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Index Model Analysis Approach to Heavy Metal Pollution Assessment in Sediments of Nworie and Otamiri Rivers in Imo State of Nigeria

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Abstract

The distribution, controlling geochemical factors and contamination status of heavy metals in sediments of Otamiri and Nworie rivers in Owerri, Imo State Nigeria, were investigated. Two groups of bed sediments samples were collected from five sample stations during February 2008 and June 2008. The sample were analyzed to determine their heavy metals (Cd, Pb, Ni, Zn, Cu, Fe and Cr), and the results showed that the heavy metal concentrations were slightly higher in February than those sampled in June. The results also showed that metal content directly correlate to flow condition of the rivers as station 2 recorded higher values than others.. Environmental assessment of sediments pollution by heavy metal was carried out using geo-accumulation index (I_{geo}), pollution load index (PLI), and enrichment factors (EF_C). EF_c not only show the class of pollution status of the river bed sediments but could be an exact indicator (i.e. showing the percentage contribution) from the sources (lithogenic or anthropogenic) of the contaminant and is very simple to use. Based on these indicators for predicting the level of heavy metal of Otamiri/Nworie river sediments, the ENRICHMENT FACTOR (EF_c) model was chosen as the best over other models.

Keywords: Heavy metal, sediment, contamination status, geoaccumulation index, pollution load index, enrichment factor.

Introduction

Heavy metals are among the most common environmental pollutants and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources. The existence of trace metals in aquatic environments has led to serious concerns about their influence on plant and animal life[1,2]. Study on the geochemistry of the River sediments in the present study area has not been undertaken by previous workers so far. However, the surface water chemistry of the river have received wide attention in the recent past. Commendable work in this line was done in 1998[3]. River borne sediments, especially the suspended matter, act as a major carrier and source of heavy metals in the aquatic system. Geochemical study of sediments to evaluate the concentration of heavy metals is necessary as it helps to assess the ecotoxic potential of the river sediments. According to study, the concentration of contaminants can be classified into three types which are: i. contamination indices – which compare the contaminants with the clean or polluted stations measured elsewhere ii. background enrichments indices – which compare the results for the contaminants with the baseline or background levels and iii. Ecological risk indices which compare the results for the contaminants with quality guidelines[4]. Environmental quality indices are a powerful tool for development, evaluation and converging raw environmental information to decision makers, managers or for the public. In recent decades, different assessment indices applied to estuarine environment here been developed[4, 5]. Sediment quality values are a useful tool to screen the potential for contaminants within sediment to induce biological effects and compare sediment contaminant concentration with corresponding quality guideline[5].

These indexes evaluate the degree to which the sediment associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and manager responsible for the interpretation of sediment quality[4]. It is also to rank and prioritize the contaminated areas or the chemicals for further investigation[6].

Material and Methods

Sampling and Sample Storage: For the purpose of this study, five sample stations 1,2,3,4 and 5 were established on the Rivers, (7^{o}2E, 5^{o}27N). Station 1 at reservoir base area, and it serves as control. Station 4 at Aba Road, about 2km downstream of Station 1, were there is massive solid waste dump. Station 2 at Nekede, about 3km downstream of station 4, where massive sand excavation is going on. Station 3 at FUTO, about 3km downstream of station 2, where fishing is going on and station 5 at Nworie, a tributary of Otamiri River about 4-5km close to the point of confluence.

Sediments were collected periodically. On each occasion, samples were taken from triplicate spots at each station to form one composite sample and the mean values noted for that season.

Sediment samples were collected using Eckman grab into plastic bags previously cleaned with detergents and preserved with 5ml of 11.3m HCl (aq). These samples were wrapped in Aluminium foils stored in an ice chest before being taken to the laboratory for analysis.

Treatment and Sample Analysis: Sediment samples were dried at about 105^{o}C in an oven to constant weight and ground to powder and then sieved through 0.5mm sieve to remove coarse materials. Digestion of all powdered sediment were according[7,8]. One gram of each sample were digested using 1.5.1 mixture of perchloric acid, conc. HNO_3 and conc. H_2SO_4 in a fume chamber at 80°C until a colourless liquid was obtained. Each digested sediment were analysed for the listed heavy metals (Cd, Pb, Ni, Zn, Cu, Fe and Cr) at their respective resonance line using Atomic Absorption spectrophotometer. The sediment pH was determined by mixing dry sediment with distilled water[9]. Total organic carbon (TOC %) was determined by Walkey and Black method[10]. Statistical Analysis using student's t-test sample were applied, to study the seasonal variation and the extend of the metal contents and their correlation in the bed sediments using Ms-Excel 2007 and Data analysis softwares. I_{geo}, EF_c and PLI for the sediment were also applied in order to classify the pollution intensity of the sediment. Another sediment index model is the *Sediment Quality Triad*. It's more complex which encompasses sediment chemistry, biological community and toxicity data.

The formula below has been applied to the study of heavy metal, to assess the anthropogenic and ithogenic contribution[11]. By re-arranging the formula for *Enrichment Factor* (EF_c), we have;

$$[M]_{lithogenic} = [Al]_{sample} \times ([M]/[Al])_{lithogenic}$$

Where ([M]/[Al])lithogenic corresponds to the average ratio of the earth crust. The anthropogenic heavy metals can be estimated as formula:

$$[M]_{anthropogenic} = [M]_{total} - [M]_{lithogenic.}$$

Results and Discussion

The results show very low concentration of Cd, Cu and Cr accross the sample stations and values are below the detection limit of the machine and background values of the upper earth crust. The concentration of Pb and Fe were highest at station 2, above the mean values of 0.3 and 147.64 respectfully for all the stations in February and similar trend was also observed in October. The concentration of Nickel (Ni) was highest at station 1 above the mean values of 1.4 for all the stations in February and similar trend was also observed in October. The concentration of Zn was highest at stations 2 during February but its value was highest at station 3 during October. This shows that the heavy metal's concentration in the sediment follows almost similar pattern in the two seasons. The results also shows that the heavy metal concentration in the sediment across the five stations is in the order SS2 > SS1 > SS3 > SS4 > SS5. Station 2 is just located after the confluence point downstream of station 4, hence, the combined influx of accumulated sediment from station 4(a dumpsite), Nworie, and land use system must have led to the highest values for station 2 and further dispersion downstream to station 3.

The high concentration of Fe over other metals is due to the reported high level of Fe in the upper earth crust of Southern Nigeria. The average I_{geo} of sediments across the sample stations show that both River sediments are in unpolluted and excellent condition, for both seasons.

There was observed no enrichment of the heavy metals across the sample stations in both seasons except for Zn and Ni at stations 1, 2, and 3 during both seasons, where Enrichment factor's grade were moderately severe enrichment. This was the same observation for Pb in the two seasons at station 2.

The PLI of the stations for both seasons show that the sediments of the Rivers are in perfect conditions.

Table-1
Pollution Intensities of selected indexes' range

Range of indexes	Pollution intensity
$I_{geo} <= 0$	Unpolluted (UNP)
$0 \leq I_{geo} < 1$	UNP to moderately polluted
$1 \leq I_{geo} < 2$	Moderately (MDTLY) polluted
$2 \leq I_{geo} < 3$	MDTLY to strongly polluted
$3 \leq I_{geo} < 4$	Strongly polluted
$4 \leq I_{geo} < 5$	Strongly to very strongly polluted
$I_{geo} \geq 5$	Very strongly polluted
0	Perfection
1	Baseline pollution
> 1	Increasing pollution level
$EF \leq 1$	No enrichment
$1 < EF \leq 3$	Minor enrichment
$3 < EF \leq 5$	Moderate enrichment
$5 < EF \leq 10$	Moderately severe enrh.
$10 < EF \leq 25$	Severe enrichment
$25 < EF \leq 50$	Very severe enrichment
$EF > 50$	Extremely severe enrichment

Table-2
Index models, mathematical expression, range and class of indexes

Index models	**Mathematical equations**	**Class of index**	**Range 0f indexes**
GEOACCUMULATION INDEX. (I_{geo})	$I_{geo} = \log_2 (Cn/1.5B_n)$ Where Cn = measured concentration of heavy metals in mangrove sediments B_n = Geochemical background values in average shale.	0 1 2 3 4 5 6	$I_{geo} <= 0$ $0 \le I_{geo} < 1$ $1 \le I_{geo} < 2$ $2 \le I_{geo} < 3$ $3 \le I_{geo} < 4$ $4 \le I_{geo} < 5$ $I_{geo} \ge 5$
POLLUTION LOAD INDEX. (PLI)	P L I = $\sqrt[n]{CF1xCF2xCF3 \; x \ldots XCFn}$ $CF = C_{metal}/C_{background\ Value}$		0 1 > 1
ENRICHMENT FACTOR. (EF_c)	$EF_c = (C_m/C_{Al})$ sample / (C_m/C_{Al}) earth crust. Where $(C_m/C_{Al})_{sample}$ is the ratio of concentration of trace metal (C_m) to that of $Al(C_{Al})$ in the sediment sample and $(C_m/C_{Al})_{earth's\ crust}$ is the same reference ratio in the earth crust.	1 2 3 4 5 6 7	$EF \le 1$ $1 < EF \le 3$ $3 < EF \le 5$ $5 < EF \le 10$ $10 < EF \le 25$ $25 < EF \le 50$ $EF > 50$
MARINE SEDIMENT POLLUTION INDEX. MSPI	MSPI = (∑ni = 1 qiwi) 2 / 100 Where qi is the sediment quality rating of the I contaminant, wi is the weight attributed to the I variable (proportion of eigenvalues obtained from results of a principal component analysis, PCA).		

Table-3
Pre- dredging data for some heavy metals in sediments dry session in mg/kg

	Cd	**Pb**	**Ni**	**Zn**	**Cu**	**Fe**	**Cr**
SS1	<0.001	0.52	2.79	7.51	<0.001	261.17	<0.001
SS2	<0.001	0.83	2.17	13.4	<0.001	284.64	<0.001
SS3	<0.001	0.07	2.1	12.89	<0.001	157.32	<0.001
SS4	<0.001	0.09	0.06	0.57	<0.001	32.14	<0.001
SS5	<0.001	0.002	<0.001	0.062	<0.001	2.9	<0.001
mean	<0.001	0.303	1.4	6.89	<0.001	147.64	<0.001

Table-4
Pre-Dredging data for some heavy metals in sediments rainy session in mg/kg

	Cd	Pb	Ni	Zn	Cu	Fe	Cr
SS1	<0.001	0.42	2.66	6.3	<0.001	251.52	<0.001
SS2	<0.001	0.63	1.83	12.01	<0.001	268.3	<0.001
SS3	<0.001	0.05	1.95	13.1	<0.001	143.81	<0.001
SS4	<0.001	0.06	0.053	0.48	<0.001	19.61	<0.001
SS5	0.0023	0.002	<0.001	0.043	<0.001	1.44	<0.001
mean	<0.001	0.232	1.29	6.387	<0.001	136.94	<0.001

Table-5
Geoaccumulation Index for Pre-Dredging Sediment (DRY)

	Cd	Pb	Ni	Zn	Cu	Cr	Fe	MEAN
SS1	-8.82	-5.18	-5.2	-3.41	-16.04	-17.04	5.33	-7.19429
SS2	-8.82	-5.85	-5.19	-4.25	-16.04	-17.04	5.2	-7.42714
SS3	-8.82	-8.74	-5.6	-3.47	-16.04	-17.04	4.47	-7.89143
SS4	-8.82	-8.38	-10.73	-7.97	-16.04	-17.04	2.18	-9.54286
SS5	-8.82	-13.87	-16.64	-11.17	-16.04	-17.04	-1.29	-12.1243
MEAN	-8.82	-8.404	-8.672	-6.054	-16.04	-17.04	3.178	-8.836

Table-6
Enrichment Factor for Pre-Dredged Sediment (Dry)

	Cd	Pb	Ni	Zn	Cu	Cr	Fe
SS1	1.02	2.505	5.37	7.61	0.0021	0.0021	5347
SS2	1.04	4.07	4.24	13.81	0.0022	0.0022	5930
SS3	1.03	0.338	4.05	13.1	0.002	0.002	3233.04
SS4	0.94	0.4	0.1	0.53	0.002	0.002	601.87
SS5	0.97	0.009	0.0018	0.06	0.002	0.002	56.2

Table-7
Geoaccumulation Index for Pre-Dredging Sediment (Rain)

	Cd	Pb	Ni	Zn	Cu	Cr	Fe	Average
SS1	-8.82	-5.57347	-5.79586	-3.57347	-15.3466	-17.04	5.24489	-7.2721
SS2	-8.82	-6.15843	-5.26534	-4.50635	-16.02	-17.04	5.15097	-7.5227
SS3	-8.82	-9.22594	-5.71786	-3.44222	-16.02	-17.04	4.34412	-7.9888
SS4	-8.82	-8.96578	-10.9092	-8.21304	-16.02	-17.04	1.46989	-9.7854
SS5	-8.82	-13.8655	-16.6388	-11.7027	-14.84	-17.04	-2.3004	-12.172
MEAN	-8.82	-8.75782	-8.86541	-6.28757	-15.6493	-17.04	2.78188	-8.9483

Table-8
Enrichment Factor for Pre-Dredged Sediment (Rain)

	Cd	Pb	Ni	Zn	Cu	Cr	Fe
SS1	1.02	2	5.08	6.33	0.0021	0.0021	5112.2
SS2	1.03	3.04	3.53	12.21	0.0043	0.0022	5513.76
SS3	1.03	0.24	3.76	13.33	0.002	0.002	2951.77
SS4	0.95	0.27	0.09	0.45	0.002	0.002	371.4
SS5	0.99	0.0093	0.0019	0.042	0.0041	0.002	28.44

Figure-1
Map of Owerri. From Wikipedia

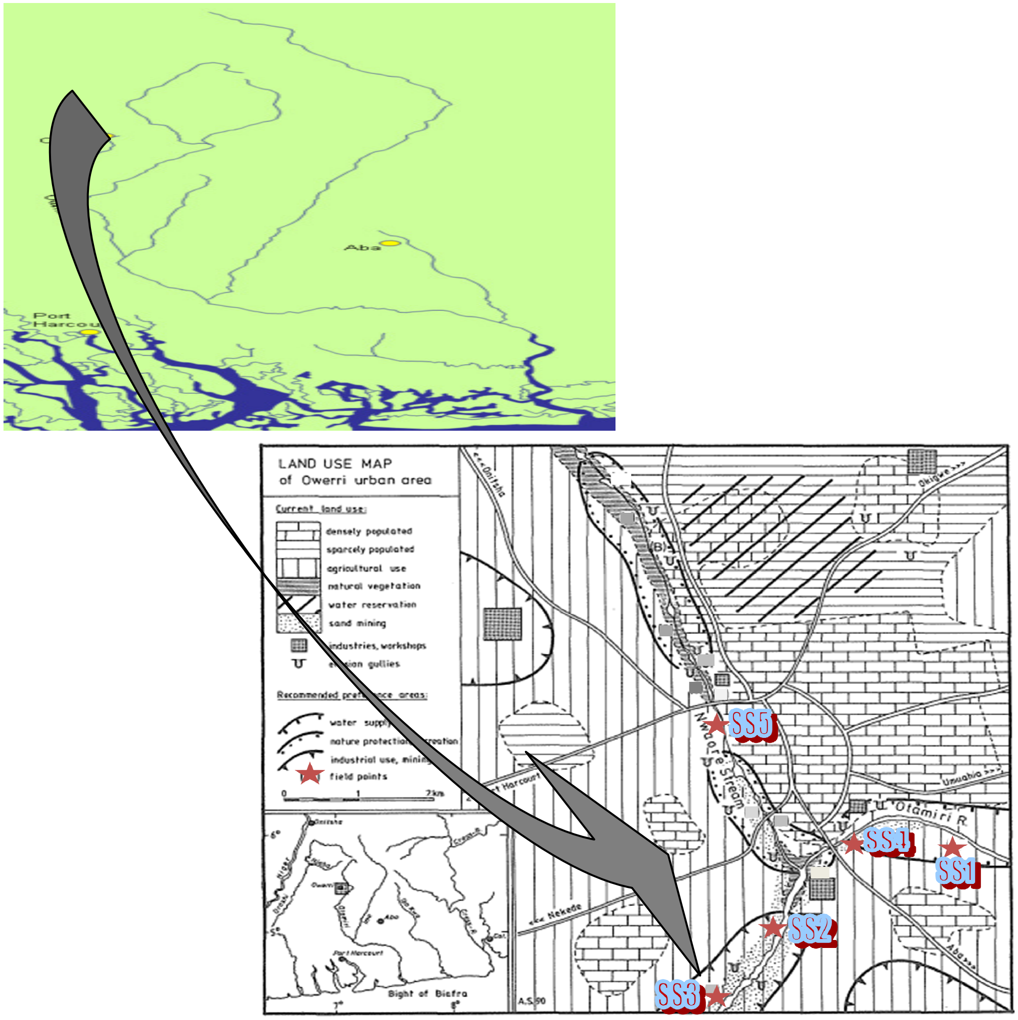


Figure-2
Map of Owerri showing sampling points and Land usage

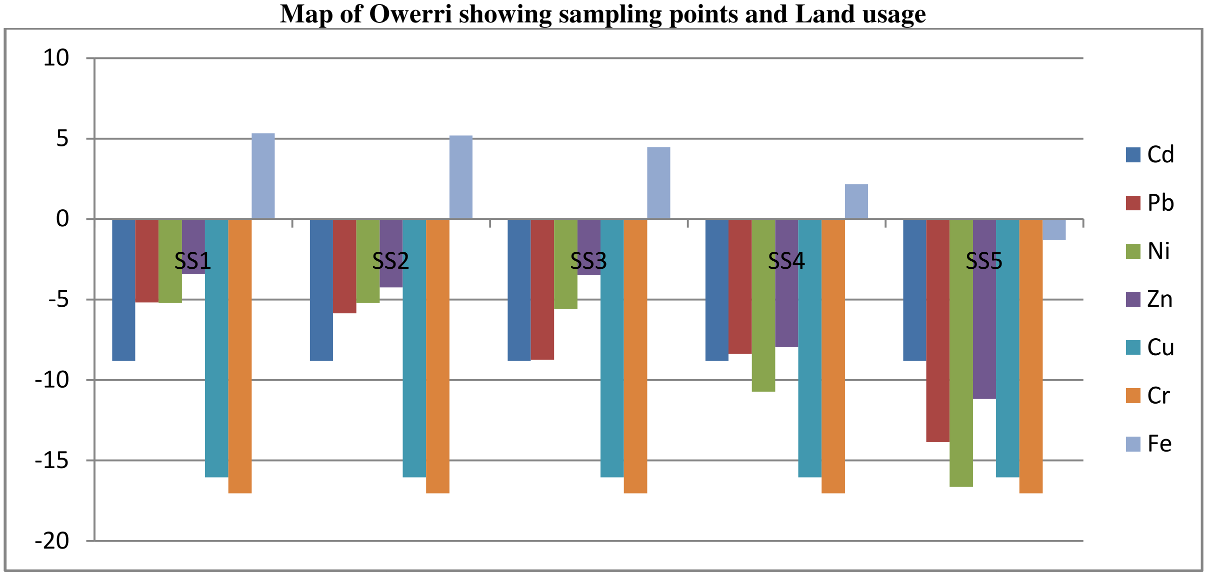


Figure-3
Geoaccumulation index of heavy metals at various sampling station sediments

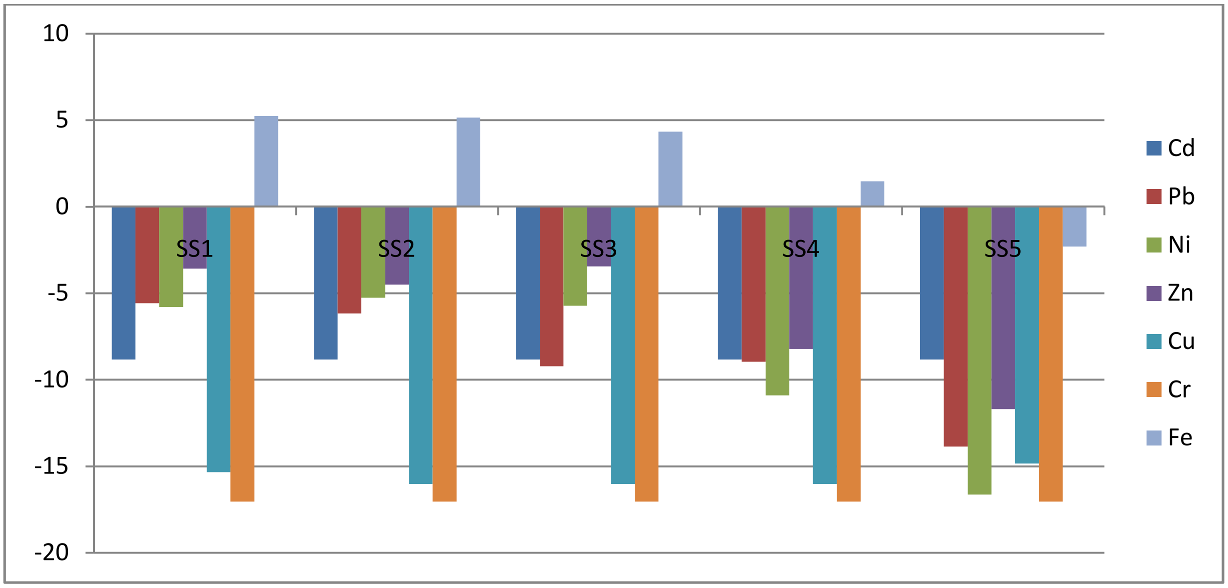


Figure-4
Geoaccumulation index of heavy metals at various sampling station sediments

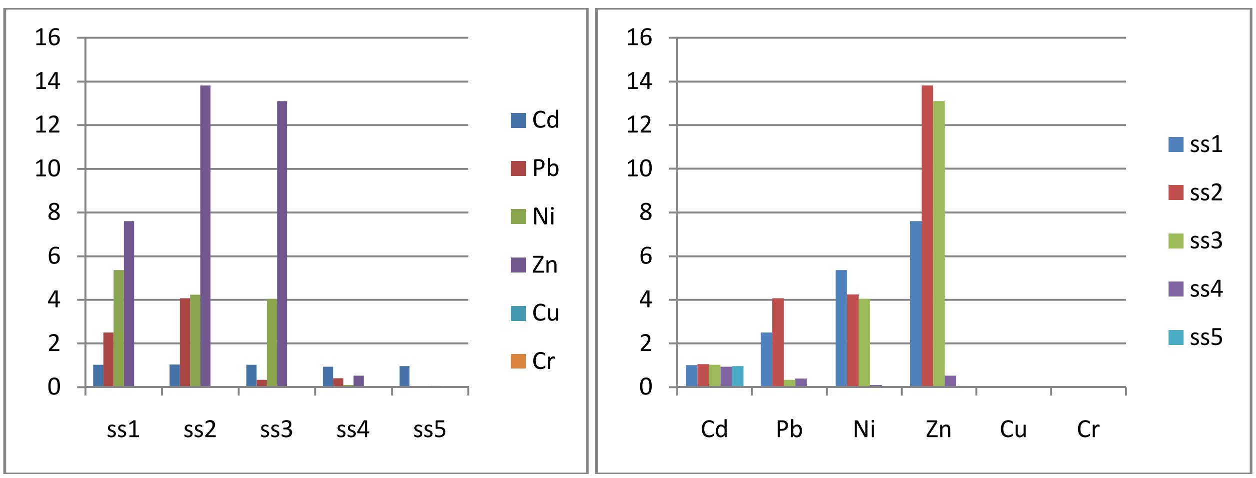


Figure-5
Enrichment factors (EF) of heavy metals at various sampling station sediments

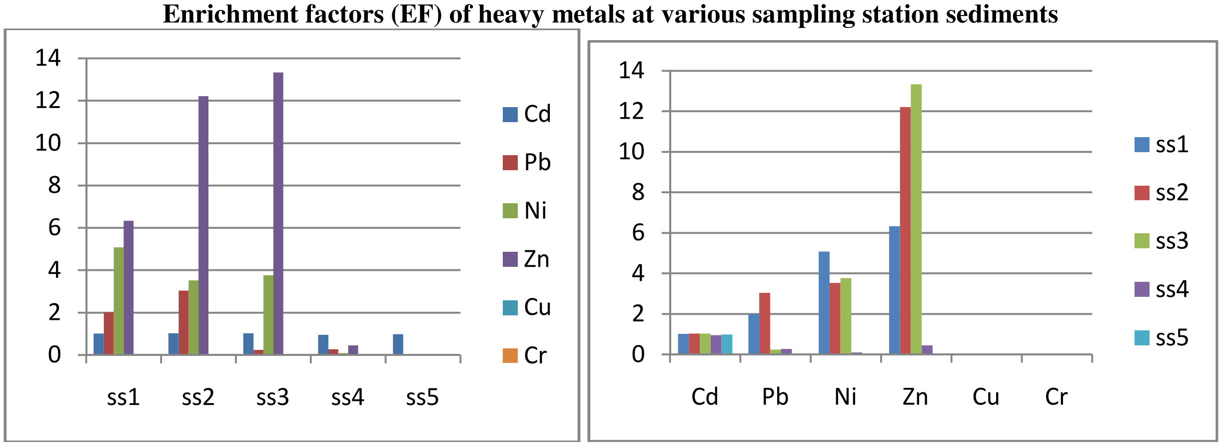
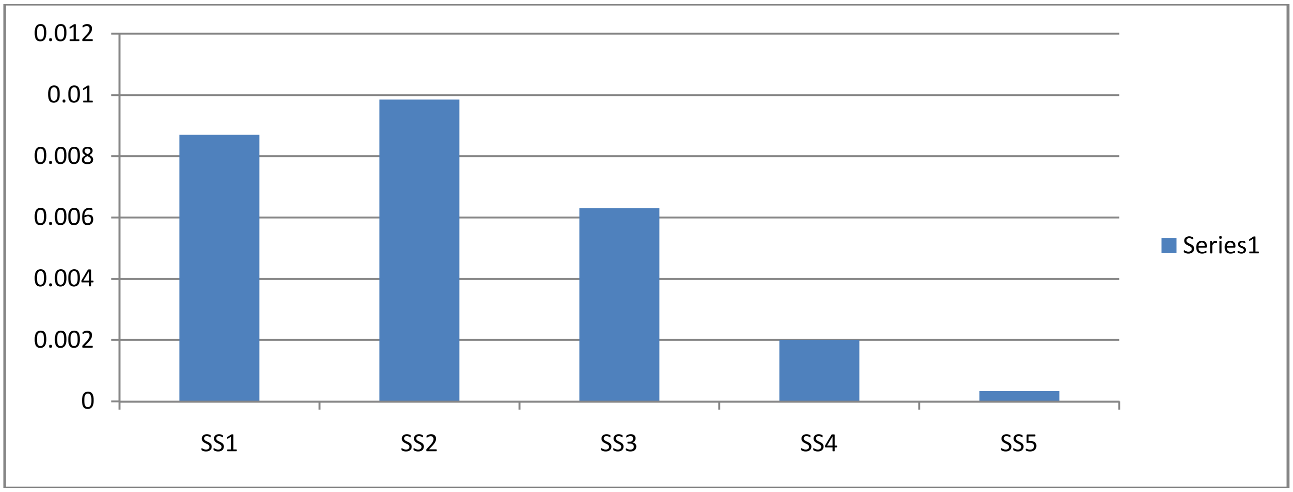
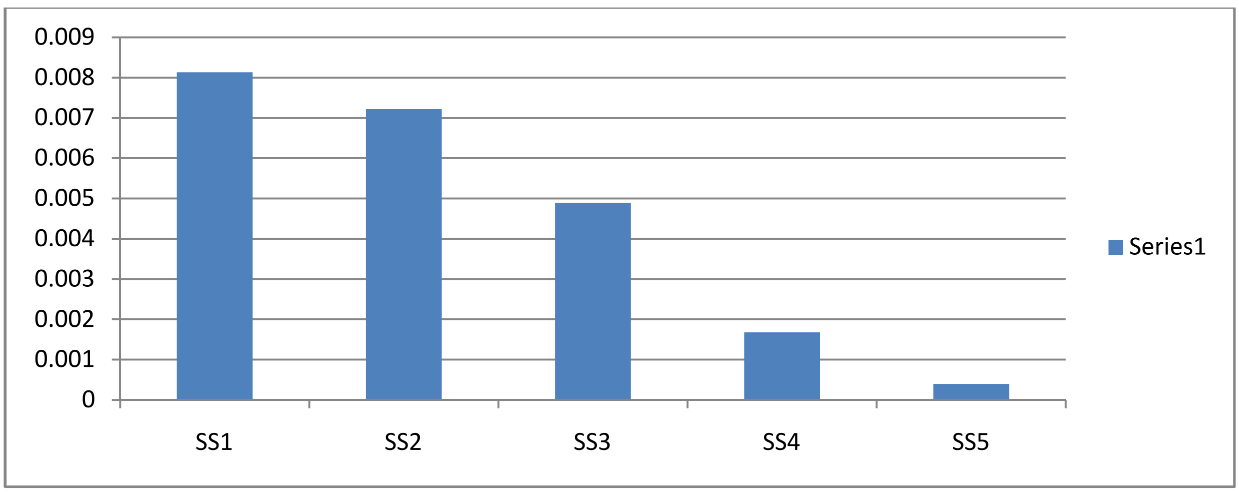


Figure-6
Enrichment factors (EF) of heavy metals at various sampling station sediments



Pollution Load Index (Dry)
Figure-7
Pollution load index of heavy metals at various sampling station sediments



Pollution Load Index (Dry)
Figure-8
Pollution load index of heavy metals at various sampling station sediments

Conclusion

More organic compounds (PAHs, PCBs, and pesticides) should be integrated into the contamination evaluation and correlated with other parameters.

Biological testing and ecological analysis of benthic structure of the river sediment should be carried out for more complete decision of the sediment quality assessment.
I_{geo} and PLI show mainly the class of pollution status of the heavy metal in the river bed sediment only and not reliable in predicting their exact sources.

PCA and Multi-variate data analysis shows more accurate value and significant correlation from which sediment pollution from *anthropogenic* sources could be traced, yet, it does not rank pollutants , it also require large sample size of at least 200 cases in order to improve the PCA loading value for the formulation of the MPSL index[12].

EF_c not only show the class of pollution status of the river bed sediments but could be an exact indicator (i.e. showing the percentage contribution) from the sources (*lithogenic* or *anthropogenic*) of the contaminant and is very simple to use. This can be achieved by using equation 1 and 2 respectively.

Based on these model indicators for predicting the level of heavy metal of Otamiri/Nworie river sediments, the enrichment factor (EF_c) model was chosen as the best over other models.

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