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Assessment of heavy metal pollution in flooded soil of kudenda, Kaduna state. Nigeria.

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Abstract: - Assessment of heavy metal pollutant: As, Cr, Cu, Fe, Mn and Ni was conducted in the flooded soil of kudenda area (latitude 10.480^{0}N and 10.481^0 N and longitude 7.394^{0}E and 7.395^{0}E) in Kaduna state, Nigeria, using contamination factor (CF) and pollution load index (PLI). Samples were taken in each of the grid area at depth 0-<5, 5-<25, 25-<50, 50-100cm and were analyzed using Energy Dispersive X-Ray Fluorescence (EDXRF). The concentrations of all the metals were found to increase to a maximum concentration at a depth of 25-<50cm then decreased. The study area was observed to be contaminated with As (maximum 2.07), Cr (maximum 2.83), Cu (maximum 2.24), Fe (maximum 1.44), Mn (maximum 1.85) and Ni (maximum 2.20) in all the sampled points and depth except 50-100cm depth. The pollution load indices (PLI) were found to be high but decrease (1.54-0.95) with increase in depth (0-100cm) indicating that the study area was polluted by all the observed heavy metals (PLI>1).

Keywords: - *Heavy metals, Pollution, CF, PLI, EDXRF*

I. INTRODUCTION

Pollution of the natural environment by heavy metals is a universal problem because these metals are indestructible and most of them have toxic effects on living organisms, when permissible concentration levels are exceeded (Mmolawa *et al.*,2011). Heavy metals are either naturally or through anthropogenic sources introduced into river water. Metals that are naturally introduced into the river come primarily from sources such as rock weathering, soil erosion, and the dissolution of water-soluble salts. Naturally occurring metals (especially the trace metals) move through aquatic environments independent of human activities and usually without any detrimental effects (Garbarino *et al.*, 1995 & Opuene *et al.*, 2008). Anthropogenic pollutants are discharged from industrial, domestic and agricultural wastewater into river water system (Ho *et al.*, 2001 & Priju *et al.*, 2007). Sediment served as sinks for most of the metals in aqueous phase (Klavins, *et al.*, 1995). The concentrations of heavy metals in soils are varied according to the rate of particle sedimentation, the rate of heavy metals deposition, the particle size and the presence or absence of organic matter in the soils (Saloman *et al.*,1987).The assessment of sediment enrichment with elements can be carried out in many ways; The most common ones are the index of geo-accumulation (I-geo) and pollution load index (PLI). The I-geo has been utilized as a measure of pollution in freshwater sediment (Singh *et al.*,1997), while pollution load index (PLI) represents the number of times by which the heavy metals concentrations in the sediment exceeds the background concentration, and give a summative indication of the overall level of heavy metal toxicity in a particular sample (Priju *et al.*,2006),this index is a quick tool used to compare the pollution status of different places (Adebowale *et al.*,2009), this type of measure has however been defined by some authors in several ways, for example, as the numerical sum of eight specific contamination factors (Hakason, 1980), whereas, Abrahim (2005) assessed the site quality as the arithmetic mean of the analyzed pollutants. In this study, the authors found it appropriate to express the PLI as the geometric mean of the studied pollutants since this method tends to reduce the outliers, which might bias the reported results.

Several analytical techniques have been extensively employed for environmental pollution monitoring, such as: instrumental Neutron activation analysis (INAA)(Coskun *et al.,2006*,Steinnes, 2000 and IAEA,2001), X-Ray Fluorescence analysis (XRF) (Cojocaru *et al.,2006* and Ene, *et al.,2009*), Particle-Induced X-ray Emission (PIXE)(Ene *et al.,2009* and Ene *et al.,2010*), Atomic Absorption Spectrometry (AAS)(Daud *et* *al.,2009*, Popescu *et al., 2009* and Al-khashman,2009) and Inductively Coupled Plasma Spectrometry-Atomic Emission Spectroscopy (ICP-AES) (Popescu *et al.*,2009). The EDXRF analysis of environmental samples has the advantage of being a rapid and inexpensive method with a simple sample preparation procedure (Ene *et al.,2010* and EPA, 2006). Quantitative and qualitative analyses by XRF techniques are performed without chemical digestion and a great number of elements can be determined simultaneously in a short time (Ene *et al.,2009*).

The objective of the present work was to use EDXRF to: (i) assess heavy metals concentration and contamination of environment by As, Cr, Cu, Fe, Mn and Ni using control soils obtained 3km away from the sampling area and (ii) assess soil contamination of study area using contamination factor (CF) and pollution load index (PLI).

II. MATERIALS AND METHODS

2.1 Study area: (Description and sampling techniques)

The study area is $60m^2$ of the kudenda area of Kaduna state, Nigeria, where the flooding of river Kaduna occurred in 2012. The area is bounded by latitude 10.480^0N, 10.481^0 N and longitude 7.394^0E, 7.395^0E. The site was divided into 9grid points (mesh) of $20m^2$ each labeled A-I with A-C, D-F and G-I parallel to the river bank but separated by 20m from each other and A-G, B-H and C-I perpendicular to the river bank and 60m away. Samples were collected at the middle of each grid from depths of 0-<5, 5-<25, 25-<50 and 50-100cm using hand auger. Control samples were collected at a distance of 3km away from the river bank. After removal of stones and vegetable matter, each soil sample was packed into its own secure water-tight polyethene bag to prevent cross contamination.

2.2 Sample preparation and analysis

Samples were each placed in an oven for drying at a temperature of 30^oC until a constant weight was reached ensuring complete removal of any residual moisture. The dried samples were pulverized into a fine powder and passed through a standard mesh (500µm). The samples were homogenized and an average of 0.5g of each of the sample was measured and pelletized at 10tons with the aid of hydraulic press (13mm dice). Each of the pellet was then irradiated in a sample chamber with X-Ray for 1000 seconds to acquire the sample spectral and each peak made up of the spectral was visually investigated to determine the elements contained in the samples by qualitative interpretation method. The quantitative interpretation was done with the aid of software called AMPTEK to obtain the concentrations of each metal.

2.3 Assessment of metal contamination

2.3.1 Contamination factor (CF)

The level of contamination of soil by metal is expressed in terms of a contamination factor (CF) calculated as:

$$CF = \frac{C_m \text{ Sample}}{C_m \text{ Background}} \qquad (1)$$

C_m Sample = metal concentration in Sample

C_m Background = metal concentration in background or control Sample

Where the contamination factor $CF < 1$ refers to low contamination; $1 \leq CF < 3$ means moderate contamination; $3 \leq CF \leq 6$ indicates considerable contamination and $CF > 6$ indicates very high contamination.

2.3.2 The Pollution Load Index (PLI)

The Pollution Load Index (PLI) is obtained as contamination Factors (CF), this CF is the quotient obtained by dividing the concentration of each metal with its control value. The PLI of the place are calculated by obtaining the n-root from the n-CFs that was obtained for all the metals. Generally pollution load index (PLI) as developed by Tomlinson *et al* (Tomlinson *et al.*,1980), is as follows:

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \times \ldots..\times CF_n)} \qquad (2)$$

Where,

CF = contamination factor, n = number of metals

The PLI value of > 1 is polluted, whereas <1 indicates no pollution (Harikumar *et al.*,2009).

III. RESULTS AND DISCUSSION

3.1 Heavy metal concentrations in soils

Fig 1(a-f) are plots of the observed elemental concentration of each grid point A-I and for each grid is a variation with depth 0-100cm in the plotted range shown, it can be observed that mean heavy metal concentrations (in ppm) in the sampled soils ranged from (14 to 41) As, (40 to 211) Cr, (15 to 63) Cu, (4713 to 21219) Fe, (173 to 930) Mn and (83 to 231) Ni.

Also Fig 1(a-f) displays the elemental concentration in each of the grid sampled area A-I as depicted for each of the elements; As, Cr, Cu, Fe, Mn and Ni, and an observed pattern is displayed consistent with all the grid points A-I analyzed. For each of the grid points A-I the metal concentration vary with sampling depths (0-100cm) with an observed increase in concentration to a depth point of 25-<50cm then decreases. This may probably be indication of soil filtration effect.

The elements are observed to accumulate at different concentrations at each of the grid points. Fig 1(a) indicates a maximum accumulation of As at the centre grid point E. Similarly fig 1(f) also has its maximum concentration of Ni at the same centre grid point. Meanwhile fig 1(d and e) had Fe and Mn accumulation to concentrate maximally at grid point B but only Cr fig 1(b)have maximum concentration at grid point C and Fig 1(c) for Cu also indicate maximum concentration at grid point A maybe due to its density when compared to the other metals. It could be observed that along the same profile is deposited the other heavy metals Fe, Mn at grid point B and Cr at grid point C.

3.2 Contamination Factor (CF)

Using equation 1, contamination factor of various metals within each grid sampled area A-I with depths were calculated and presented in table 1. At depth 0-<5, 5-<25 and 25-<50cm most of the grid points were observed to be moderately contaminated with As, Cu, Cr, Mn and Ni but Fe is observed with most of the grid points to indicate low contamination. Whereas, at 50-100cm depth most of the grid points were observed to be moderately contaminated with Ni but As, Cu, Cr, Fe and Mn were observed with most of the grid points to indicate low contamination.

3.3 Pollution Load Index (PLI)

To effectively know the measure of degree of overall contamination, the pollution load index (PLI) was calculated using equation 2 for each grid sampled area A-I with depth and presented in table 1.

Based on the results presented in table 1, it was observed that at depth 0-<5, 5-<25 and 25-<50cm all the grid sampled points were polluted (>1) except grid point D at depth 25-50cm which is unpolluted (<1) and at depth 50-100cm all the grid sampled point were unpolluted (<1) except grid point C and I which were polluted (>1).

Fig 2 is a plot of the variation of pollution load index with depth. According to fig 2 the pollution load index (PLI) decreases (1.54-0.95) with depth (0-100cm) which confirm that the study area is facing probable environmental pollution especially with dangerous heavy metals (As, Cu, Cr, Mn and Ni) which could be as a result of increased rate of non-treated industrial waste discharged into river Kaduna and deposited in the area due the flood activity.

IV. CONCLUSION

A study of the flood profile using the elemental concentrations at the site indicates most of the toxic element to accumulate at a depth 25-<50cm. this could be due to the common source of the metals and to have the same grain size hence filtered to the same depth into the soil.

Anthropogenically impacted and control soils of the study area were assessed using contamination factors and pollution load index for As, Cu, Cr, Fe, Mn and Ni. The contamination factors were observed generally to indicate low to moderate contamination by heavy metals across the grid points and depths; the background soil was higher than that of the study area for some of the element and grid points which could be attributed to human activity such as sewage deposit.

The measure of degree of overall contamination (PLI) at the sampled grid area indicate strong signs of pollution deterioration by the six measured metals at depth 0-<5, 5-<25 and 25-<50cm and no overall contamination at 50-100cm depth. The pollution load index (PLI) (1.54-0.95) vary with depth(0-100cm) which confirm that the study area is facing probable environmental pollution especially with dangerous heavy metals which result from increased rate of non-treated industrial waste discharged into river Kaduna and deposited at the river bank due to flood activity.

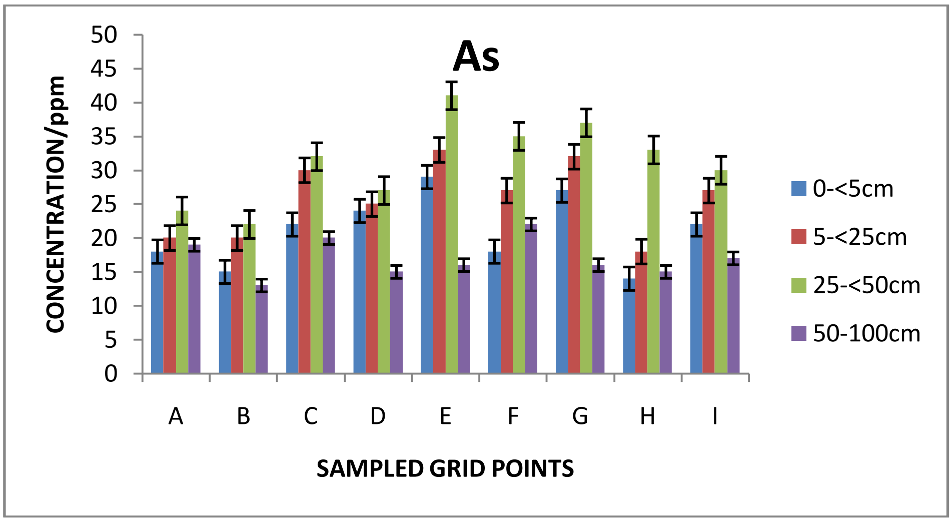

Fig 1(a): Concentration of As of Sampled grid points

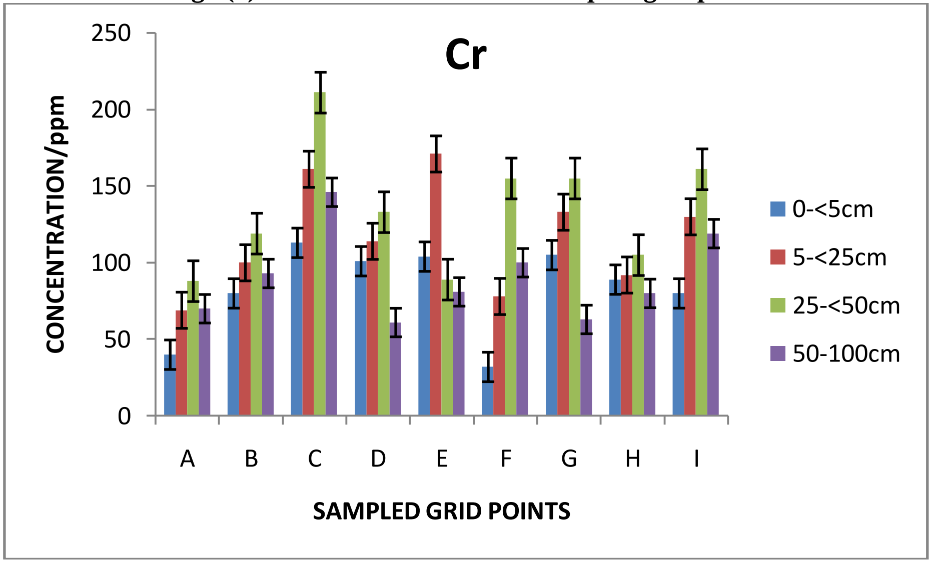

Fig 1(b): Concentration of Cr of Sampled grid points

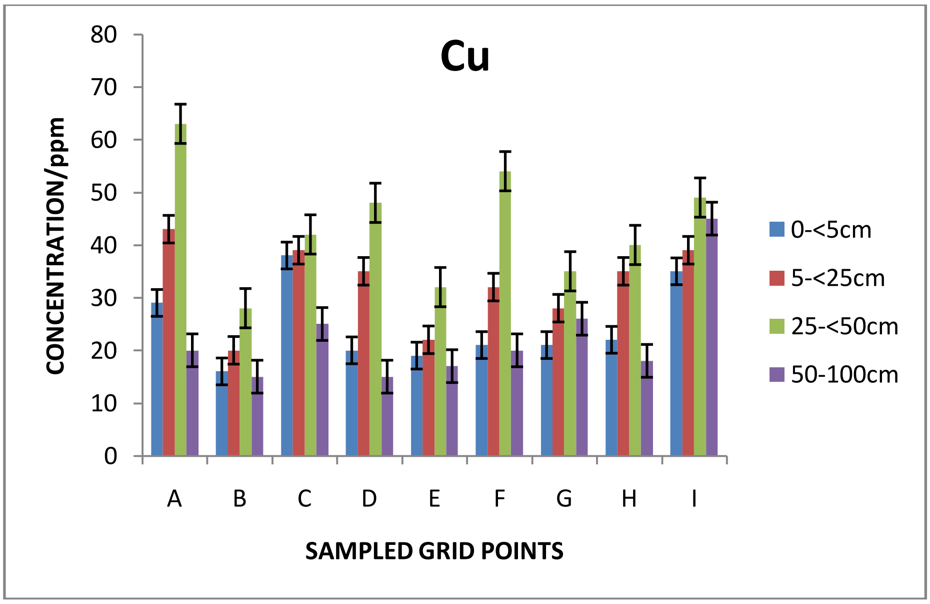

Fig 1(c): Concentration of Cu of Sampled grid points

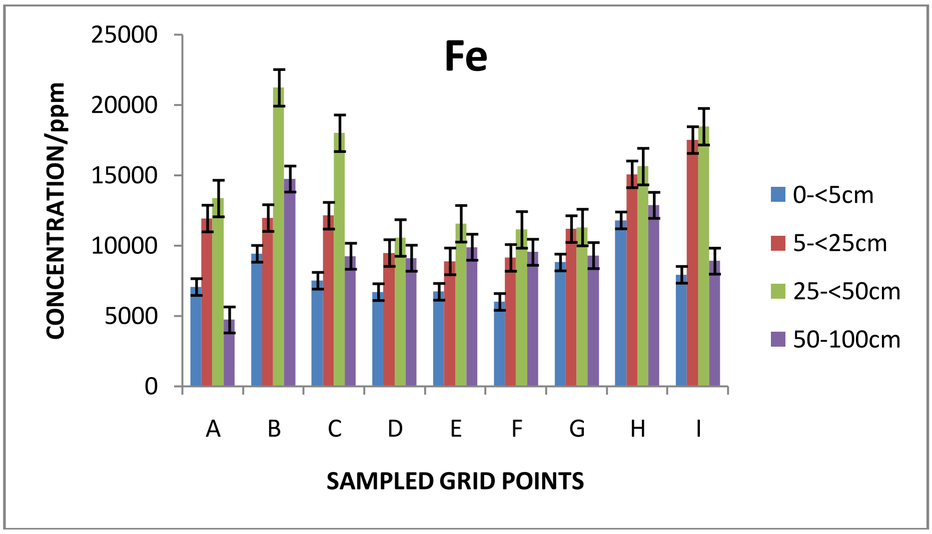

Fig 1(d): Concentration of Fe of Sampled grid points

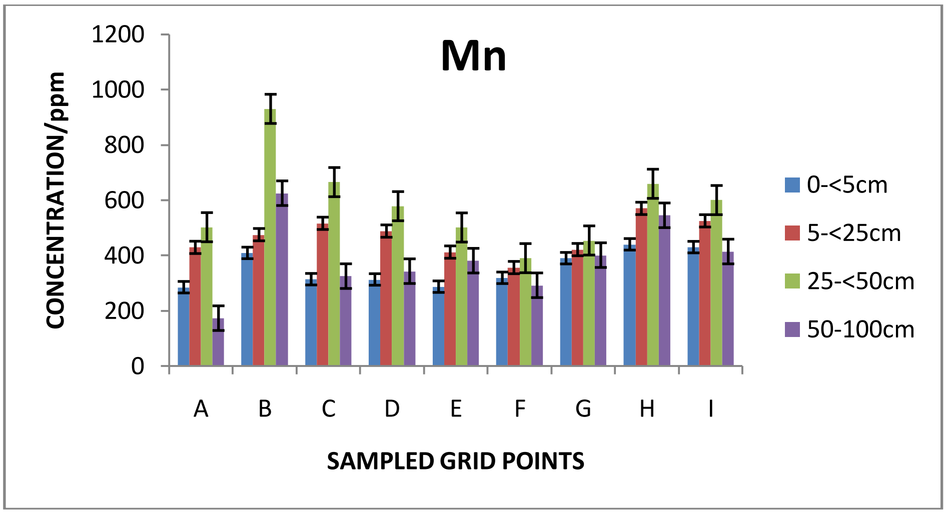

Fig 1(e): Concentration of Mn of Sampled grid points

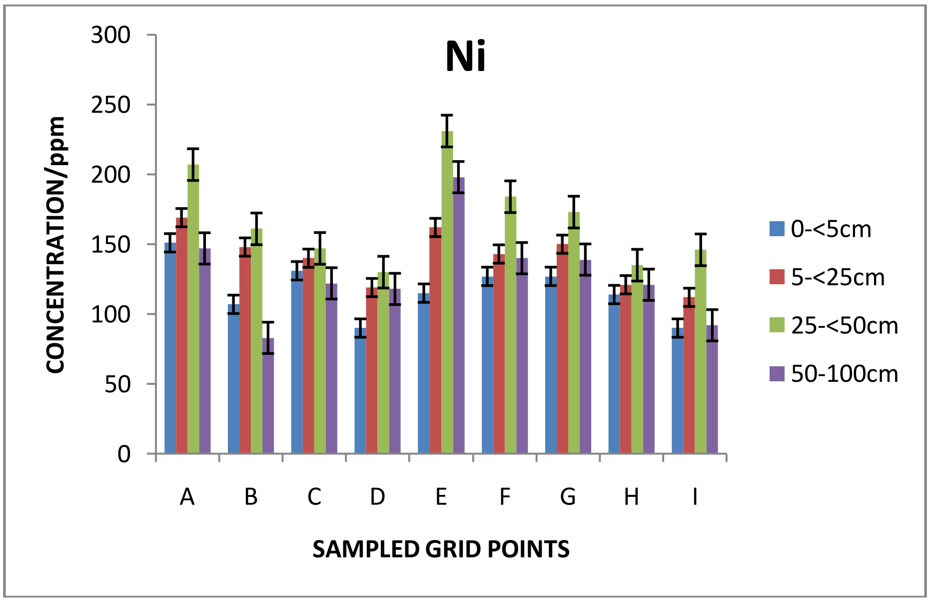

Fig 1(f): Concentration of Ni of Sampled grid points

Table (1): Contamination factor (CF) and Pollution Load Index (PLI) for the sampled area.

Location/Depth	CF As	CF Cu	CF Cr	CF Fe	CF Mn	CF Ni	PLI
0-<5cm							
A	1.29	1.71	1.00	0.78	1.00	1.70	1.20
B	1.07	0.94	2.00	1.04	1.44	1.20	1.24
C	1.57	2.24	2.83	0.83	1.11	1.47	1.54
D	1.71	1.18	2.53	0.74	1.10	1.01	1.27
E	2.07	1.12	2.60	0.74	1.01	1.29	1.34
F	1.29	1.24	0.80	0.66	1.12	1.43	1.05
G	1.93	1.24	2.63	0.98	1.37	1.43	1.51
H	1.00	1.29	2.23	1.31	1.55	1.28	1.40
I	1.57	2.06	2.00	0.88	1.51	1.01	1.43
5-<25cm							
A	1.11	1.54	0.96	0.86	1.08	1.40	1.13
B	1.11	0.71	1.39	0.86	1.19	1.22	1.06
C	1.67	1.39	2.24	0.87	1.29	1.16	1.38
D	1.39	1.25	1.58	0.68	1.22	0.98	1.15
E	1.83	0.79	2.38	0.64	1.03	1.34	1.20
F	1.50	1.14	1.08	0.66	0.89	1.18	1.04
G	1.78	1.00	1.85	0.80	1.06	1.24	1.23
H	1.00	1.25	1.28	1.08	1.43	1.00	1.16
I	1.50	1.39	1.81	1.26	1.32	0.93	1.34
25-<50cm							
A	1.00	1.75	0.79	0.81	1.00	1.48	1.09
B	0.92	0.78	1.07	1.30	1.85	1.15	1.13
C	1.33	1.17	1.90	1.10	1.32	1.05	1.28
D	1.13	1.33	1.20	0.64	1.15	0.21	0.81
E	1.71	0.89	0.80	0.71	0.99	1.65	1.06
F	1.46	1.50	1.40	0.68	0.77	1.31	1.13
G	1.54	0.97	1.40	0.69	0.90	1.24	1.08
H	1.38	1.11	0.95	0.95	1.31	0.96	1.10
I	1.25	1.36	1.45	1.13	1.19	1.04	1.23
50-100cm							
A	0.95	0.83	0.75	0.46	0.37	1.63	0.74
B	0.65	0.63	1.00	1.44	1.34	0.92	0.95
C	1.00	1.04	1.57	0.90	0.69	1.36	1.06
D	0.75	0.63	0.66	0.89	0.73	1.31	0.80
E	0.80	0.71	0.87	0.97	0.81	2.20	0.97
F	1.10	0.83	1.08	0.93	0.62	1.56	0.98
G	0.80	1.08	0.68	0.91	0.86	1.54	0.94
H	0.75	0.75	0.86	1.26	1.16	1.34	0.99
I	0.85	1.88	1.28	0.87	0.88	1.02	1.08

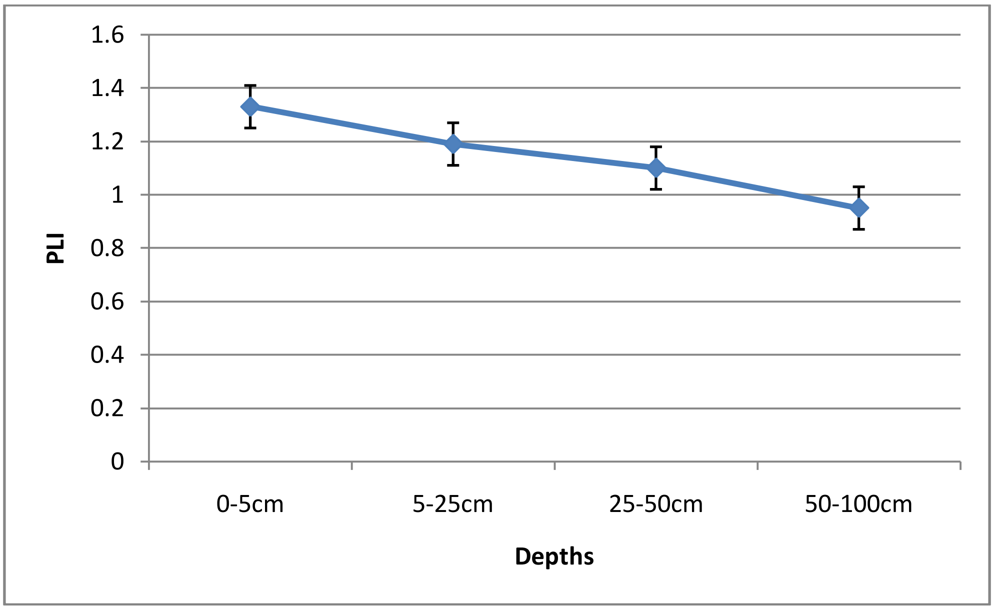

Fig.(2): Variation of pollution load index (PLI) with depth

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