atasi	43	0.4	1	1	3.8	12.1	1.3	0	71.9	0.4	1.5	1	4.4	14.6	1.6	0
Ukpenekang	9.5	0.7	2.5	1	1.5	11.8	1.3	0	107.4	0.5	2.3	1	2	14.8	1.7	0
Douglas creek	41.4	0.6	3.5	1	2	11.6	1.2	5	7.5	0.4	2	1	2.6	15	1.6	0
Egerton Port	48	0.8	2.7	1	2	11.9	1.1	4	45.8	0.3	2.5	1	3.1	14.1	1.6	0
Stubbs creek	69	2.3	3.3	1	3.5	11.9	1	0	25.7	1.3	2.9	1	4.9	15.5	1.2	0
Mean	44.26	0.81	2.98	1	2.64	11.7	1.2	1.8	50.1	0.5	3.2	1	4.13	14.8	1.4	0

The result of enrichment factor (EF) for both wet and dry seasons in the study area.

According to these researchers, possible enrichment of Cd in bottom sediments was attributed to anthropogenic inputs from fertilizers and pesticides used in agricultural activities. Manaf, Samah, and Zukki (2009) reported that domestic wastes is the primary source of the generation of solid wastes as a result the high concentration of Cd in Malaysia and its coast.

Sediment bacteria may also assist in the partitioning of cadmium from water to sediments. Studies indicate that concentrations of cadmium in sediments are at least one order of magnitude higher than in the overlying water. The mode of sorption of cadmium to sediments is important in determining its deposition and remobilization into water column (Harisson & De Mora, 1996). Cadmium, associated with carbonate minerals or co-precipitated with hydrous iron oxides, is less likely to be mobilized by re-suspension of sediments or biological activity. Cadmium that is adsorbed to mineral surfaces such as clay, or to organic materials, is more easily bioaccumulated or released in the dissolved state when the sediment is disturbed. Cadmium may re-dissolve from sediments under varying ambient conditions of pH, salinity, and redox potential (Di Toro et al., 1991). Cadmium is not known to form volatile compounds in the aquatic environment, so partitioning from water to the atmosphere does not occur. The geo-accumulation index was introduced by Muller in 1979. The model was used to assess metal pollution in sediments from Qua Iboe river estuary besides the enrichment factor. Geo-accumulation Index is expressed as:

$$I_{geo} = \log_2 \left(\frac{c_n}{1.5B_n} \right) \quad (5)$$

where c_n is the measured concentration of the heavy metal (n) in the <63 μ m fraction of the sediment, B_n is the geochemical background value in average shale (Turekian & Wedepohl, 1961) of element n, and 1.5 is the background correction factor due to lithogenic effects. The index of geo-accumulation includes seven grades which show various degrees of enrichment above the background value ranging from unpolluted to much polluted water and sediment quality (Table 3). The highest grades (class six) reflect 100-fold enrichment above the background values (Sing, Hasnain, & Banerjee, 2003).

Table 4. Muller's classification for geo-accumulation index

Igeo value	Class	Sediment quality
≥ 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately polluted to strongly polluted
3-4	4	Strongly polluted
4-5	5	strongly polluted to extremely polluted
> 5	6	Extremely polluted

Muller's classification for geo-accumulation index.

Table 5. Results of geo-accumulation index (Igeo)

Stations	WET SEASON								DRY SEASON							
	Cd	Cr	Cu	Fe	Pb	Zn	Ni	Hg	Cd	Cr	Cu	Fe	Pb	Zn	Ni	Hg
IkotIwang	8.2	1.3	1.0	-0.5	1.2	1.9	6.5	1.2	2.6	0.7	1.0	-0.9	1.1	1.9	6.3	0.0
Iwoachang	3.4	1.1	0.9	-0.5	0.8	2.0	6.5	0.0	2.9	0.5	0.6	0.9	0.6	1.8	6.4	0.0
Ukpenekang	3.2	1.1	0.6	-0.5	0.8	1.9	6.6	0.0	3.3	0.2	0.5	-0.9	0.6	1.8	6.4	0.0
Atasi	3.2	0.7	-0.5	-0.6	0.8	1.9	6.0	0.0	3.4	0.5	-0.5	-0.9	0.6	1.8	6.5	0.0
Mkpanak	1.7	1.4	0.4	-0.6	-0.2	1.9	6.6	0.0	3.6	0.7	-0.2	-1.1	-0.3	1.7	6.5	0.0
Douglas creek	3.2	0.6	0.7	-0.5	0.2	1.9	6.6	1.2	5.7	0.5	-0.2	-0.9	0.03	1.8	5.4	0.0
Egerton Port	3.4	1.6	0.5	-0.5	0.2	2.0	6.5	1.2	2.9	0.2	0.01	-0.9	0.2	1.8	6.5	0.0
Stubbs creek	3.8	2.6	0.7	-0.5	0.8	2.0	6.5	1.2	2.4	1.7	0.2	-0.9	0.7	1.9	6.2	1.2
Mean	3.8	1.3	0.5	-0.5	0.6	1.9	6.5	0.6	3.4	0.6	0.2	-0.9	0.4	1.8	6.3	0.2

Results of geo-accumulation index (Igeo) for both wet and dry seasons in the study area.

Results from the mean geo-accumulation index (Equation 5. and Table 4) reveal the following trend $Ni > Cd > Zn > Cr > Cu > Pb > Hg > Fe$ (Figure 7). Based on Muller (1979) classification (Table 3), marine sediment for geo-accumulation of metals, Ni belongs to class 6 (extremely polluted), Cd belongs to class 4 (strongly polluted), Zn belongs to class 2 (moderately polluted), Cr, Cu, Pb, and Hg belongs to class 1 (unpolluted to moderately polluted) and Fe belongs to class 0 (background concentration) making it a suitable normalizer for sediments of the study area. The geo-accumulation is important because on a weight per square meter basis, the uppermost superficial sediments serve as the largest heavy metal sinks in marine ecosystem. Once these heavy metals accumulate in sediments, they tend to pose threats to aquatic life as a result of re-suspension into the water column from geochemical cycling, bioaccumulating in benthic organisms that feed on substrate nutrient and also biomagnified through the aquatic food web.

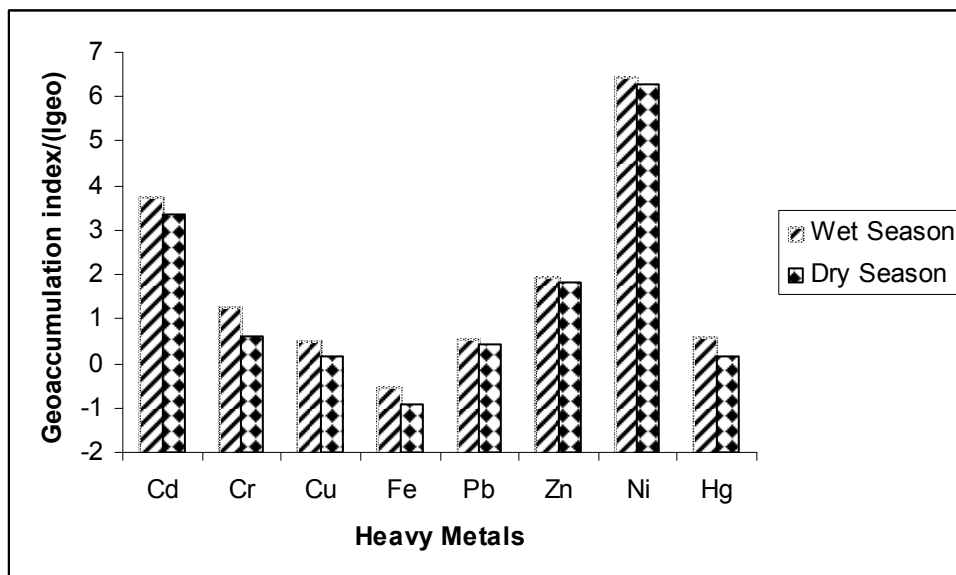


Figure 2. Seasonal variations in geo accumulation index of heavy metals in sediments of the study area

Modified degree of contamination (mC_d) is based on the calculation for each pollutant of a contamination factor (C_f). However, the C_f requires that at least five surficial sediment samples are averaged to produce a mean pollutant concentration which is then compared to baseline pristine reference level, according to the equation below:

$$CF = \frac{C_{Sample}}{C_{background}} \quad (6)$$

where C_{sample} and $C_{background}$ respectively refer to the mean concentration of a pollutant in the contaminated sediments and the pre-industrial “baseline” sediment or average shale. The numeric sum of the K specifies contamination factors which express the overall degree (Hakanson, 1980) of sediment contamination (C_d) using the following formula:

$$C_d = \sum_{i=1}^k cf_i \quad (7)$$

The C_d is aimed at providing a measure of the degree of overall contamination in surface layers of the sediment. Furthermore, all n species must be analyzed in order to calculate the correct C_d for the range of classes defined by (Hakanson, 1980). The modified formula is generalized by defining the degree of contamination mC_d as the sum of all the contamination factors C_f for a given set of estuarine pollutants divided by the number of analyzed pollutants. The modified equation for a generalized approach to calculating the degree of contamination is given:

$$mC_d = \frac{\sum_{i=1}^k Cf_i}{n} \quad (8)$$

where n is the number of analyzed elements and (i) is i_{th} element (or pollutant) and C_f is formula to calculate M_{cd} . It allows the incorporation of as many metals as the study may analyze with no upper limit. Table 5 shows the model for classifying estuarine sediment.

Table 6. Hakanson (1980) classification of the modified degree of contamination (Abraham et al., 2007)

m_{Cd} values	Sediment quality
$mCd < 1.5$	Nil to low degree of contamination
$1.5 \leq mCd < 2$	Low degree of contamination
$2 \leq mCd < 4$	Moderate degree of contamination
$4 \leq mCd < 8$	High degree of contamination
$8 \leq mCd < 16$	Very high degree of contamination
$16 \leq mCd < 32$	Extremely high degree of contamination
$mCd > 32$	Ultra high degree of contamination

Table 7. Results of modified degree of contamination

Stations	mCd	
	Dry season	Wet season
IkotIwang	40.00	36.00
Iwoachang	7.20	2.90
Ukpenekang	0.91	0.88
Atasi	2.73	2.10
Mkpanak	0.80	0.61
Douglass creek	3.08	2.69
Egerton Port	10.50	8.98
Stubbs creek	10.40	8.99
Mean	9.34	7.78

Modified degree of contamination using pristine values (Ekwere et al., 1992) for heavy metals in bottom sediments from Qua-Iboe River estuary and associated creeks, South Eastern Nigeria.

The earlier indices (EF and Igeo) gave diverse classification of sediment quality of the study area. The modified degree of contamination has an advantage over other indices and provides a measure of the overall degree of contamination of all the chemical parameters in each sampling station. Based on Hakanson classification (Equation 8 and Table 5), Ikot Iwang shows an ultra high degree of contamination during both seasons, Iwoachang is moderately contaminated from the wet season results but highly contaminated from the dry season results, Ukpenekang shows low degree of contamination, Atasi moderately polluted while Mkpanak shows low degree of contamination during both seasons, Douglass Creek is moderately polluted, Egerton Port and Stubbs Creek show very high degree of contamination. However, on the average, the sediments of Qua Iboe River estuary and some associated creeks were found to be highly contaminated during both seasons.

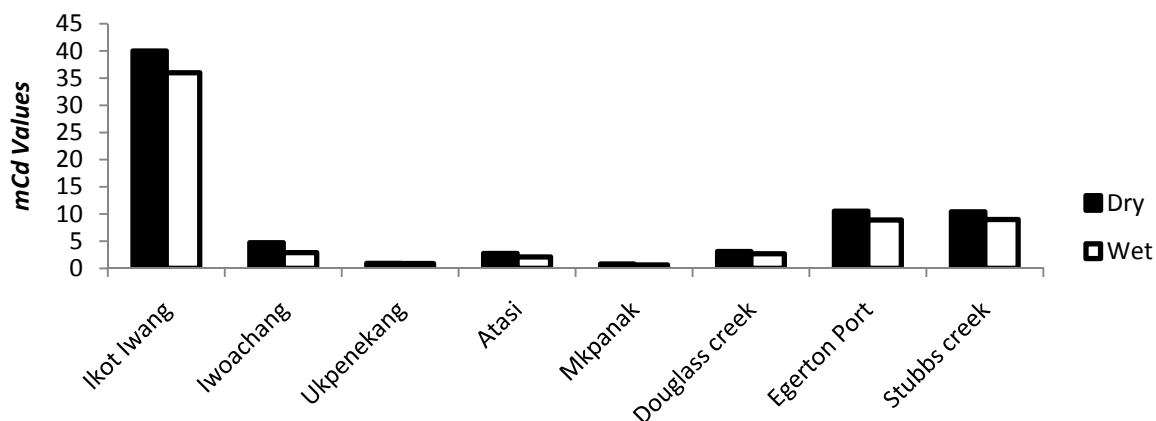


Figure 3. Modified degree of contamination

5. Conclusion

Identification and quantification of heavy metal sources, as well as their enrichment in marine sediments are important environmental scientific issues. Descriptive statistics showed that the mean concentrations of Cr, Cu, Fe, Pb, Ni, and Hg were lower than marine sediment quality standard (MSQS) but the mean concentration of Cd and Zn were significantly higher than MSQS. There were significant higher concentrations of heavy metals during the dry season than the wet season. Analysis of the data using Pearson correlation matrix showed significant correlation between the metals, Fe and Clay suggesting that Fe is the best chemical normalizer for other metals. Different metal assessment indices were applied in order to interpret the sediment's quality of Qua Iboe River estuary and associated creeks. All the EF's values of Cr, Fe and Hg were less than 1.5. However, the EF's values for Cd, Cu, Pb, Zn, and Ni were greater than 1.5 signifying greater percentages from anthropogenic inputs. The sources of pollution were mainly high surface runoffs, domestic effluents from the coastal dwellers and possibly from the oil exploration in the area. The high Igeo values for Ni may be attributed to oil spill and the slow water movement along the creeks. With regards to an overall degree of contamination as proposed by Hakanson (1980) sediment quality equation, the sediments of Qua Iboe River estuary and associated creeks fall between $8 \leq mCd < 16$ indicating high degree of contamination.

Acknowledgements

The authors would like to thank the following for assisting during sampling process, Eno Sampson, Evelyn Sampson and Patience Ekpenyong of the Department of Pure & Applied Chemistry. We are also grateful to Mr Effiom and Mr Charles, the laboratory staff who assisted immensely in the analytical work.

References

- Abdullah, M. H., Sidi, J., & Aris, A. Z. (2007). Heavy metals (Cd, Cu, Cr, Pb, and Zn) in meretrix Roding, water and sediments from Estuaries in Sabah, North Borneo. *International Journal of Environmental & Science Education*, 2(3), 69-74.
- Abraham, J. (1998). Spatial distribution of major and trace elements in Shaw Reservoir Sediments: An example from Lake Waco, Texas. *Environmental Geology*, 36, 3-4. <http://dx.doi.org/10.1007/s002540050351>
- Acevedo-Figueroa, D., Jiménez, B. D., & Rodríguez-Sierra, C. J. (2006). Trace metals in sediments of two estuarine lagoons from Puerto Rico. *Environmental Pollution*, 141, 336-342. <http://dx.doi.org/10.1016/j.envpol.2005.08.037>
- Alloway, B. J. (1990). *Heavy Metals in Soils*. Glasgow, London: John Wiley and Sons.
- Ankley, G. T., Lodge, K., Call, D. J., Balcer, M. D., Brooke, L.T., Cook, P. M., . . . McAllister, J. J. (1992). Heavy metal concentrations in surface sediments in a nearshore environment, Jurujuba Sound, Southeast Brazil. *Environmental Pollution*, 109, 1-9.
- Asuquo, F. E. (1998). Water pollution monitoring of Great Kwa River at Calabar (pp. 1-12). In *proceedings of the 1st conference of Nigeria water and sanitation*, Port Harcourt.

- Babtista, J. A., Smith, B. J., & McAllister, J. J. (2000). Heavy metal concentrations in surface sediments in a nearshore environment, Jurujuba Sound, Southeast Brazil. *Environ. Pollut.*, 109, 1-9. [http://dx.doi.org/10.1016/S0269-7491\(99\)00233-X](http://dx.doi.org/10.1016/S0269-7491(99)00233-X)
- Barakat, A., Baghdadi, M. E., Rais, J., & Nadem, S. (2012). Assessment of heavy metal in surface sediments of Day River at Beni-Mellal Region, Morocco. *Research Journal of Environmental and Earth Sciences*, 4(8), 797-806.
- Barnes, K. H., Meyer, J. L., & Freeman, B. J. (1998). Sedimentation and Georgia's Fishes: An analysis of existing information and future research. *1997 Georgia Water Resources Conference*, March 20-22, 1997, the University of Georgia, Athens Georgia.
- Bascomb, C. L. (1994). Physical and chemical analysis of < 2 mm samples. Soil survey laboratory methods. In B. W. Averg, & C. L. Bascomb (Eds.), *Soil Survey Technology Monographs*, 6, 14-41
- Berg, S. B. (1999). Iron as a reference element for determining trace metal enrichment in Southern California coast shelf sediments. *Mar. Environ. Res.*, 48, 161-176.
- Calmano, W., Hong, J., & Forstner, U. (1993). Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. *Water Sci. Technol.*, 28(8-9), 223-235.
- Chatterjee, M., Silva-Filho, E. V., Sarkar, S. K., Sella, S. M., Bhattacharya, K., Satpaty, K. K., . . . Bhattacharya, B. D. (2006). Distribution and Possible Source of Trace Element in Sediment Core of Tropical Macrotidal Estuary and Their Ecotoxicological Significance. *Environment International*, 3, 346-356.
- Dahilia, A., Apodaca, C., Emerson, J., Tui, N. G., & Allyn, S. V. (2003). Remediation of Pb^{2+} , Ca^{2+} and Zn^{2+} metal ions in waste water samples using iota-carrageenan. *Research Journal of Chemistry and Environment*, 7(2), 23-45.
- Di Toro, D. M., Zarba, C. S., Hansen, D. J., Berry, W. J., Swartz, R. C., Coman, C. E., . . . Pasquin, R. P. (1991). Technical basis for establishing sediment quality criteria for non ionic organic chemicals by using equilibrium partitioning. *Environ. Toxicol. Chem.*, 10, 1541-1583. <http://dx.doi.org/10.1002/etc.5620101203>
- Ekwere, S. J., Akpan, E. B., & Ntekim, E. E. (1992). Geochemical studies of sediments in Qua Iboe estuary and associated creeks, South Eastern Nigeria. *Tropical Journal of Applied Science*, 2, 91-95.
- Ergin, M., Saydam, C., Basturk, O., Erdem, E., & Yoruk, R. (1991). Heavy metal concentrations in surface sediments from the two coastal inlets(Golden Horn Estuary and Izmit Bay) of the northeastern Sea of Marmara. *Chem. Geo.*, 91, 269-285. [http://dx.doi.org/10.1016/0009-2541\(91\)90004-B](http://dx.doi.org/10.1016/0009-2541(91)90004-B)
- Forstner, U., & Wittmann, G. T. W. (1981). *Metal pollution in aquatic environment*. New York: Springer. <http://dx.doi.org/10.1007/978-3-642-69385-4>
- Forstner, U., & Wittmann, G. T. W. (1983). *Metal Pollution in the Aquatic Environment*. Berlin, Heidelberg, New York, Tokyo: Springer-Verlag.
- Ghreif, H., & Yusuf, N. (2006). Assessing Mn, Fe, Cu, Zn and Cd pollution in bottom sediments of Wadi Al-Arab Dam, Jordan. *Chemosphere*, 65, 2114-2121. <http://dx.doi.org/10.1016/j.chemosphere.2006.06.043>
- Gibbs, R. J. (1973). Water chemistry of the Amazon River. *Geochim. Cosmochim Acta*, 36, 1006-1066.
- Habes, G., & Nigem, Y. (2006). Assessing Mn, Fe, Cu, Zn, and Cd pollution in bottom sediments of wadi Al-rab Dam, Jordan. *Chemosphere*, 1-6.
- Hakanson, L. (1980). Ecological risk index for aquatic pollution control, a sedimentological approach. *Water Research*, 14, 975-1001. [http://dx.doi.org/10.1016/0043-1354\(80\):90143-8](http://dx.doi.org/10.1016/0043-1354(80):90143-8)
- Harrison, R. M., & De Mora, S. J. (1996). *Introduction chemistry for the Environmental Sciences* (2nd ed.). Cambridge: University Press.
- Kamau, J. N. (2002). Heavy metals distribution and enrichment at port-Reitz Creeks, Mombasa Western Indian Ocean. *Journal Marine Science*, 1, 65-70.
- Kehing, H. A., Pinto, F. N., Moreira, I., & Malm, O. (2003). Heavy metals and methyl mercury in a tropical coastal estuary and a mangrove in Brazil. *Organic Geochemistry*, 34, 661-669. [http://dx.doi.org/10.1016/S0146-6380\(03\)00021-4](http://dx.doi.org/10.1016/S0146-6380(03)00021-4)
- Khaled, A., El-Nemr, A., & El-Sikaily, A. (2006). An assessment of heavy-metal contamination in surface sediments of the Suez Gulf using geo-accumulation indices and statistical analysis. *Chem. Ecol.*, 22(3), 239-252. <http://dx.doi.org/10.1080/02757540600658765>

- Leivouri, M. (1998). Heavy metal contamination in surface sediment in the Gulf of Finland and comparison with the Gulf of Bothnia. *Chemosphere*, 36, 43-59. [http://dx.doi.org/10.1016/S0045-6535\(97\)00285-3](http://dx.doi.org/10.1016/S0045-6535(97)00285-3)
- Maher, W. A., & Aislabe, J. (1992). Polycyclic aromatic hydrocarbons in nearshore marine sediments of Australia. *Sci. Total Environ.*, 11(3), 143-164. [http://dx.doi.org/10.1016/0048-9697\(92\)90184-T](http://dx.doi.org/10.1016/0048-9697(92)90184-T)
- Manaf, L. A., Samah, M. A. A., & Zukki, N. I. M. (2009). Municipal Solid Wastes Management in Malaysia: Practices and Challenges. *Wastes Management*, 29, 2902-2906. <http://dx.doi.org/10.1016/j.wasman.2008.07.015>
- Manahan, S. E. (1991). *Environmental chemistry* (5th ed., pp. 565). Lewis Publishers.
- Mashiatullah, A., Chaudhary, M. Z., Ahmed, N., Javel, T., & Ghaffar, A. (2013). Metal pollution and ecological risk assessment in marine sediments of Karachi Coast, Pakiatan. *Environmental Monitoring and Assessment*, 185(2), 1555-65. <http://dx.doi.org/10.1007/s10661-012-2650-9>
- Muller, G. (1979). Schwermetalle in den sedimenten des Rheine-Vera Enderungenseit. *Umschau*, 79, 778-783.
- Nriagu, J. O. (1989). A global assessment of the natural sources of atmosphere trace metals. *Nature*, 338, 47-49. <http://dx.doi.org/10.1038/338047a0>
- Qu, C. H., Chen, C. Z., Yang, L. Z., & Lu, Y. L. (1993). Geochemistry of dissolved and Particulate Elements in the Major Rivers of China (The Huanghe, Changjiang, and Zhunjiang Rivers). *Estuaries*, 16, 475-467. <http://dx.doi.org/10.2307/1352595>
- Razae, K. H., Saion, E. B., Yap, C. K., Abdi, M. R., & Riyahi, B. A. (2010). Vertical Distribution of heavy Metals and Enrichment in the South China Sea Sediment Cores. *International Journal of Environment*, 4(4), 877-886.
- Rubio, B., Nombela, M. A., & Vilas, F. (2000). Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): An assessment of metal pollution. *Marine pollution Bulletin*, 40(11), 968-980. [http://dx.doi.org/10.1016/S0025-326X\(00\)00039-4](http://dx.doi.org/10.1016/S0025-326X(00)00039-4)
- Schiff, K. C., & Weisberg, S. B. (1999). Iron as a reference element for determining trace metal enrichment in Southern California coast shelf sediments. *Mar. Environ. Res.*, 48, 161-176. [http://dx.doi.org/10.1016/S0141-1136\(99\)00033-1](http://dx.doi.org/10.1016/S0141-1136(99)00033-1)
- Sieve analysis. (2013). In Wikipedia, the free encyclopedia. Retrieved July 17, 2013 from en.wikipedia.org/wiki/sieve_analysis
- Singh, A. K., Hasnain, S. I., & Banerjee, D. K. (2003). Grain Size and Geochemical Portioning of heavy metals in sediments of the Damodar River – A tributary of the lower Ganga, India. *Environmental Geology*, 39, 90-98. <http://dx.doi.org/10.1007/s002540050439>
- Soto-Jimenez, M. F., & Pac-Osuna, F. (2001). Distribution and Normalization of heavy metal concentrations in mangrove and lagoonal sediments from Mazatlan Harbour (S.E. Gulf of California). *Estuarine, Coastal and Shelf Science*, 53, 259-274. <http://dx.doi.org/10.1006/ecss.2000.0814>
- Turekian, K. K., & Wedepohl, K. H. (1961). Distribution of the elements in some major units of the earth's crust. *Bulletin Environ.*
- Wen, X. A., & Allen, H. E. (1999). Mobilization of heavy metals from Len River sediments. *Sci. Total Environ.*, 227, 27-38. [http://dx.doi.org/10.1016/S0048-9697\(99\)00002-9](http://dx.doi.org/10.1016/S0048-9697(99)00002-9)

Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).