Contamination Status: Geo-Investigation of Stream Sediments of Ilubirin Bitumen Rich Area of Ondo State, Southwest Nigeria Using Oxide and Trace Metals

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Abstract: The stream sediments of Ilubirin bitumen rich area was investigated for contamination using enrichment factor (EF), contamination factor (CF), geo-acummulation index (I-geo), and pollution load index (PLI).Statistical analysis was used to determine the anthropogenic or natural sources of the contamination if any.The result of EF shows that majority of the elements in the stream sediment are minimally enriched in the sediments as their values are less than 2 (EF < 2). Co is moderately enriched since it has values that are greater than 3 in locations 3 and 7. Major oxides were determined by the use of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), while the trace elements were analysed withthe use of X-Ray Fluorescence (XRF) analytical technique in the laboratory of the Stellenbosch University ,South Africa. CF results showthat Cs and Cr have moderate contamination on the sediments because they both have values higher than 1 but less than 3 (1<CF<3) and all other elements have values that are less than 1 (CF > 1) an indication of low contamination. I -geo values indicate that Cs, Ni, Cr, and Mo have uncontaminated to moderate contamination having values in the class range of0-1. Other elements have no contamination impact on the environment because they have values below zero. Zr and Co in locations 3 and 7 have the highest concentration levels which suggest a threat of concern in the stream sediments of the study area. Statistical analysis indicates that the trace metals have mutually, strong and positively correlated relationships indicative of a single natural source contamination suggestive of bitumen. It is suggested that regular geochemical work should be carried out in this area so as to monitor any rise in contamination level and the residents should be advised to avoid making use of the nearby stream water.

*IndexTerms:*Ilubirin, stream sediments, source contamination, investigation.

I. INTRODUCTION

Ilubirin is one of the bitumen-rich areas of Ondo State, in Southwestern part of Nigeria. It lies between latitudes $6^0 28^1$N and $6^0 37^1$N and longitudes $4^0 32^1$E and $4^0 50^1$E of theGreenwich meridian. The elevation ranges between 50 and 250 m above the sea level. Some major towns surrounding the study area include: Agbabu, Okitipupa, Ode Aye, Ode Irele and Arogbo. These major towns are generally accessible through a network of road that links it with other parts of the country (Fig 1).
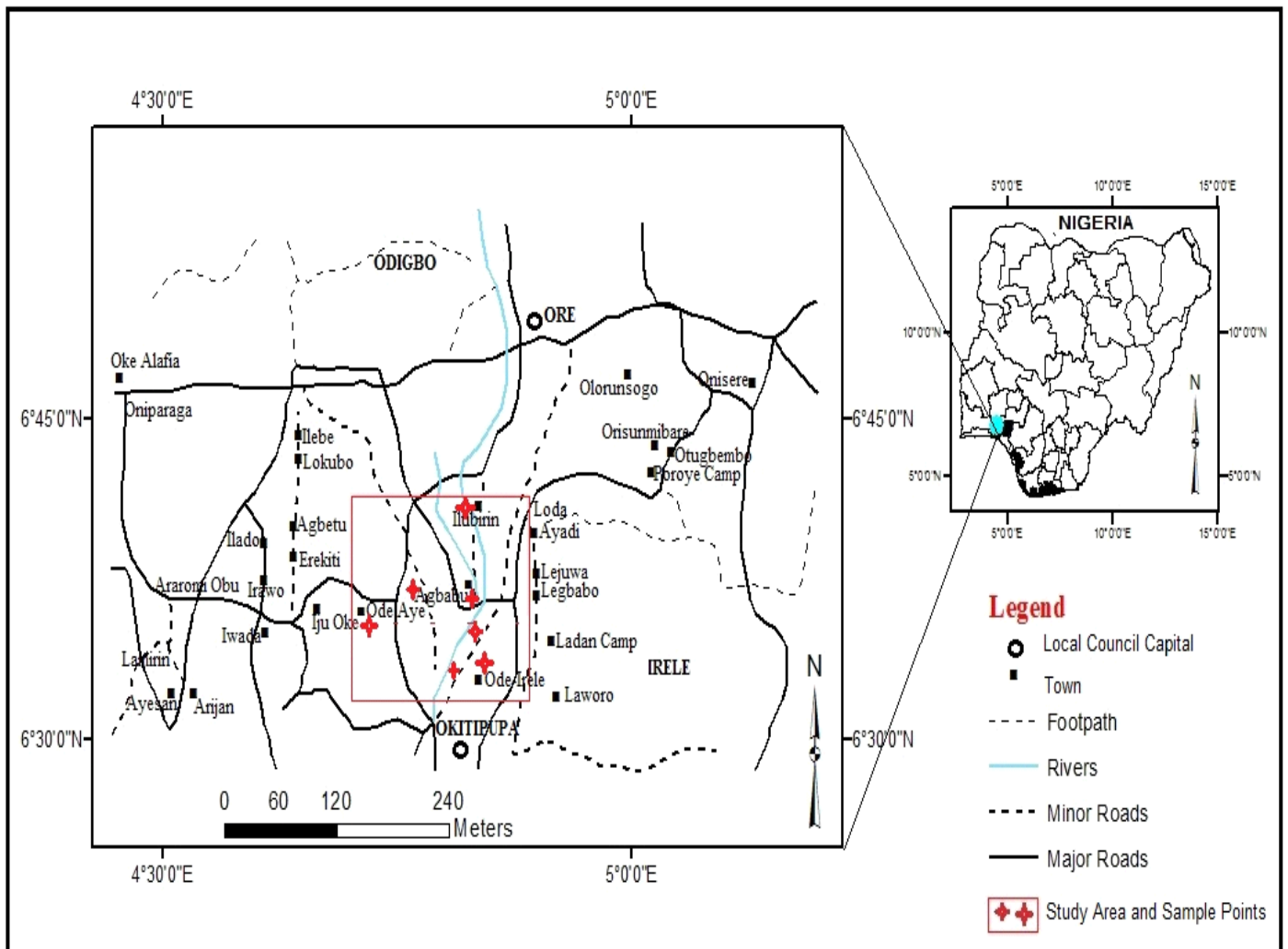
. **Fig 1: The Topographic Map of the Study Area (Inset Ondo State)**

The village has nucleated settlements with people whose occupations are mainly trading and peasant farming. During hot weather, the bitumen melts and stains the water which the local people use for their drinking and domestic purposes. Stream sediment is one of the recipient avenues that can readily be contaminated by trace and rare earth elements at lethal levels. Trace elements such as As, Fe, Hg, Mn and Pb contained in bitumen contaminate rivers and stream sediments leading to health hazards when their values exceed Standard Safety levels (Nartey et al., 2011). Other elements like Cu, Fe and Zn are essential micronutrients but can be detrimental to man and other living organisms at higher concentration (Kar et al.,2000). Heavy metals and rare earth elements are commonly distributed in the earth's environment. They are persistent, non-degradable, toxic and can be bio-accumulated leading to environmental hazards (Townsend et al., 2013). Heavy and trace metals enter the aquatic environment from natural and anthropogenic sources. The natural source could be as a result of weathering processes, land run-offs, wet and dry deposition from the atmosphere, while the anthropogenic source include; direct discharge of industrial and domestic wastes ,oil drilling, agricultural practices and other daily activities of man. Metal pollution in the aquatic environment is fast becoming a global concern. In the recent years, many researchers around the globe have investigated the distribution of heavy, trace and rare earth in sediments of rivers, lakes and oceans in an attempt to estimate the potential risks associated with metal contaminations (Qian et al., 2005. Zhang et al.,2012,).

The contamination or otherwise of the stream sediments in Ilubirin area by bitumen is what this work intends to investigate. The approach adopted to investigate if the stream sediments have been naturally or anthropogenically impacted upon is through the use of the following indices , enrichment factors (EF) (Huu et al.,2010), contamination factor, (CF), pollution load index (PLI) as well as the use of statistical analysis.

1.1. Geologic setting of Ilubinrin

The study area belongs to Ise formation of the Cretaceous Abeokuta group and overlies unconformably on the basement (Jones and Hockey,1963). Omatsola and Adegoke (1981) on the lithostratigraphy of Dahomey basin recognized three formations belonging to the Abeokuta group based on lithologic homogeneity and similarity of origin. The Ise formation is the thickest sedimentary unit within the basin . The formations from oldest to youngest are Ise, Afowo and Araromi formation. Afowo formation overlies the Ise formation, and composed of coarse to medium grained sandstone with variable but thick interbedded shale, siltstone and claystone. The sandy facies are tar-bearing while shales are enriched in organic materials. The youngest Cretaceous formation in the group is Araromi formation, which conformably overlies the Afowo formation. It is composed of fine-medium grained sandstone at the base, overlain by shale, siltstone with interbedded limestone; marl and lignite. The geological map of the study area is shown in Fig . 2 as modified.
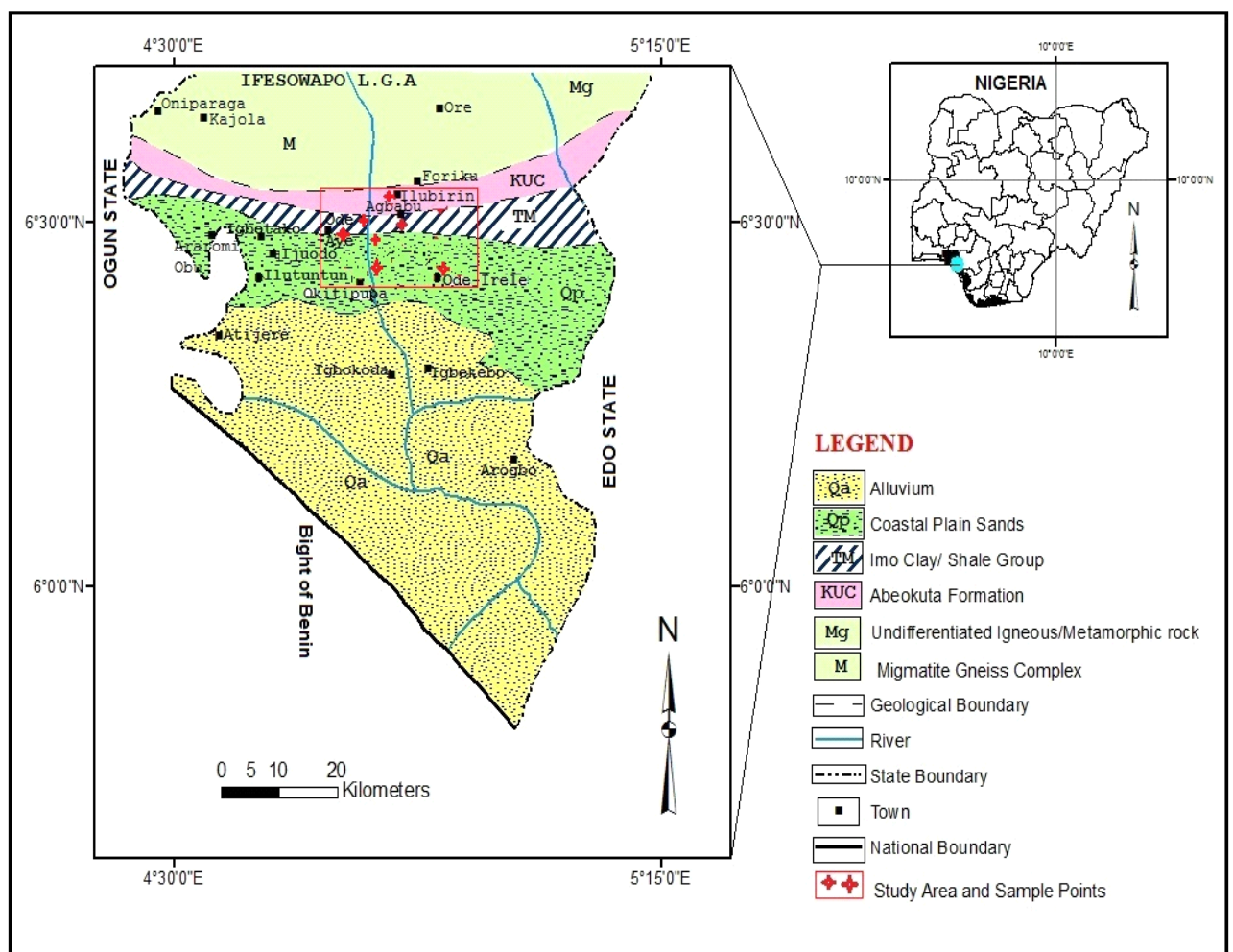
Fig 2: Geological map of Ilubirin area (Enclosed).

Omatola and Adegoke (1981) assigned a Maestrichian to Paleocene age to this formation based on faunal content. The Abeokuta group is overlain by the Imo shale lateral equivalent are the Ewekoro and Akinbo formations (Jones and Hockey, 1963).

II. MATERIALS AND METHOD

Samples of surface sediments were collected from seven sampling stations along the Olubinrin stream course at regular distances of fifteen meters apart .Sediment samples were taken at a depth of 0-10cm.The samples were air dried, sievedand ground using mortar and pestle and pulverized into fine powder (particle size < 70µm) in a tungsten-carbide Zibb mill prior to the preparation of a fused disc for major and trace metal analysis. The mill was cleaned with uncontaminated quartz between samples to avoid cross contamination. Glass disks were prepared for X-Ray Fluorescence (XRF) analysis using 7g of high purity trace. Whole rock major element compositions were determined by XRF spectometry on a Panalytical Axios Wavelength dispersive spectrometer at the Central Analytical Facilities, Stellenbosch University. Major elements were analyzed on a fused glass disk using a 2.4 kw Rhodium tube. Matrix effects in the samples were corrected by applying theoretical alpha factors while the measured line overlap factors to the raw intensities were measured with the SuperQ Panalytical software. To check the accuracy of the analysis, the concentration of the control standards were used in the calibration procedures for major element analysis. Amongst the standards were NIM-G (granite from the council for Mineral Technology, South Africa) and BE-N (Basalt from the International working group). The chemical determination of the trace and rare earth elements was carried out using the Inductively Coupled Plasma –Mass spectrophotometer, (ICP-MS) technique. Details of ICP- MS methods are given in Longerich et al., (1990). This analysis provided data on trace.The data were used in all computations using the statistical package for social sciences (SPSS 17) software.

III. RESULTS AND DISCUSSION

Major element concentrations of the stream sediments are presented in Table. The SiO_2 content ranges from 93.86 to 94.81 wt %. while Al_2O_3 varies from 1.52 to 1.81wt%. The high concentration of silica reflects the tar sand nature of the bitumen impregnated area. The data on Table 1 show that mean silica content (94.43 wt %) is higher than the shale average values of 58.9 wt% .The mean of the other oxides is far less than the shale average values. The high proportion of silica is suggestive of intensive weathering of the parent granite of the southwest basement complex underlying the Ise Formation. It is also observed that the values of Al_2O_3 that would have formed aluminium silicate with silica is strongly depleted, hence not much of the clay/shale cover could form the seal to prevent outflow of bitumen in the study area. This explains why the bitumen often emerges to the surface without hindrance.

Table 1 : Major oxide concentration of the stream sediments of Ilubirin area. (Wt .%).

Sample	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO		P_2O_5	TiO_2
1	94.06	1.5	0.03	0.87	0.03	0.06	0.02		0.04	0.84
2	94.63	1.78	0.04	1.1	0.06	0.07	0.02		0.05	0.79
3	93.86	1.81	0.03	0.96	0.06	0.02	0.02		0.05	1.14
4	94.7	1.7	0.03	0.83	0.06	0.01	0.01		0.04	0.69
5	94.21	1.65	0.03	0.78	0.05	0.01	0.01		0.04	0.71
6	94.74	1.57	0.04	0.59	0.06	0.01	0.01		0.04	0.58
7	94.81	1.67	0.03	0.94	0.05	0.01	0.01		0.04	0.63
Min	93.86	1.52	0.03	0.59	1.78	0.01	0.01		0.04	0.58
Max	94.81	1.81	0.04	1.1	1.78	0.02	0.02		0.05	1.14
Mean	94.41	1.67	0.03	0.86	0.43	0.01	0.01		0.04	0.79
Bgv	58.9	16.7	2.20	6.90	3,60	2.60	-		-	0.78

3.1 Sediment Characterization

It has been reported severally that sediments form reservoirs and repositories of heavy metals (Ravanelli et al., 1997; Ranjbar, 1998; Kamau, 2001; Mathew et al., 2003; Sekhar et al., 2003; Panda et al., 2006; Nemr et al., 2006; Veen et al., 2006) and have been used as environmental indicators to assess the anthropogenic influence. The results of trace element composition (heavy metals) in the stream sediments, with their ranges, means, and average shale concentrations are presented in Table 2.The data show that Zr ranges from 653.83 to 1212.60 ppm (mean 787.60)with the maximum at location 3 and minimum at location 7. Co (58.23- 558.42) with a mean value of 222.84 ppm , the maximum at location 7 and minimum at location 6. Pb (4.95-7.55) with a mean of 19.46, with maximum concentration at location 3 and minimum at location 6 while Zn varies from 18.29ppm at

location 7 to 27.15 ppm at location 2. In the order of increasing mean Zr > Co > Cr (Fig 3) The   mean values of Zr (787.3) are five times higher than the upper crust (170) and the average world-wide shale value (160) while Co mean values are significantly higher than those of the average shale of 19 (Turekian and Wedepohl, 1961.), and the upper crust of 17 (Wedephol, 1995) respectively.Elements Zr and Co deviated wildly from the other elements within the environment . Zr is found in the mineralogical content of granitic rocks and it is a source of Hf (Levinson, 1974). The high Zr content in the stream sediment might be due to weathering of Ise formation to which the study area belongs and which is unconformably overlying the basement complex. (Jones and Hockey 1963, Omatsola and Adegoke, 1981). Erosion of the nearby rocks also may have contributed to the load.

Table 2: Trace element concentration in PPM

Sample	Zr	V	Cr	Co	Ni	Cu	Pb	Sr	Nb	Ba	Rb	Zn
1	655.44	37.83	36.01	64.62	8.30	10.29	5.64	17.05	20.53	24.68	1.92	24.16
2	801.63	37.28	37.39	136.38	9.26	8.44	6.22	21.06	18.64	32.23	2.73	27.15
3	1212.60	34.95	40.30	558.42	8.51	3.98	7.55	18.13	34.71	28.48	2.51	26.12
4	844.69	36.04	37.68	104.51	16.32	12.34	6.63	19.64	15.18	28.47	2.68	19.63
5	674.96	35.79	37.42	80.86	6.82	5.80	5.80	20.33	27.85	29.87	2.55	18.90
6	667.67	30.78	29.28	58.23	7.75	5.23	4.95	20.48	13.46	30.68	2.54	7
7	653.83	34.81	33.71	556.89	10.66	7.83	5.95	19.56	14.86	27.52	2.63	18.29
Range	653.83-1212.60	30.78-37.83	29.28-40.30	58.23-558.42	6.82-10.66	3.98-10.29	4.95-7.55	17.05-21.06	13.46-34.71	24.68-32.23	1.92-2.73	18.29-27.15
Mean	787.26	30.50	36.04	222.84	9.66	7.78	6.11	19.46	20.75	28.85	2.51	21.86
Average shale (worldwide)	160	130	90	19	50	45	20	170	11	580	140	95
Upper Crust	170	140	69	17	55	39	17	35 0	15	570	110	67
Std Dev	202.7	2.31	3.55	230.2	9.66	2.95	0.82	1.41	7.84	2.42	0.27	3.82

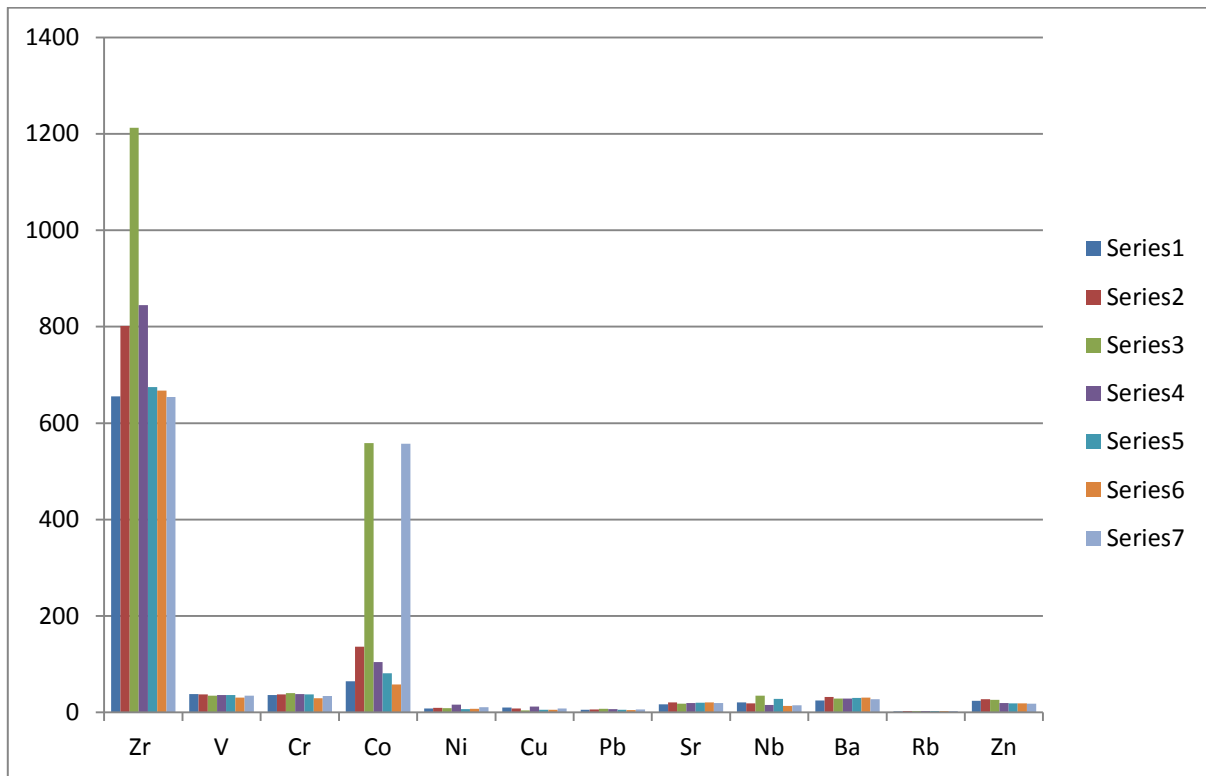Shale average; (Turekian and Wedephol, 1961) , Upper crust ; (Wedephol,1995).

Fig.3: Metal concentration in the sediments of the study area.

Cr, Pb and Ni are toxic metals that are found in the sedimentin the aquatic ecosystem and their presence could be dangerous to flora and fauna including man. Cr ,Pb, and Ni contents in the present Olubirin stream sediment are significantly less than the worldwide shale average values as well as the upper crust and therefore do not pose any health risk(Fig 3). Cr varies from 29.28 to 40.30 ppm, although less than the shale average of 90 is less risky to the ecosystem. However, according to Chiba and Masironi, (1992), the biological effects of Cr depend on its valency. In the trivalent form, Cr is essential element but in the hexevalent form it is carcinogenic. Katz and Salem (1994) reported that Cr contamination is common in soils and in both ground and surface waters in industrial areas. However in this study, Cr in the sediment has no contaminating effect since the area is not an industrial area that can generate such a metal to lethal level.Pb is regarded as a good indicator of pollution sourced by urban run-off water as well as from gasoline (fuel) in automobiles. Mukai et al., (1994) and Legret and Pagotto, (1999) reported that gasoline was responsible for Pb pollution in the 20th century in Japan.The study area is however predominantly locally forestedand cannot generate robust run-off and gasoline levels that can generate contamination in the sediments.

3.2 Enrichment factor (EF)

In order to determine the degree of contamination of the trace metals in the sediment, indices such as the enrichment factor (EF), geoaccumulation index (Igeo) and pollution load index (PLI) are applied for this study (Covelli and Fontolan,1997; Ghrefat and Yusuf, 2006; Gonzales-Macias et al., 2006; Chen et al., 2007) . The world-wide average shale concentration as given by Turekian and Wedepohl (1961) is used as reference for unpolluted sediments to quantify the trace metal enrichment. Enrichment factor is a convenient measure of geochemical trends and is used for comparison between areas (Hernandez et al., 2003).It can be used to compare the necessary enrichment of different types of elements for their recovery to be economically viable (Loska et al., 2005).

The normalized enrichment factor (EF) of the metals used in this study is asoriginally introduced by Buat-Menard and Chesselet, (1979) and Rubio, et al., and Vilas, F. (2000) in equation 1.

$$EF= [Cn/Cref]sample/[\ Bn/Bref\ ]\qquad \text{Equation}\quad 1$$

where Cn (sample) is the concentration of the examined metal in the sample, Cref (sample) is the concentration of the reference sample. Bn and Bref are concentrations of the examined metal in the average shale and reference metal in the average shale respectively. Elements such as Al (Chen et al.,2007) and Fe have been widely used for normalization. (Ogusola et al.,1994.,

Gaiero et al.,1997., Sutherland et al.,2000., Kamau, 2002., Valdes et al., 2005., Ghrefat and Yusuf.,2006, Abrahim and Parker, 2008., Akoto et al.,2008., Dragovic et al.,2008., Charkravarty and Patgiri, 2009., Harikumar and Jisha, 2010) but for this work, copper (Cu) has been used as a conservative tracer to differentiate the natural from the anthropogenic components. The metal contamination has been expressed with respect to the average shale in order to quantify the extent and degree of pollution around the area of study.

Table 3: Enrichment Factor (EF) values (ppm) for Trace elements

LOCATION	V	Cr	Co	Ni	Pb	Sr	Nb	Mo	Ba	Rb	Zn	Zr
1	0.14	0.59	0.35	0.72	0.53	0.06	0.29	0.60	0.003	0.01	0.16	0.10
2	0.15	0.62	0.75	0.81	0.58	0.07	0.27	0.47	0.004	0.015	0.19	0.10
3	0.14	0.67	3.06	0.75	0.70	0.06	0.51	0.76	0.004	0.014	0.01	0.21
4	0.14	0.63	0.57	1.43	0.62	0.07	0.22	0.67	0.004	0.013	0.01	0.12
5	0.14	0.62	0.44	0.59	0.07	0.07	0.41	0.85	0.004	0.014	0.01	0.12
6	0.12	0.48	0.32	0.68	0.46	0.07	0.19	0.44	0.004	0.014	0.01	0.10
7	0.13	0.56	3.06	0.93	0.55	0.06	0.22	0.60	0.003	0.013	0.01	0.10

A five-category ranking system as proposed by Sutherland, (2000) and Kartal et al., (2006) is used in this paper to denote the degree of anthropogenic contamination. When the enrichment factor is less than 2 (EF < 2) it means that the sediment is not contaminated or that it has a minimal contamination, when the EF = 2–5, it means moderate contamination, EF = 5–20 significant contamination, EF = 20–40 very high contamination, and EF > 40 extremely high contamination. The enrichment factor (EF) values of sediments at the various locations points are presented in Table 3. The EF value for Co ranges from 0.32 to 3.06, Ni (0.68-1.43), Pb (0.46-0.70)and Mo (0.44-0.85) in the elements of the study area.

The values of EF presented in Table 3 shows that only Co in locations 3 and 7 has values that are more than 3 and it is therefore considered to have moderatecontamination . Other elements that have their EF values < 2 suggest that the environment is deficiently to minimally contaminated implying that they have no anthropogenic input but have input from natural processes whereas those whose EF is higher than 2 (EF> 2) gives an indication that their sources are likely to be anthropogenic (Ergin et al.,1991., Angelidis and Aluopi,1997 and Liaghati et al., 2003).

3.3 **Contamination Factor (CF)**

The degree of contamination is expressed by the contamination factor (CF); (Hakanson,1980). The EF is the ratio obtained by dividing the value of the element in the sediment by the background values . Håkanson, (1980) used four terminologies to express the level of contamination in any sediment; thus CF<1 indicates low contamination, 1≤CF<3, moderate contamination, 3≤ CF ≤6 considerate contamination, and CF>6 means very high contamination. The contamination factor (CF) valuesas presented in Table 4 indicate that Cr, (locations 1-5 and 7) Ni (locations 4 and7) and Cs (all locations) satisfied the category with values higher than 1 but less than 3(1≤CF<3),and is therefore considered to havemoderate contamination effects. All other elements show low CF values that are less than 1 except for Co (locations 3 and 7) and Ni (locations 4 and 7) thus indicating low contamination (.Fig 4).

Table 4: Contamination Factor (EF) values (ppm) for Trace Elements

| Location	V	Cr	Co	Ni	Cu	Pb	Sr	Nb	Mo	Cs	Ba	Rb	Zn	Zr
1	0.44	1.19	0.15	0.81	0.53	0.23	0.25	0.07	0.75	1.25	0.04	0.03	0.36	0.12
2	0.43	1.25	0.32	0.90	0.43	0.26	0.28	0.07	0.70	1.50	0.06	0.05	0.40	0.14
3	0.40	1.34	1.30	0.83	0.20	0.31	0.24	0.12	0.81	1.07	0.05	0.04	0.39	0.22
4	0.42	1.25	0.24	1.59	0.63	0.27	0.26	0.05	0.88	1.32	0.05	0.05	0.29	0.15
5	0.41	1.25	0.19	0.67	0.30	0.24	0.28	0.10	0.88	1.04	0.05	0.04	0.28	0.12
6	0.36	0.97	0.14	0.76	0.27	0.20	0.27	0.05	0.61	1.39	0.05	0.04	0.28	0.12
7	0.40	1.12	1.29	1.04	0.39	0.25	0.26	0.05	0.81	1.36	0.05	0.04	0.27	0.12
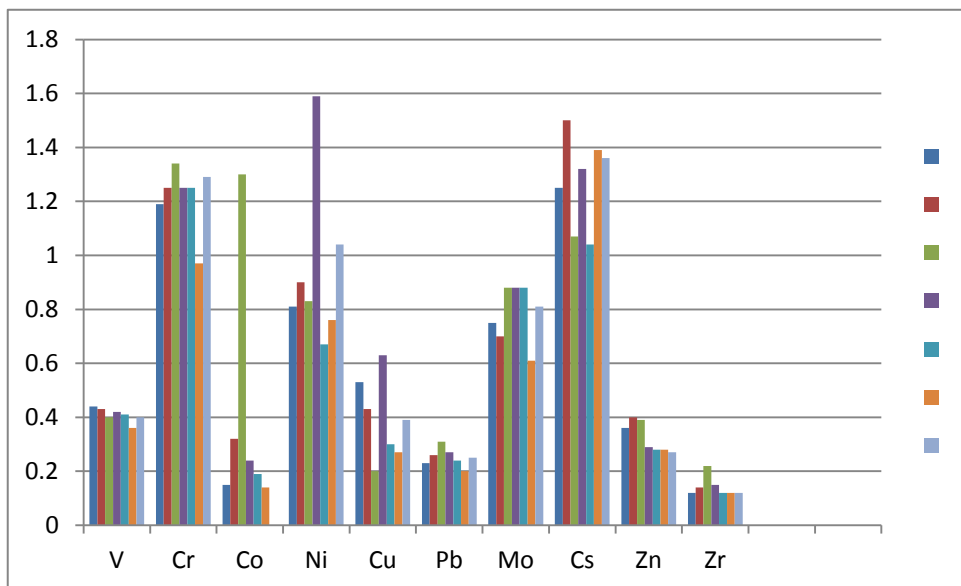
Fig: 4. Contamination factor (EF) values (ppm) for trace metals .

3.4 Pollution Load Index (PLI)

The pollution load index, proposed by Thomlinson et al., (1980) was calculated using;

$$PLI = [CF_1 \times CF_2 \times CF_3 \times \text{---} \times CF_N]^{1/N} \qquad \text{Equation 2}$$

The worked out data of the PLI and the degree of contamination (Cd) are presented in Table 5. The essence of these two parameters (PLI and Cd) is to pin point the sites that are heavily contaminated or polluted. The PLI values are less than unity suggesting perfection or no overall pollution, but the values of Cd in Table 5 using the equation 2 as proposed by Pekey et al.,2004; Caeiro et al., 2005 and Abrahim, (2005) show the range of between 5.51 and 7.45. Using the Cd terminologies: Cd < 8 means low degree of contamination, $8 \leq Cd < 16$, moderate degree of contamination, $16 \leq Cd < 32$ considerable degree of contamination, Cd> 32 very high degree of contamination. Since the highest value of Cd is 7.45 (Fig 5) and not up to 8, it means there is low degree of contamination especially at locations 7, 3 and 4 in the study area.

Table 5:Pollution load index and degree of contamination by trace elements

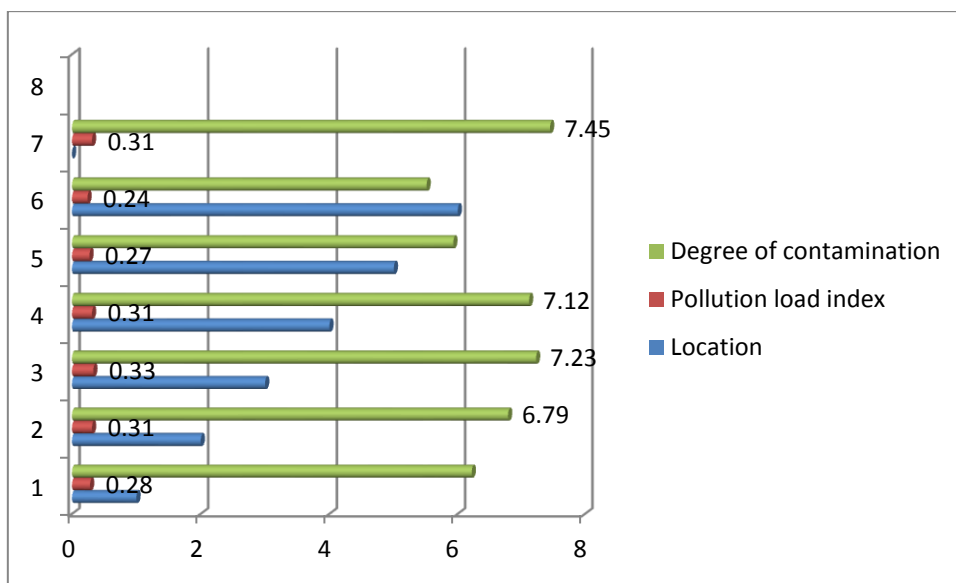| Location	Pollution load index	Degree of contamination
1	0.28	6.22
2	0.31	6.79
3	0.33	7.23
4	0.31	7.12
5	0.27	5.93
6	0.24	5.51
7	0.31	7.45

Fig: 5: Pollution load index (PLI) and degree of contamination (Cd) of the study area.

3.5 Geoaccumulation Index (Igeo)

The geoaccumulation index is a quantitative measure of the degree of pollution in aquatic sediments and can be calculated by using equation 3:

$$Igeo = log_2 \; Cn \; / \; 1.5 \; Bn \qquad \text{Equation} \quad 3$$

where Cn is the measured concentration of the examined metal in the sediment and Bn is the geochemical background concentration of the metal. The factor 1.5 is used because of possible variations in background values due to lithological variability. Müller (1969) proposed the seven enrichment classes based on the increasing numerical values of the index.

Table 6: Geo-accumulation Index (Igeo) (Muller, 1969) of Heavy Metal Concentration in Sediment

Table 6: Geo-accumulation Index (Igeo) (Muller, 1969) of Heavy Metal Concentration in Sediment

Geoacumulation index	Class	Pollution Intensity
0	0	Background concentration
0-1	1	Unpolluted
1-2	2	Moderately to unpolluted
2-3	3	Moderately polluted
3-4	4	Moderately to highly polluted
4-5	5	Highly polluted
>5	6	Very highly polluted

Source: Singh et all, (2003)

Table 7: Geoaccumulation index (Igeo) values.

Location /Element	V	Cr	Co	Ni	Cu	Pb	Sr	Nb	Mo	Cs	Ba	Rb	Zn	Zr
1	-1.79	0.34	-3.47	0.89	-1.51	-2.64	-2.73	-4.32	-1.00	0.26	-5.05	-5.64	-2.05	-3.64
2	-1.79	0.26	-2.25	0.73	1.84	-2.55	-2.39	-4.64	-1.08	0.00	-4.64	-5.05	1.88	-3.47
3	-1.89	0.17	0.21	0.86	-2.83	-2.25	-2.64	-3.64	0.89	0.49	-5.05	-5.05	-1.94	-2.73
4	-1.84	0.25	-2.64	0.08	-1.25	-2.47	-2.55	-4.64	0.76	0.18	-5.05	-5.05	-2.39	-3.32
5	-1.84	0.26	-3.05	-1.18	-2.39	-2.64	-2.47	-3.83	0.76	0.53	-5.05	-5.05	-2.39	-3.64
6	-2.06	0.21	-3.47	-1.00	-2.47	-2.83	-2.47	-5.05	-1.28	0.10	-5.05	-5.05	-2.39	-3.64
7	-1.89	0.42	0.21	0.54	-1.94	-2.64	-2.55	-4.64	0.89	0.13	-5.05	-5.05	-2.39	-3.64

The Igeo value of Co ranges from -2.25 to 0.21, Ni -1.00 to 0.89, Cu -1.25 to 1.84, Pb -2.25 to 2.83 and Zn -2.05 to 1.88 in the sediment of the study area.(Table 7).Co andNi fall in the class of 0-1 and is therefore unpolluted. Cu and Zn at location 2 fall between 1-2 class and therefore remain moderately to unpollutedin intensity. (Fig 6)V, Pb Sr Nb Rb, Zr metals fall in class 0 as they are negative in all locations suggesting that the study area sediments are in background level with respect to these metals. These negative Igeo values found in these metals relate them to low levels of contamination.The variations of Igeo for each metal with locations are shown in Fig 6.
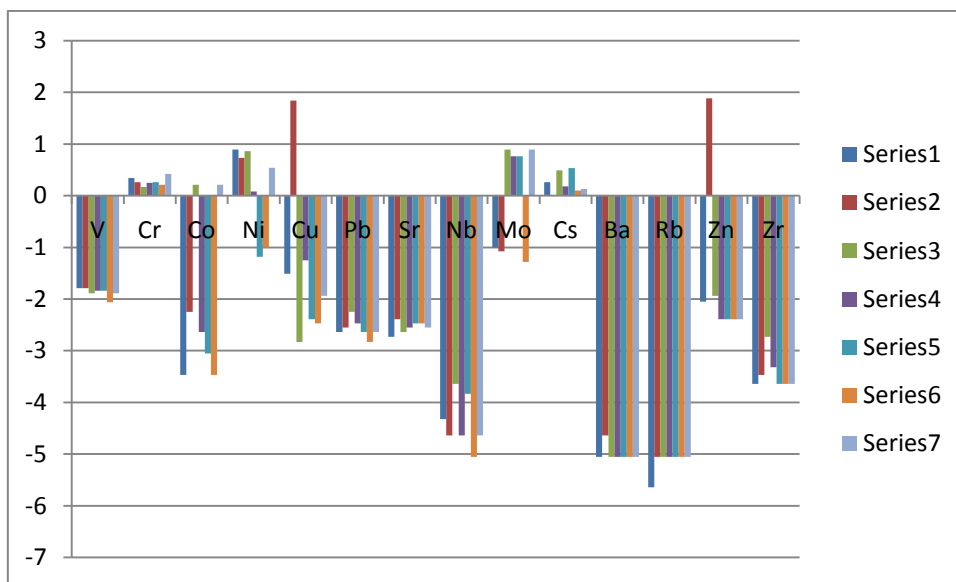

Fig 6:Geoaccumulation index (Igeo) of sediment of studied area.

3.6 Statistical Analysis

Inter-oxide association was evaluated by Spearman's rank correlation coefficient, ρ and the results are shown in Table 3. Table 3 shows some major oxide pairs, examples are SiO_2/CaO (r= 850), and SiO_2/ Fe_2O_3, SiO_2/K_2O, SiO_2/MnO (r=874), Other pairs are Al_2O_3 /CaO , Al_2O /Fe_2O_3, Al_2O_3/K_2O and all show strong correlations. Strong correlations signify that each paired elements have common contamination sources.

Table 8: Correlation co-efficient of the major elements of the study area

	SiO$_2$	Al$_2$O$_3$	CaO	Fe$_2$O$_3$	K$_2$O	MgO	MnO	P$_2$O$_5$
SiO2	1							
A$_2$O$_3$	.967	1						
CaO	.850**	.854**	1					
Fe$_2$O$_3$	.874**	.870 **.983**	1					
K$_2$O	.874**	870*	.983**	1.00	1			
MgO	.874	.866**	.979**	.996**	.996**	1		
MnO	.874**	.870**	.983**	1.00	1.00	.996**	1	
P$_2$O$_5$	.578	.720	.882**	.899	,988**	895**	.899**	1

The spearman,s rho correlation indicates that the oxides are highly positive, correlated and associated suggesting that they are of the same source of enrichment (natural process) .

The correlation matrix of the trace metals is also calculated and presented in Table 8. The inter-element correlations show that V is strongly correlated with V/Cr and V/Zn. Other pairs are Cr (Cr/Zn, Cr/Nb. Cr/Cs), CO (Co/ Nb) , while Zn correlates with Nb. while Nb strongly associates with Cs. The repetitive correlation of these elements is an indication of their common source occurrences that are devoid of any anthropogenic input. Strong correlations shows also that each paired elements have common contamination sources. The component plots of the elements showed the clustering of these elements into one component (Fig 7) thus confirming the common source of origin most probably bitumen.

Table 9; Correlation Matrix of trace elements.

Correlation	V	Cr	Co	Ni	Zn	Zr	Nb	Cs	Ba
V	1.000								
Cr	**.710**	1.000							
Co	-.083	.258	1.000						
Ni	.179	.181	.029	1.000					
Zn	**.520**	**.573**	.116	-.196	1.000				
Zr	-.336	-.302	-.247	.039	-.285	1.000			
Nb	.050	**.667**	**.524**	.125	**.568**	-.261	1.000		
Cs	.236	**.718**	.350	-.430	.461	-.365	**.679**	1.000	
Ba	-.086	-.498	-.202	.317	.054	.431	-.366	-.829	1.000

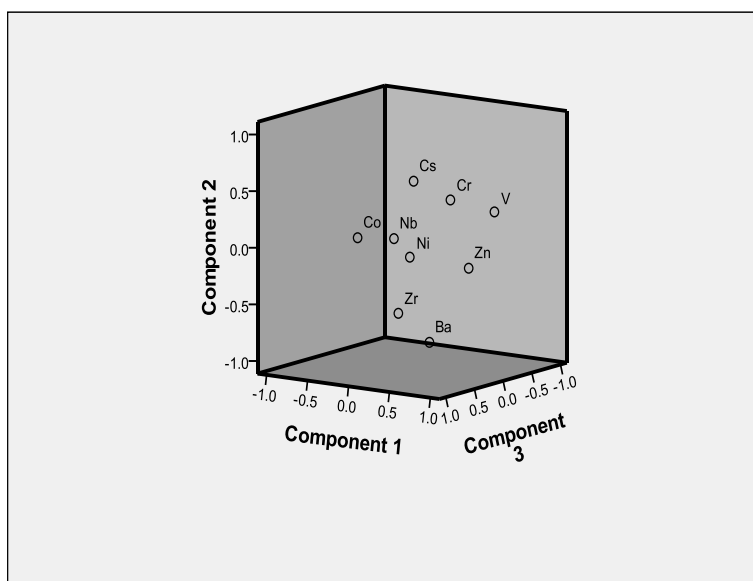| Correlation	V	Cr	Co	Ni	Zn	Zr	Nb	Cs	Ba
V	1.000								
Cr	**.710**	1.000							
Co	-.083	.258	1.000						
Ni	.179	.181	.029	1.000					
Zn	**.520**	**.573**	.116	-.196	1.000				
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Nb	.050	**.667**	**.524**	.125	**.568**	-.261	1.000		
Cs	.236	**.718**	.350	-.430	.461	-.365	**.679**	1.000	
Ba	-.086	-.498	-.202	.317	.054	.431	-.366	-.829	1.000

Component Plot in Rotated Space

FIG 7: COMPONENT PLOT OF TRACE METALS IN THE STREAM SEDIMENT.

IV. CONCLUSION

The stream sediments of Ilubirin bitumen impregnated samples were collected and evaluated for contamination using the major and tracemetal elements. The evaluation iscarried out with indices such as enrichment factor (EF), contamination factor (CF), and geoacummulation index (Igeo). The results of the EF indicated that most elements are deficiently enriched in the sediment having EF values less than 2 (EF < 2). CF indicates that Cr at locations 1-5, and 7 and Ni at locations 4 and 7 showed moderate contamination having values higher than 1 and less than 3 (1<CF<3). Igeo value indicates that Cs, Ni, Cr, and Mo have uncontaminated to moderate contamination degrees because they have values in the class range of0-1. Zr and Co (locations 3 and 7) have the highest concentrations that suggesta threat on the sediments. Correlation analysis for trace elements shows that elements Rb, Sr, Nb, Cs, Ba, are highly and positively correlated with other elements suggesting a similar contamination source.It

is suggested that regular geochemical work should be carried out in this area so as to monitor any rise in contamination level and the residents should be advised to avoid making use of the water from streams within the environment of study.

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