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Full Length Research Paper

Survey of heavy metals in sediments of Kolo creek in the Niger Delta, Nigeria

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Concentrations of Fe, Pb, Cr, Ni and V were measured in sediments taken from eight (8) sampling stations along a section of Kolo creek which traverses an oil flow station and a point in Epie creek which receive effluent discharges from human and industrial activities. The study was conducted in four seasons (Dry, Late Dry, Rainy and Late Rainy Seasons). Vanadium was less than 0.001 mg/Kg in all the samples analysed. Fe, Pd, Cr and Ni had annual means of 5109.85, 1.60, 14.22 and 10.18 mg/Kg respectively. One way ANOVA at 95% confidence limit showed no significant difference in the nine (9) sampling stations. However, there was significant difference in the four (4) seasons that the study was conducted. Cluster analysis of the data further classified the four seasons into two groups. Geoaccumulation indices showed that the Creek is not polluted by Pb, Cr and Ni, however, it is highly polluted with Fe. The highest positive correlation was between Pb and Cr while the highest negative correlation was between Fe and Ni. Compared to DPR intervention values, Kolo creek is free from pollution by Pb, Cr and Ni.

Key words: Heavy metals, sediment, Kolo creek, cluster analysis, geoaccumulation index.

INTRODUCTION

Kolo creek, a fresh water non-tidal creek flows through a region of Niger Delta that has been urbanised and industrialized due to the quest for crude oil and natural gas, a natural resource that is in abundance in this area. As a result of these activities, Kolo creek receives loads of human and industrial effluents which may be detrimental to the quality of the creek. This calls for urgent attention since the creek serves as the major source of water for domestic and recreational use for the communities that it traverses. Often times as these components get to the water body, they finally settle at the bottom as sediments which acts as sinks for contaminants in aquatic systems (Adams et al., 1992; Burton and Scott, 1992; Mucha et al., 2003)

In this study, the following heavy metals were considered: Pb, Fe, Cr, V and Ni. Ni and V were considered based on the fact that they are the substantial metals in crude oil and gross indices of the biodegraded oil (Osuji et al., 2006). Pb, Fe and Cr are considered mainly due to their association in piping system and corrosion inhibition as well as an anti-knocking agent in automobile engines.

Heavy metal discharged into the environment rapidly associates with particulates and ultimately settles in bottom sediments of water bodies either through direct discharge or surface run-offs (Hanson et al., 1993; Binning and Baird, 2001). The accumulation of metals from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, electrical conductivity and the available surface area for adsorption caused by the variation in grain size distribution (Davies et al., 1991). Digenetic processes in the sediments can change and redistribute these contaminants between the solid and the dissolved phases, but most of the elemental contaminants are immobilised through sedimentation (Hanson et al., 1993).

The objectives of this paper are to illustrate the distribution and levels of sediment contamination by

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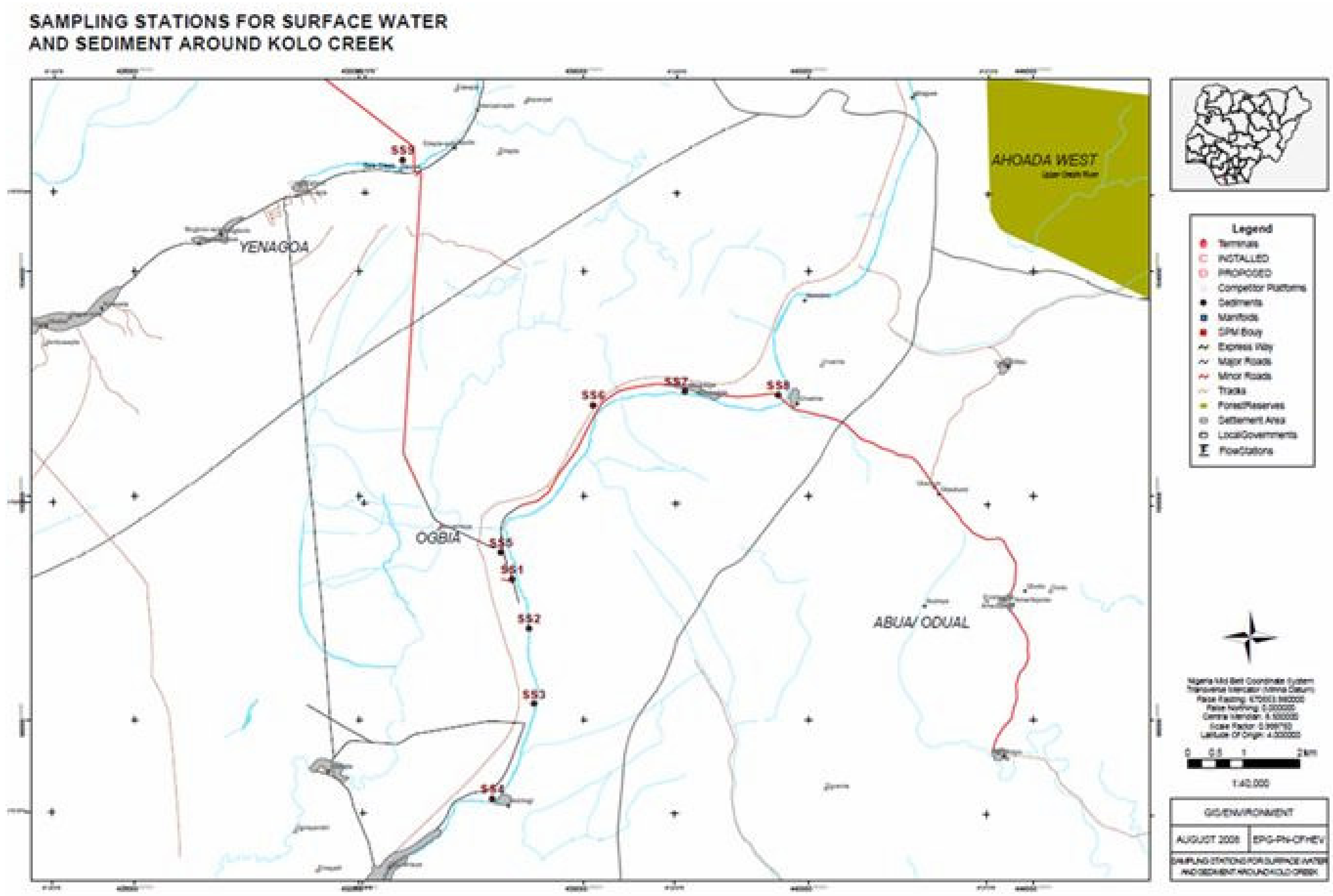

Figure 1. Map showing sampling stations for surface water and sediment.

heavy metals in the Kolo creek sediments and to compare data with Department of Petroleum Resources (DPR) 2002 guideline values.

MATERIALS AND METHODS

Sampling sites

Nine points were sampled, eight along Kolo creek and one point located at Epie creek (Figure 1). Three points (SS1, SS2, SS5) were around Kolo creek flow station, SS4, SS7 and SS8 were within Imiringi, Otuasega and Oruma communities respectively, while SS3 and SS6 were within uninhabited environments. SS9 was in Epie creek within Tombia junction which is urbanised and densely populated.

The sampling field data for surface water and sediment are as shown in Table 1.

Sampling

Sediment samples were collected using a Van Veen grab sampler as described by Inengite et al. (2010). Triplicate sediment samples were collected at each point to form one composite sample and another composite sample collected about 5 m away from the first point at the same sampling station, forming a total of 72 composite sediment samples for the four sampling months, 6th April, 2008 (Late Dry Season); 29th June, 2008 (Rainy Season); 19th October, 2008 (Late Rainy Season) and 24th January, 2009 (Dry Season) (Table 1). The samples were wrapped in aluminium foil stored in an ice chest and taken to the laboratory and stored at -20°C prior to analysis.

Some physico-chemical parameters of the surface water such as temperature, pH, conductivity, total dissolved solids, turbidity and dissolved oxygen were determined *in-situ* using the appropriate field sampling meters. The results are as shown in Table 2.

Determination of heavy metals

The soil samples were air-dried and gently crushed and sieved to 2 mm. ASTM method D3110 (1995) was employed. 2 g of the sieved sediment samples were first digested using mixed acids. 1 ml perchloric acid, 4 ml concentrated Sulphuric acid, 3 ml concentrated Nitric acid and 1 ml hydrochloric acid were added to the sediment and swirled to disperse the particles. 5 cm^3 of deionized water was added and the crucible heated gently in a fume cupboard and later strongly to partial dryness. After cooling the crucible, deionized water was added and the suspension stirred with a glass rod. This was filtered into a 100 ml volumetric flask and diluted to volume with deionized water. The heavy metal levels were determined with Perkin Elmer Atomic Absorption Spectrophotometer (AAS), model

Table 1. Sampling field data for surface water and sediment.

Sampling stations (SS)	Dates sampled	Times sampled	Station location	Latitude (N)	Longitude (E)
SS1	6th April, 2008; 29th June,2008 19th Oct.,2008; 24th Jan., 2009	10:03am; 9:45am 10:30am; 9:30am	Kolo creek flow station	4° 53' 15.855''	6° 22' 25.640''
SS2	6th April, 2008; 29th June,2008 19th Oct.,2008; 24th Jan., 2009	10:40am; 10:32am 11:05am; 9:50am	Kolo creek flow station	4° 52' 47.289''	6° 22' 35.497''
SS3	6th April, 2008; 29th June,2008 19th Oct.,2008; 24th Jan., 2009	11:10am; 11:05am 11:30am; 10:30am	Imiringi	4° 52' 03.614''	6° 22' 38.551''
SS4	6th April, 2008; 29th June,2008 19th Oct.,2008; 24th Jan., 2009	11:45am; 11:40am 12:00pm; 11:05am	Imiringi	4° 51' 08.229''	6° 22' 14.620''
SS5	6th April, 2008; 29th June,2008 19th Oct.,2008; 24th Jan., 2009	12:35pm; 12:30pm 12:45pm; 11:30am	Kolo creek flow station	4° 53' 31.426''	6° 22' 19.121''
SS6	6th April, 2008; 29th June,2008 19th Oct.,2008; 24th Jan., 2009	1:25pm; 1:25pm 1:48pm; 12:40pm	Otuasega	4° 54' 56.765''	6° 23' 12.185''
SS7	6th April, 2008; 29th June,2008 19th Oct.,2008; 24th Jan., 2009	2:10pm; 2:15pm 2:45pm; 1:50pm	Otuasega	4° 55' 05.089''	6° 24' 04.921''
SS8	6th April, 2008; 29th June,2008 19th Oct.,2008; 24th Jan., 2009	3:05pm; 3:05pm 3:40pm; 3:05pm	Oruma	4°55'03.037''	6°24'58.92''
SS9	6th April, 2008; 29th June,2008 19th Oct.,2008; 24th Jan., 2009	4:10pm;4:15pm 4:40pm;4:00pm	Tombia junction Yenagoa	4°57'18.776''	6°21'21.604''

LD = 6th April, 2008; R= 29th June, 2008; LR=19th Oct., 2008; D=24th Jan., 2009.

3100, using calibration curve method.

RESULTS AND DISCUSSION

The concentrations of heavy metals in the sampling stations are shown in Table 3. Fe was in the range 552 - 15379.50 mg/Kg, with mean concentration of 1128.38; 1184.38; 3255.74 and 1055.16 mg/Kg for Dry (D), Late Dry (LD), Rainy (R) and Late Rainy (LR) seasons respectively. In an increasing order, it is LR<D<LD<R.

The highest concentrations were in the rainy season(R). This could be attributed to the contribution from run-offs from storm water into the creek, which serves as a drainage route for the area. Owing to the fact that the soil in this environment has high Fe content (Iwegbue et al., 2006), most of the run-offs will be loaded with high contents of Fe. The highest concentration of Fe was recorded at SS6, where metal construction across the creek was going on. This activity may have contributed greatly to the extremely high concentration of Fe at this point (Ohimain et al., 2008).

Dendrograms from the Cluster Analysis for the four seasons D, LD, R and LR classified D and LD together, R was outstanding and LR was closer to the cluster of D and LD (Figure 2). This clustering pattern could be attributed to high levels of rain during the period of June, 2008. This high levels of rain invariably increased the volume of storm water that is evacuated into the creek and therefore increasing its Fe content.

Pb recorded its highest concentration in the Late Dry Season (LD) for all the stations sampled except SS6 and SS7 which had highest Pb concentrations in the Rainy Season (R). Pb concentration was in the range <0.001 - 3.76 mg/Kg. The highest concentration was in the LD Season. The seasonal mean concentrations were 1.64; 2.31; 1.54 and 0.91 mg/Kg for D, LD, R and LR respectively. In an increasing order, LR<R<D<LD. Pb which is likely to be associated with automobile combustion could be transported by air through exhaust fumes and deposited on water bodies (Morillo et al., 2008). This point to the direction why lead is higher in the LD season when the weather is relatively dry and industrial activities tend to be at its peak (Puyate et al.,

Table 2. Physico-chemical characteristics of surface water in Kolo creek.

Sampling stations	pH				Conductivity uS/cm				Turbidity (NTU)				Dissolved oxygen (%)				Temperature (°C)				Total dissolved solids (mg/l)			
	D	LD	R	LR	D	LD	R	LR	D	LD	R	LR	D	LD	R	LR	D	LD	R	LR	D	LD	R	LR
SS1	6.70	5.90	6.80	6.80	50.5	49	51.5	51.0	52.0	50.0	57.5	55.5	5.20	5.2	5.90	5.80	26.5	27.0	26.1	26.0	29.1	35.5	27.0	28.1
SS2	6.60	6.10	6.85	6.85	50.5	49.5	50.8	50.8	50.2	48.0	55.6	55.5	5.10	5.3	5.98	5.98	27.0	26.5	25.8	25.8	27.5	35.0	27.0	26.9
SS3	6.70	6.20	6.85	6.85	51.0	48	51.0	51.1	52.1	51.0	55.0	54.0	5.10	5.2	5.86	5.90	27.0	26.5	26.2	25.8	31.0	36.5	28.0	30.3
SS4	6.50	6.00	6.88	6.88	71.4	69.4	72.1	72.8	55.0	60.0	59.1	59.0	6.00	6.1	6.50	6.50	27.2	27.0	26.3	26.3	39.3	43.2	36.4	38.6
SS5	6.80	6.20	7.10	6.80	47.8	46.5	49.5	48.8	55.8	62.0	72.0	64.8	6.20	6.2	6.80	6.60	27.0	28.2	28.1	26.1	30.0	35.0	26.0	28.9
SS6	6.80	5.90	6.95	7.10	52.1	52	55.0	55.0	58.0	53.0	61.2	58.2	6.50	6.1	6.36	6.20	28.0	28.0	28.0	26.0	38.2	45.1	31.2	38.8
SS7	6.90	6.10	6.85	7.30	51.0	52.1	51.0	31.3	45.6	49.0	50.3	49.5	5.50	5.7	5.90	5.70	28.0	28.0	28.3	26.0	29.9	35.0	27.0	16.6
SS8	6.80	6.00	6.80	6.95	51.2	54	51.0	51.5	45.1	42.0	48.0	46.0	5.50	5.7	5.88	5.80	29.1	29.5	28.0	26.2	28.7	36.0	27.0	28.6
Tombia	6.80	6.20	6.80	6.80	51.0	54	51.5	51.5	52.2	50.00	48.6	48.1	5.80	5.6	5.83	5.83	29.5	29.7	29.5	29.5	28.4	36.4	27.0	27.3

Table 3. Heavy metals in Kolo creek sediment in mg/kg.

	Fe				Pb				Cr				Ni			
DPR intervention value	NA				530				380				210			
	D	LD	R	LR	D	LD	R	LR	D	LD	R	LR	D	LD	R	LR
SS1	1668.00	552.00	8687.00	5072.00	2.56	3.48	1.52	1.63	11.05	9.04	14.15	21.57	15.05	20.00	7.35	11.02
SS2	2281.00	900.00	4563.00	4964.00	0.79	1.90	0.65	0.00	12.85	10.95	6.54	24.39	15.96	20.60	3.58	10.42
SS3	3171.00	2560.00	7841.00	6536.00	1.28	1.78	1.35	0.99	12.56	10.55	7.06	22.26	12.42	16.40	3.55	8.54
SS4	3855.00	2836.00	9435.00	5648.00	2.54	3.76	1.80	1.46	13.02	13.56	16.16	25.61	4.01	4.40	6.93	9.92
SS5	4765.00	1050.00	9396.50	7144.00	2.03	2.42	1.44	1.44	13.29	11.28	11.69	19.88	8.33	10.00	6.48	10.10
SS6	4062.00	2694.00	15379.50	5960.00	0.98	1.80	2.44	1.71	11.98	10.08	18.03	21.47	11.25	14.20	8.47	9.22
SS7	3990.00	900.00	6619.00	7642.00	0.88	0.96	1.96	0.00	11.22	10.20	9.47	22.95	9.14	12.40	4.36	9.87
SS8	4675.00	2685.00	9356.50	7815.00	2.09	2.98	1.40	0.93	10.54	9.52	9.82	21.33	9.00	10.20	5.90	10.25
Tombia	4900.00	3960.00	4550.00	5842.00	1.58	1.72	1.30	0.00	14.95	14.04	5.62	23.28	14.98	20.80	3.08	8.42
Mean	3707.44	2015.22	8425.28	6291.44	1.64	2.31	1.54	0.91	12.38	11.02	10.95	22.53	11.13	14.33	5.52	9.75
Std. Dev	1128.38	1184.38	3255.74	1055.16	0.70	0.92	0.50	0.73	1.36	1.72	4.39	1.74	3.91	5.65	1.94	0.87

D = Dry Season; LD = Late Dry Season; R = Rainy Season; LR = Late Rainy Season; NA = Not Available.

2007).

The highest concentration of 20.80 mg/Kg for Ni was recorded in Tombia junction during the LD season, while the least was 3.08 mg/Kg during the rainy season. The mean concentrations of Ni were11.13; 14.33; 5.52 and 9.75 mg/Kg for D, LD, R and LR seasons respectively, giving a pattern R<LR<D<LD. Nickel had higher concentrations in the dry seasons as compared to the rainy seasons. Its pattern is similar to that of Pb.

Chromium (Cr) recorded its highest concentration of 25.61 mg/Kg in SS4 during the LR season

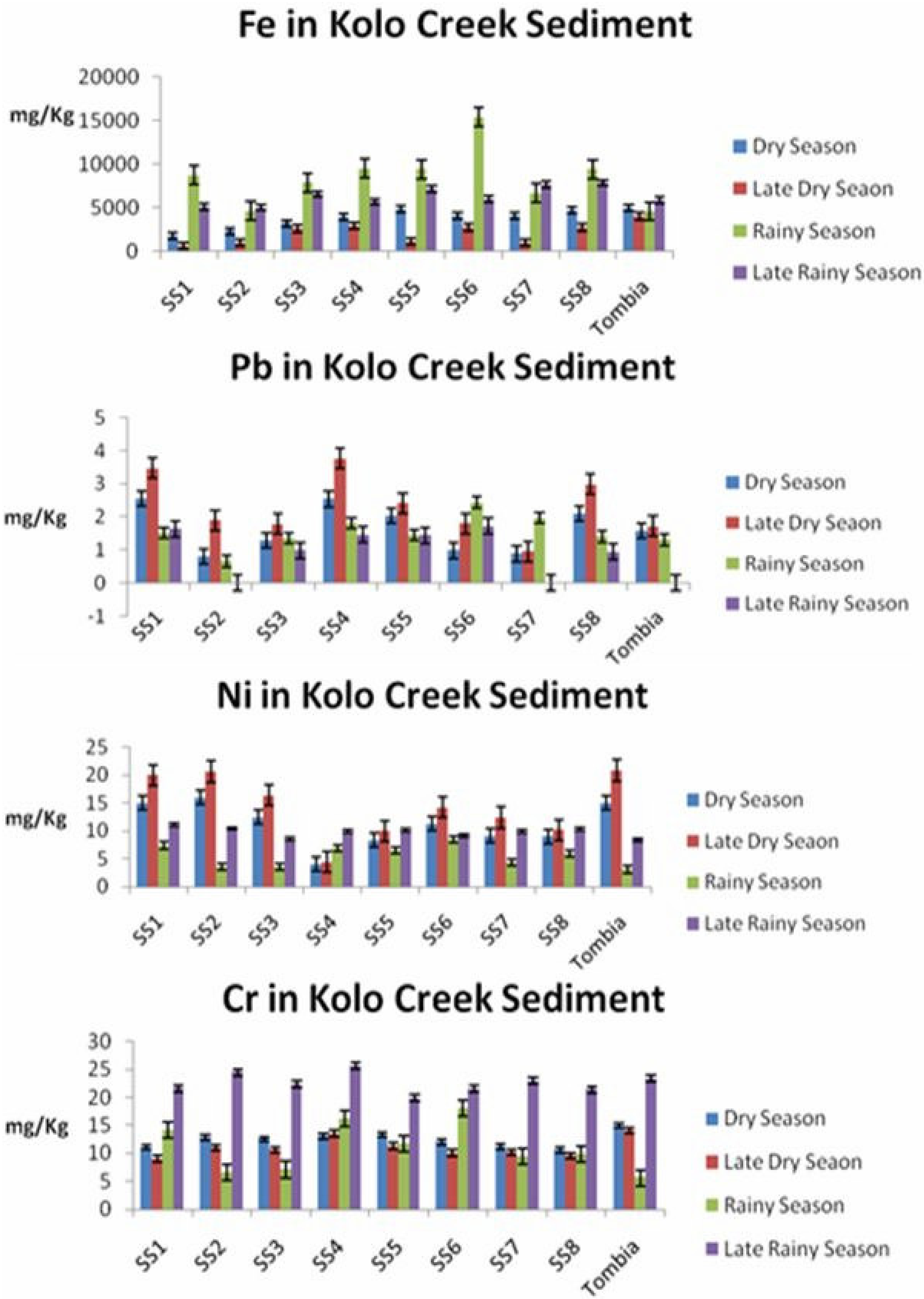

Figure 2. Heavy metals in Kolo creek sediment.

Plate 1. On-going metal construction work at sampling station 6.

and its lowest concentration of 5.62 mg/Kg at Tombia Junction during the R season. The mean concentrations for D, LD, R and LR seasons were 12.38; 11.02; 10.95 and 22.53 respectively. The following pattern R<LD<D<LR was recorded.

Dendrograms of Ni and Pb separated the seasons into two D and LD in one set and R and LR in the second set. This is expected since the two recognised seasons in this geographical location are majorly Dry and Rainy Seasons (Puyate et al., 2007).

The dendrogram for Cr separated LR season from the rest which indicates that there may be a major contributor of chromium to the environment during the LR season since it also recorded significantly high concentrations.

The physicochemical parameters of the surface water of Kolo Creek had characteristics of a fresh water swamp in the Niger Delta (Table 2) (Opuene, 2005). It is therefore not an implication of a recent pollution that may have been responsible for the variations in the heavy metal content of the sediment. The possibilities of discharges and run-offs into the creek are there but the effluents may have almost immediately settled to the bottom sediment which serves as the ultimate sink.

Geoaccumulation index

The geoaccumulation index proposed by Muller (1979) has been utilized to evaluate the pollution by heavy metals in sediments (Wakida et al., 2008).

The index proposed by Muller (1979) is:

$$I_{GEO} = Log_2[CM/(1:5*CB)]$$

Where CM is the concentration in the fraction analyzed of the sample (<63 µm) and C.B. is the concentration in the same fraction of the sediments in the background site and the factor 1.5 is used to take into account the possible litological variability).

The Muller index has seven classes depending of its value: <0 or 0 no pollution, values from 0 - 1 not polluted to moderately polluted (class 1), 1 - 2, moderately polluted (class 2); 2 - 3, moderately polluted to polluted (class 3); 3 - 4, polluted to strongly polluted (class 4); 4 - 5, strongly polluted (class 5); 5 to 6 strongly polluted to very polluted (class 6); and >6 very polluted (class 7).

Background concentrations for the heavy metals studied in this area are Fe = 40; Pb = 20; Ni = 38; and Cr = 30 (Puyate et al., 2007).

All the heavy metals had geoaccumulation indices below zero which indicates no pollution except Fe which had geoaccumulation index in the range 3.2 - 8.0. This indicates polluted to very pollute. The highest was in SS6 during the rainy season. The metal construction across the creek during this season is a suspect contributor of Fe to the creek at this point (Plate 1).

Comparisons of the heavy metals concentrations and DPR intervention values (Table 3) showed that the heavy metals concentrations where far below the intervention limits except for Fe that the intervention value was not available. This indicates that there is virtually no imminent danger, however bioaccumulation in the aquatic organisms could be a concern, since the Kolo Creek

Table 4. Muller Geoaccumulation index for the different sampling stations.

Heavy metal	Fe				Pb				Cr				Ni			
Background value	**40**				**20**				**30**				**38**			
Season	**D**	**LD**	**R**	**LR**	**D**	**LD**	**R**	**LR**	**D**	**LD**	**R**	**LR**	**D**	**LD**	**R**	**LR**
SS1	4.8	3.2	7.2	6.4	-3.6	-3.1	-4.3	-4.2	-2.0	-2.3	-1.7	-1.1	-1.9	-1.5	-3.0	-2.4
SS2	5.2	3.9	6.2	6.4	-5.2	-4.0	-5.5	NA	-1.8	-2.0	-2.8	-0.9	-1.8	-1.5	-4.0	-2.5
SS3	5.7	5.4	7.0	6.8	-4.6	-4.1	-4.5	-4.9	-1.8	-2.1	-2.7	-1.0	-2.2	-1.8	-4.0	-2.7
SS4	6.0	5.6	7.3	6.6	-3.6	-3.0	-4.1	-4.4	-1.8	-1.7	-1.5	-0.8	-3.8	-3.7	-3.0	-2.5
SS5	6.3	4.1	7.3	6.9	-3.9	-3.6	-4.4	-4.4	-1.8	-2.0	-1.9	-1.2	-2.8	-2.5	-3.1	-2.5
SS6	6.1	5.5	8.0	6.6	-4.9	-4.1	-3.6	-4.1	-1.9	-2.2	-1.3	-1.1	-2.3	-2.0	-2.8	-2.6
SS7	6.1	3.9	6.8	7.0	-5.1	-5.0	-3.9	NA	-2.0	-2.1	-2.2	-1.0	-2.6	-2.2	-3.7	-2.5
SS8	6.3	5.5	7.3	7.0	-3.8	-3.3	-4.4	-5.0	-2.1	-2.2	-2.2	-1.1	-2.7	-2.5	-3.3	-2.5
Tombia	6.4	6.0	6.2	6.6	-4.2	-4.1	-4.5	NA	-1.6	-1.7	-3.0	-1.0	-1.9	-1.5	-4.2	-2.8

Table 5. Correlation of Heavy Metals in Kolo Creek.

	Fe	Cr	Pb	Ni
Fe	1			
Cr	0.273364	1		
Pb	0.384043	0.491724	1	
Ni	-0.52628	-0.38722	-0.3265	1

serves as a means of livelihood in terms of fishing activities (Agbozu et al., 2007).

Correlations

The annual correlation for the heavy metals studied is as shown in Table 5. The highest positive correlation was between Pb and Cr while the highest negative correlation was between Fe and Ni (Table 5). These correlations determine the relationships between the sources of these heavy metals. Positive correlations points to similar sources of heavy metal pollution. Pb is used as an anti-knocking agent in automobile engines while Cr is used as an anti-corrosion agent in piping systems. It is likely that the correlation between Pb and Cr may be directed to a common source, the Kolo creek flow station which has a combination of automobile engines and complex piping systems.

Analysis of variance

Statistically, there is no significant difference among the sampling stations (SS), However, One-Way Analysis of Variance (ANOVA) at 95% confidence level, using Microsoft Excel showed significant difference between the four seasons.

Calculating the least significant difference separated the seasons into groups as shown in the dendrograms (Figure 3).

$$s\sqrt{\left(\frac{2}{n}\right)}\ x\ t_{h(n-1)}$$ (Miller and Miller, 2000).

s = within sample estimate of σ; n = number of replications; h = number of cases.

The dendrograms in Figure 3 illustrates the classification, using cluster analysis with squared Euclidean distance as distance measure. The classifications show two major groups. Dry season and late dry season in one group and rainy season and late rainy season in the other group. This further confirms the two characteristics seasons in this geographical location, the dry and rainy seasons (Iwegbue et al., 2006; Essien et al., 2009).

Conclusion

Levels of Pb, Cr and Ni concentrations in the Kolo creek sediment are low in the period of this study and may not be lethal to the environment. Also, cluster analysis of the seasons studied further grouped the seasons into two major seasons, the Dry and Rainy seasons. However, Fe concentrations in the Kolo creek are exceptionally high and the creek has been classified as very polluted in term

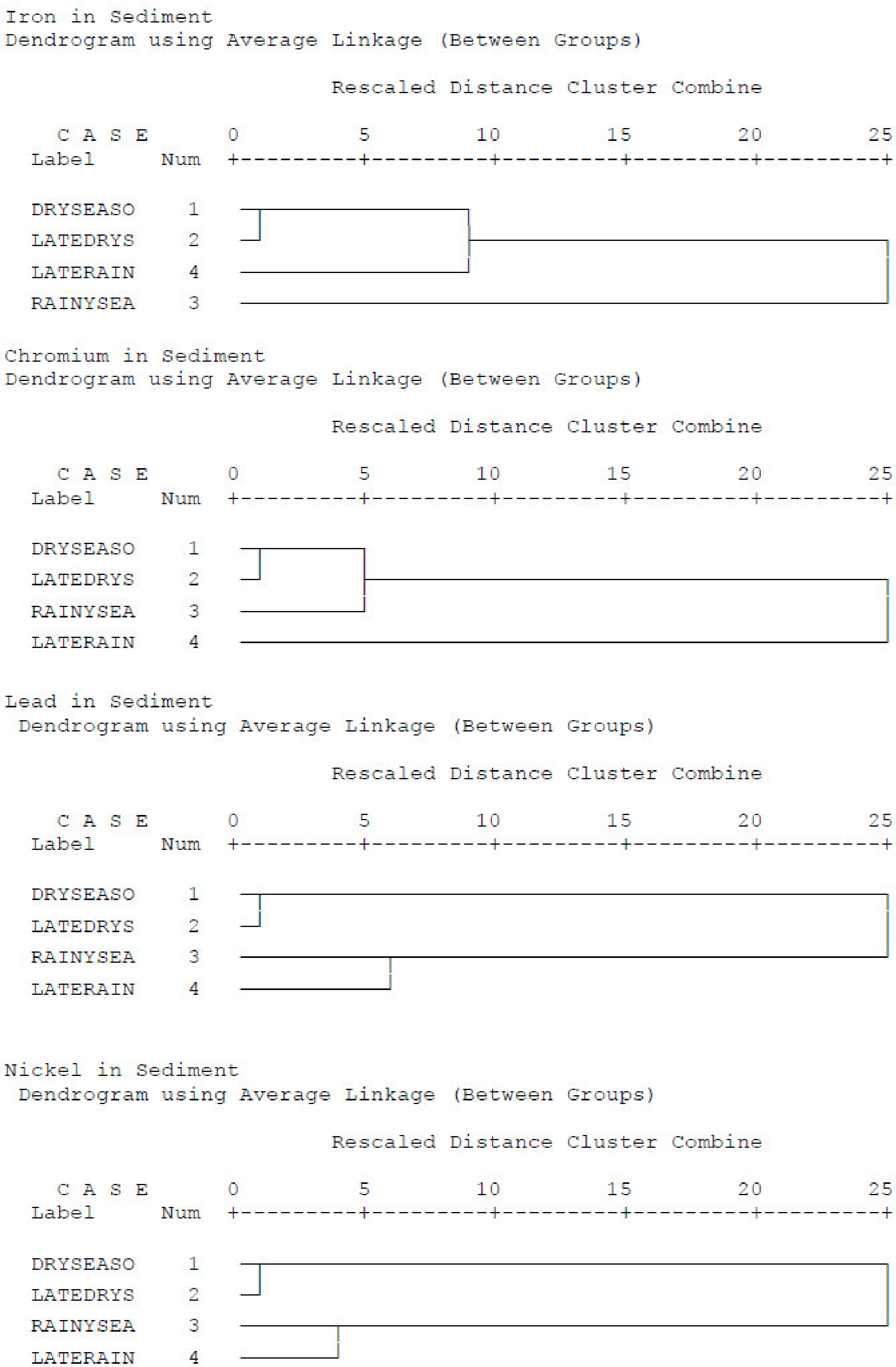

Figure 3. Dendrograms of seasonal clusters in Kolo creek.

of Fe. This is an issue of great concern which should be addressed diagnostically.

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