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Heavy Metals Pollution Assessment of Asa River Sediments in Ilorin, Kwara State, Nigeria

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Abstract: Asa River sediment samples (26) were collected and analyse to determine seasonal concentrations, spatial and assessment contamination of heavy metals which includes Pb, Cu, Co, Cr, Ni, Zn, Al, Fe and Mn. The purpose of this research is to assess concentrations of heavy metals and degree of contamination in the Asa River sediments. The mean concentrations are as follows 0.75 mg/kg for Pb, 47.70 mg/kg for Cu, 34.88 mg/kg for Co, 54.35 mg/kg for Cr, 25.06 mg/kg for Ni, 34.70 mg/kg for Zn, 30.53 mg/kg for Al, 16.74 mg/kg for Fe and 11.84 mg/kg for Mn. To assess metal contamination in sediments, sediment quality guidelines were applied. The mean concentration of Cu and Co exceeded the USEPA guidelines. The metal contamination in the sediments was also evaluated by applying Enrichment Factor (EF), Contamination Factor (CF), Geoaccumulation Index (I_{geo}) and Pollution Load Index (PLI). Based on EF, the Asa River sediments have less deficiency for Pb, Cr, Ni, Zn, Al, Fe and Mn while Cu and Co have moderate enrichment. According to CF: Cu, Co, Cr, Zn and Al have moderate contamination while Pb, Ni, Fe and Mn have low contamination. According to I_{geo}, the Asa River sediments are unpolluted to moderately polluted. Based on PLI, most sampling sites suggest no overall pollution of site quality.

Keywords: Asa River Sediments, Contamination Factor, Heavy Metals, Pollution

1. Introduction

Bottom sediments have been described as a long term sink for contaminants and it has also been taken to be their shelter for various life forms including both micro and macro benthic organisms. Contaminants in the sediment pose threats to human health, aquatic life and the environment. The study of toxic effects and heavy metals in Asa River is more important in comparison with other pollutants due to their non-biodegradability nature, accumulative properties and long biological half-lives. With the increase use of wide varieties of metals and petrochemicals in industries coupled with African lifestyle of dumping wastes around indiscriminately, there is now a greater awareness of toxic metal pollution of the environment. Many of these metals tend to remain in the ecosystem and eventually move from one component of the food chain to another [1]. The rapid industrialization is also having a direct and indirect adverse effect on our environment. Industrial development manifested due to setting up of new industries or expansion of the pre-existing ones resulting into the generation of industrial effluents, spatially small scale cottage industries which discharge untreated effluents that causes sediment pollution. Industrial growth and its associated environmental

problems such as water and sediment contamination is fast increasing [2, 3].

Heavy metal contamination in sediments have been reviewed and surveyed by most researchers till date [4-7]. Heavy metals accumulation has occurred in different regions. In Asa River sediments, study distributions undertaken have been found to be limited [8-10].

The aim of this work is to assess concentrations of heavy metals and degree of contamination in the Asa River sediments.

2. Materials and Methods

2.1. Study Area

Asa River Ilorin, Kwara State is of particular influence on the direction of growth of the city [11]. The River catchments basin is about 1040 km in area and lies between latitude (8°24' and 8°36'N) and between longitude (4°10' and 4°36'E), figure 1. Tropical wet and dry climate each lasting for about six months with mean annual rainfall of 1200 mm. Temperature varies between 25°C to 30°C in March, which makes the hottest month [12].

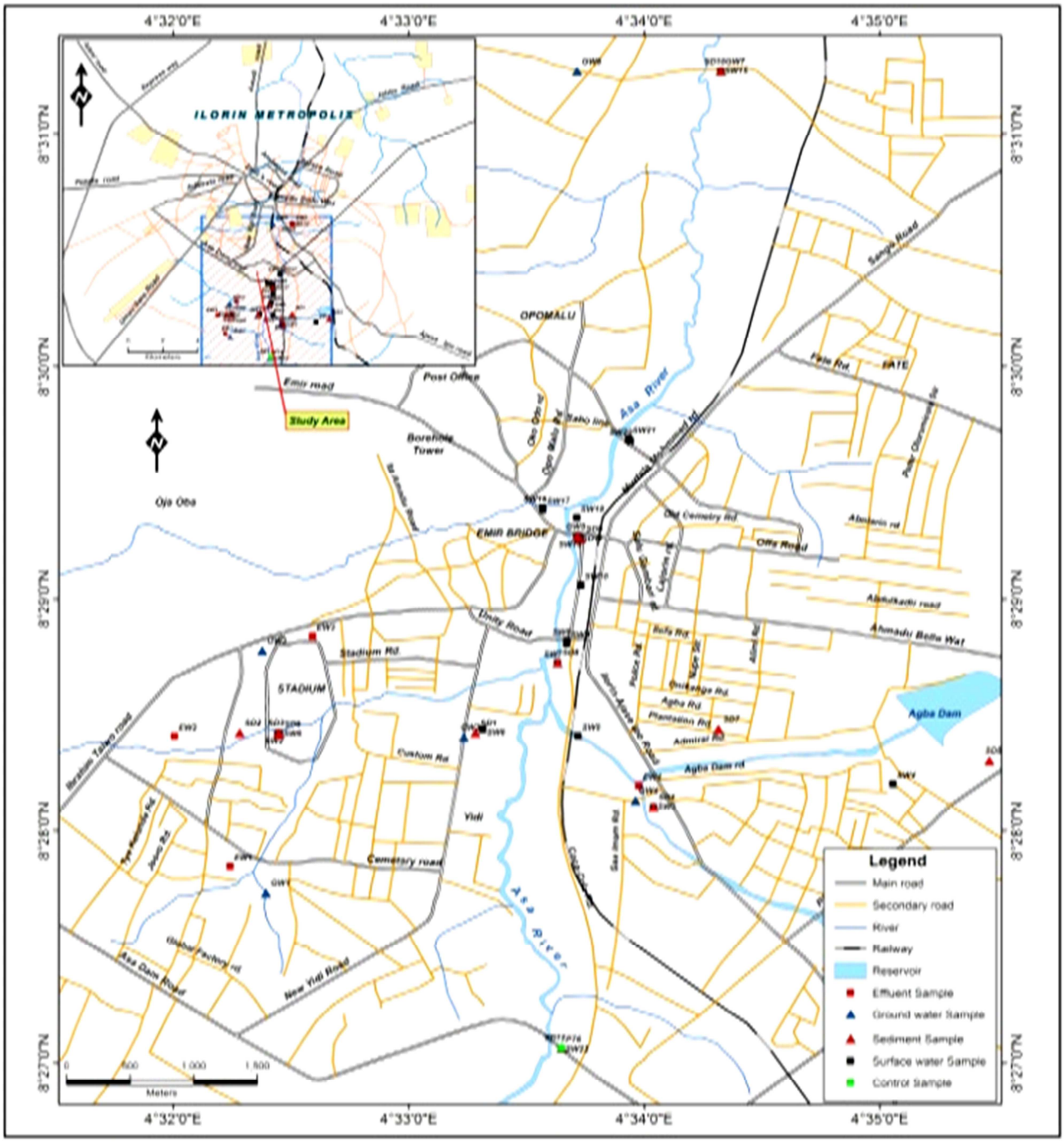

Figure 1. *Map Locationof study area.*

2.2. Sampling Collection and Analysis

Asa River sediments (26) sampling sites were chosen for collection (Figure 2, table 1). Global Positioning System (Garmin) locator was used. Sediment sampling was done with Auger tube. Sediment samples were collected seasonally for two years (February, 2013 – April, 2015). Samples were placed in polyethylene bags and transported to the laboratory under frozen condition (at 4°C). The samples were dried in the laboratory at 104°C for 48 hours, ground to a fine powder and sieved through 106 micrometer stainless steel mesh wire. The samples were then stored in a polyethylene container ready for digestion and analysis [13-14]. 0.5-1.0 g of sediment sample was put into a clean 100 ml Teflon beaker and wet with 5 ml distilled water. Conc. $HClO_4$ acid of 2 ml was added with 12 ml conc. HF acid and heated to near dryness, 8 ml conc. HF acid was added and heated to near dryness. The remaining residue was dissolved in 8 ml conc. HCl acid and 20 ml distilled water was added, and also make up 100 ml volume and stored in polyethylene bottles. Heavy metals were determined with Atomic Absorption Spectrometry (AAS) at different wavelength in the sediment samples.

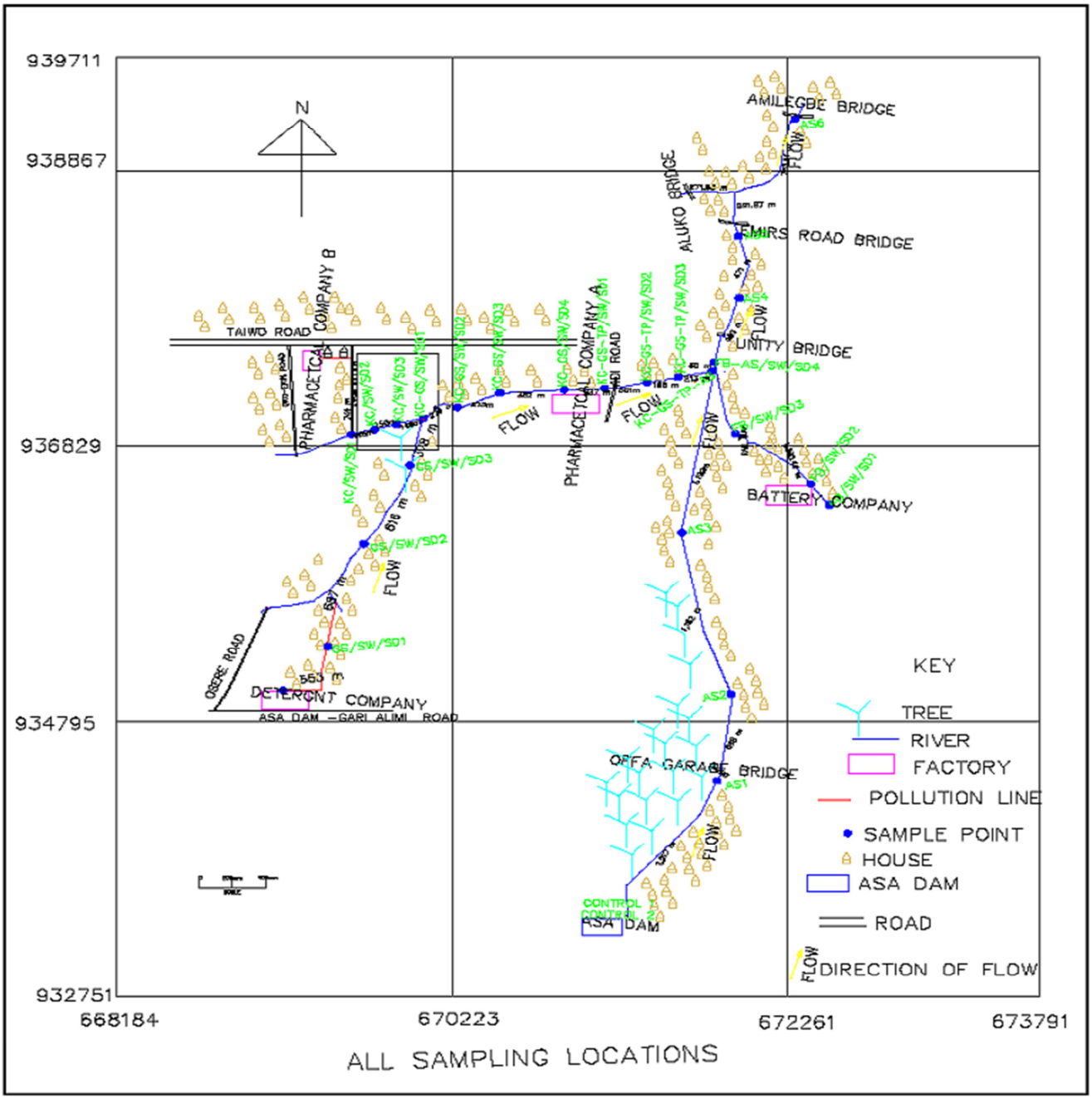

Figure 2. *Sampling sites map.*

Table 1. *Sampling locations details of Asa River.*

S/No.	Site Code	Name of site	Latitude - N	Longitude – E
1	GS/SD1	Detergent company pointone	8 °27' 27.84"N	4°32' 20.57" E
2	GS/SD2	Detergent company point two	8°27'58.83" N	4 °32'28.96"E
3	GS/SD3	Detergent company point three	8°28'17.54" N	4°32'38.32" E
4	KC/SD1	Pharmaceutical company B point one	8°28'25.14"N	4°32'26.62" E
5	KC/SD2	Pharmaceutical company B point two	8°28'26.42"N	4°32'31.33"E
6	KC/SD3	Pharmaceutical company B point three	8°28'27.51" N	4°32'35.68" E
7	KC-GS/SD1	Pharmaceutical company B- Detergent company point one	8°28'29.15"N	4°32'40.95" E
8	KC-GS/SD2	Pharmaceutical company B- Detergent company point two	8°28'31.76"N	4°32'47.86"E
9	KC-GS/SD3	Pharmaceutical company B- Detergent company point three	8°28'35.12"N	4°32'56.31"E
10	KC-GS/SD4	Pharmaceutical company B- Detergent company point four	8°28'35.59" N	4°33'9.61"E
11	KC-GS-TP/SD1	Pharmaceutical company B- Detergent company point-Pharmaceutical company A meeting point one	8°28'36.21" N	4°33'16.91" E
12	KC-GS-TP/SD2	Pharmaceutical company B- Detergent company point-Pharmaceutical company A meeting point two	8°28'37.41"N	4°33'25.55"E
13	KC-GS-TP/SD3	Pharmaceutical company B- Detergent company point-Pharmaceutical company A meeting point three	8°28'38.72"N	4°33'31.67"E
14	KC-GS-TP-AS/SD	Pharmaceutical company B- Detergent company point-Pharmaceutical company A as it enters Asa River	8°28'39.93"N	4°33'38.44"E
15	FB/SD1	Battery company point one	8°28'7.97"N	4°34'1.36"E
16	FB/SD2	Battery company point two	8°28'12.73"N	4°33'57.46"E
17	FB/SD3	Battery company three	8°28'25.23"N	4°33'42.89"E
18	FB-AS/SD	Battery company as it enters Asa River	8°28'41.98"N	4°33'38.81"E
19	AS1/SD1	Asa River after the dam	8°27'1.29"N	4°33'39.25"E
20	AS2/SD2	Asa River Dangote Area	8°27'22.63"N	4°33'41.86"E
21	AS3/SD3	Asa River 7UP Bridge	8°28'1.28"N	4°33'32.30"E
22	AS4/SD4	Asa River Unity Bridge	8°28'57.88"N	4°33'43.58"E
23	AS5/SD5	Asa River Emir Bridge	8°29'12.56"N	4°33'43.80"E
24	AS6/SD6	Asa River Amilegbe Bridge	8°29'40.90"N	4°33'55.07"E
25	CTRL1/SD	Asa Dam water corporation	8°26'30.76"N	4°33'21.02"E
26	CTRL2/SD	Egbejila before Asa Dam site	8°26'16.08"N	4°33'20.05"E

2.3. Assessment of Metal Contamination

The degree of contamination in sediments was evaluated using four parameters: Enrichment Factor (EF), Contamination Factor (CF), Geo-accumulation Index (I_{geo}).

Enrichment Factor (EF): Metals Enrichment Factor (EF) presented in table 2 is a useful indicator reflecting the status and degree of environmental contamination [15]. The EF calculations, compare each value with a given background level, either from the local site, using older deposits formed under level similar conditions, but without anthropogenic impact, or from a regional or global average composition [16].

The EF was calculated using the method proposed which is

$$EF = (Me/Fe)sample/(Me/Fe)background$$

Where: $(Me/Fe)_{sample}$ is the metal to Fe ratioin the sampleof interest.

$(Me/Fe)_{background}$ is the natural value of metal to Fe ratio.

Fe used as the element ofnormalization (1.5%).

Mean Shale concentration (mg/kg): Pb = 20, Cu = 11.2, Co = 29, Cr = 90, Ni = 68, Zn = 95, Al = 15.53, Fe = 46700 and Mn = 850.

Contamination Factor (CF): The level of contamination of sediment in table 3 by metal is expressed in terms of a contamination factor (CF) calculated as:

$$CF = CmSample/CmBackground$$

Where: Cm_{Sample} = Sample concentration ofa given metal in river sediment.

$Cm_{Background}$ = Background value concentration of the metal which is equal to the Worldsurface rock average.

World surface rock average (mg/kg): Pb = 16, Cu = 32, Co = 13, Cr = 71, Ni = 49, Zn = 20, Al = 15.6, Fe = 35900 and Mn = 750.

Geo-accumulation index (I_{geo}): The geo-accumulation index was used to determine the pollution level of sediments and presented in table 4.

$$Igeo = Log2\,[CnSample/1.5 * Bn]$$

Where: C_n= Concentration of theheavy metal in the sample.

B_n= Geochemical background value (world surface rock average givenby Muller quoted by [17].

Factor 1.5 = minimize the effect of possible variation in the background values which may be attributed to lithogenic variations in the sample.

World surface rock average (mg/kg): Pb = 16, Cu = 32, Co = 13, Cr = 71, Ni = 49, Zn = 20, Al = 15.6, Fe = 35900 and Mn = 750.

The overall total geo-accumulation index (I_{tot}) is defined as the sum of I_{geo} for all trace elements obtain from the site [18].

Pollution Load Index (PLI): Pollution Load Index (PLI) for a particular site, has been evaluated following the method proposed by [19-20]. This parameter is expressed as

$$PLI = (CF1 * CF2 * CF3 * \ldots..CFn)1/n$$

Where n is the number of metals.

Table 2. *Enrichment Factor (EF) calculations [7, 6].*

Enrichment Factor	Enrichment Factor (EF) classifications
EF<2	Deficiency to minimal enrichment
2≤EF<5	Moderate enrichment
5≤EF<20	Significant enrichment
20≤EF<40	Very high enrichment
EF≤40	Extremely high enrichment

Table 3. *Contamination Factor (CF) and their levels [17].*

Contamination Factor	Contamination level
CF<1	Low contamination
1≤CF<3	Moderate contamination
3≤CF<6	Considerable contamination
CF>6	Very high contamination

Table 4. *Muller's classification for geo-accumulation (I_{geo}) [17].*

I_{geo} value	Class	Sediment Quality
≤0	0	Unpolluted
0-1	1	from unpolluted to moderately polluted
1-2	2	moderately polluted
2-3	3	from moderately polluted to strongly polluted
3-4	4	strongly polluted
4-5	5	from strongly polluted to extremely polluted
>6	6	extremely polluted

3. Results and Discussion

The descriptive statistics of the data set pertaining to Asa River sediments are presented in table 5. Intermetallic correlation, seasonal and spatial variations were delineated in table 6 and shown in figure 3. The EF values of heavy metals in the Asa River sediments are presented in table 7 and displayed in figure 4. The calculated CF for various heavy metals in sediments of Asa River are presented in table 8 and shown in figure 5. The calculated I_{geo} values based on the world surface average are presented in table 9.

The PLI provides simple but comparative means for assessing a site quality, were a value of PLI<1 denotes perfection, PLI = 1 presents that only baseline levels of pollutants are presented and PLI>1 would indicate deterioration of site quality [19-20]. The PLI values for heavy metals in the Asa River Sediments are listed in table 10 and shown in figure 6. Pb concentration Pb varied from 0.74 to 0.76 mg/kg with a mean value of 0.75 mg/kg. It was less than the world surface rock average and the shale concentration as background level. In comparison with sediment quality guidelines, the mean did not exceed the limits, and this result reveals that the Asa River sediments are not polluted by Pb. Pb expressed a strong positive correlation with Fe at 0.05 level. The strong correlation indicated that the two elements have common sources. Pb have EF values in Asa River sediments ranged from 0.02 to 0.12. The EF values for Pb were found to be less than 20 in all sampling sites (table 7), suggesting that these sites are deficient to minimal enrichment for Pb. Lead CF values varied from 0.00 to 0.15 with a mean of 0.03, table 8. All the sampling sites have CF < 1, which denotes low contamination (table 3).

Lead (I_{geo}) values were less than 0 (<0) in all sampling sites, table 9 reveal negative values which indicated that Asa River sediments in this study area are unpolluted by Pb. This result was in good agreement with the results of [17, 24]. Copper concentrationvaried from 47.68 to 47.71 mg/kg, and mean value was 47.70 mg/kg. The mean concentration obtained in this study was higher than the world surface rock average concentration as a geochemical background level for seventeen sites and lower for nine sites.

Table 5. *Concentration of heavy metals in the sediment samples of Asa River during the study period.*

Metal	Minimum	Maximum	Mean	Standard deviation	World Surface Rock Average	Mean Shale Concentration	WHO	USEPA	CCME
Pb (mg/kg)	0.74	0.76	0.75	0.49	16	20	-	40	35
Cu (mg/kg)	47.68	47.71	47.70	11.17	32	11.2	25	16	35.7
Co (mg/kg)	33.20	36.55	34.88	21.85	13	29	-	-	-
Cr (mg/kg)	53.05	55.64	54.35	10.61	71	90	25	25	37.3
Ni (mg/kg)	24.15	25.97	25.06	1.92	49	68	20	16	-
Zn (mg/kg)	32.29	37.11	34.70	1.57	20	95	123	110	123
Al (mg/kg)	28.15	32.90	30.53	0.70	15.6	15.53	-	-	-
Fe (mg/kg)	15.33	18.14	16.74	0.74	35900	46700	-	30	-
Mn (mg/kg)	10.32	13.36	11.84	0.81	750	850	-	30	-

Ref [21-23, 4, 13].

Table 6. *Pearson's correlation coefficient of heavy metals in Asa River sediments.*

Metals	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn
Pb	1.00								
Cu	0.99	1.00							
Co	1.00	0.99	1.00						
Cr	0.95	1.00	0.99	1.00					
Ni	1.00	0.95	-1.00	0.99	1.00				
Zn	0.86	-1.00	0.95	-1.00	0.99	1.00			
Al	1.00	0.86	-1.00	0.95	-1.00	0.99	1.00		
Fe	1.00	1.00	0.86	-1.00	0.95	-1.00	0.99	1.00	
Mn	1.00	1.00	1.00	0.86	-1.00	0.95	-1.00	0.99	1.00

Table 7. *Enrichment Factor (EF) values of heavy metals in Asa River Sediments.*

Sampling sites	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn
GS/SD1	0.02	5.27	1.42	0.85	0.32	0.36	1.29	0.00	0.01
GS/SD2	0.01	5.21	1.24	0.77	0.39	0.31	1.49	0.00	0.01
GS/SD3	0.02	4.67	1.27	0.80	0.43	0.37	1.34	0.00	0.01
KC/SD1	0.03	5.42	1.34	0.55	0.22	0.35	2.07	0.00	0.01
KC/SD2	0.03	4.95	1.26	0.74	0.40	0.37	1.49	0.00	0.01
KC/SD3	0.02	4.33	1.46	0.64	0.44	0.34	1.51	0.00	0.01
KC-GS/SD1	0.01	3.79	1.82	0.39	0.48	0.30	1.87	0.00	0.01
KC-GS/SD2	0.00	2.19	1.58	0.70	0.41	0.34	1.83	0.00	0.01
KC-GS/SD3	0.01	2.76	1.43	0072	0.44	0.32	2.12	0.00	0.00
KC-GS/SD4	0.00	2.42	1.67	0.61	0.47	0.37	2.27	0.00	0.02
KC-GS-TP/SD1	0.02	4.64	1.36	0.70	0.29	0.27	2.33	0.00	0.02
KC-GS-TP/SD2	0.02	2.71	0.88	0.53	0.42	0.32	2.56	0.00	0.01
KC-GS-TP/SD3	0.02	2.54	1.68	0.59	0.38	0.33	2.19	0.00	0.01
KC-GS-TP-AS/SD	0.03	3.44	0.99	0.56	0.39	0.35	2.39	0.00	0.01
FB/SD1	0.12	5.98	1.32	0.58	0.39	0.35	1.67	0.00	0.02
FB/SD2	0.11	6.34	1.47	0.61	0.51	0.39	1.79	0.00	0.01
FB/SD3	0.02	3.47	1.11	0.63	0.30	0.37	1.84	0.00	0.02
FB-AS/SD	0.01	2.63	1.10	0.56	0.35	0.43	1.94	0.00	0.02
AS1/SD1	0.02	2.35	1.19	0.53	0.32	0.35	1.69	0.00	0.01
AS2/SD2	0.02	3.76	1.71	0.71	0.30	0.32	1.62	0.00	0.01
AS3/SD3	0.02	3.96	1.19	0.68	0.23	0.35	1.90	0.00	0.01
AS4/SD4	0.01	4.36	0.93	0.61	0.42	0.47	2.30	0.00	0.02
AS5/SD5	0.01	3.42	1.00	0.61	0.37	0.54	2.95	0.00	0.02
AS6/SD6	0.02	2.63	1.12	0.50	0.44	0.58	3.20	0.00	0.03
CTRL1/SD	0.03	3.83	0.96	0.58	0.25	0.28	1.32	0.00	0.01
CTRL2/SD	0.01	2.73	1.06	0.39	0.22	0.31	1.42	0.00	0.01

In comparison with sediment quality guideline (SQG), the mean value exceed the limit for WHO and USEPA guidelines and not for CCME, and this results shows that Asa River sediment is slightly polluted by Cu. EF values for Cu vary from 2.19 at KC-GS/SD2 to 6.34 at FB/SD2. EF values for all sampling sites is greater than 2 but less than 20, suggesting significant enrichment for Cu [9]. Copper CF values ranged from 0.77 at KC-GS/SD2 to 2.22 at FB/SD2 with a mean value of 1.34. The CF values for Cu were $1 \leq CF < 3$ at most sampling sites. According to table 3, all sampling sites face moderate contamination. Copper I_{geo} values were ranged from -0.97 to 0.57. According to Muller's classification, Asa River sediments at most sampling sites were unpolluted, except for sites FB/SD2 and FB/SD1 which had ($0 < I_{geo} < 2$) that is from unpolluted to moderately polluted. This result was in good agreement with results of [9]. Co concentration varied from 33.20 to 36.55 mg/kg, and mean value was 34.88 mg/kg.

Table 8. *Contamination Factor (CF) values of heavy metals in Asa River Sediments.*

Sampling sites	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn
GS/SD1	0.03	1.84	3.17	1.07	0.45	1.73	1.28	0.00	0.01
GS/SD2	0.01	1.82	2.77	0.97	0.54	1.49	1.48	0.00	0.01
GS/SD3	0.02	1.63	2.83	1.01	0.60	1.75	1.34	0.00	0.01
KC/SD1	0.03	1.90	2.98	0.69	0.31	1.65	2.06	0.00	0.01
KC/SD2	0.03	1.73	2.81	0.93	0.55	1.76	1.48	0.00	0.01
KC/SD3	0.03	1.52	3.25	0.81	0.61	1.62	1.50	0.00	0.01
KC-GS/SD1	0.02	1.33	4.06	0.50	0.66	1.41	1.86	0.00	0.02
KC-GS/SD2	0.00	0.77	3.52	0.88	0.57	1.59	1.82	0.00	0.01
KC-GS/SD3	0.01	0.97	3.20	0.92	0.60	1.51	2.12	0.00	0.02
KC-GS/SD4	0.00	0.85	3.73	0.77	0.65	1.76	2.26	0.00	0.02
KC-GS-TP/SD1	0.02	1.63	3.04	0.89	0.41	1.28	2.32	0.00	0.01
KC-GS-TP/SD2	0.02	0.95	1.96	0.67	0.58	1.51	2.55	0.00	0.01
KC-GS-TP/SD3	0.02	0.89	3.75	0.74	0.53	1.56	2.18	0.00	0.02
KC-GS-TP-AS/SD	0.04	1.20	2.21	0.71	0.53	1.66	2.38	0.00	0.02
FB/SD1	0.15	2.09	2.94	0.74	0.55	1.65	1.67	0.00	0.01
FB/SD2	0.14	2.22	3.27	0.77	0.71	1.88	1.78	0.00	0.01
FB/SD3	0.03	1.22	2.48	0.79	0.42	1.75	1.83	0.00	0.02
FB-AS/SD	0.01	0.92	2.45	0.71	0.48	2.05	1.93	0.00	0.02
AS1/SD1	0.02	0.82	2.65	0.67	0.44	1.66	1.68	0.00	0.01
AS2/SD2	0.02	1.32	3.81	0.91	0.42	1.50	1.61	0.00	0.02
AS3/SD3	0.02	1.38	2.65	0.87	0.31	1.65	1.89	0.00	0.02
AS4/SD4	0.02	1.53	2.08	0.77	0.59	2.23	2.29	0.00	0.02
AS5/SD5	0.02	1.20	2.24	0.77	0.52	2.55	2.93	0.00	0.03
AS6/SD6	0.02	0.96	2.50	0.63	0.61	2.73	3.19	0.00	0.03

Sampling sites	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn
CTRL1/SD	0.04	1.34	2.14	0.74	0.34	1.33	1.31	0.00	0.01
CTRL2/SD	0.01	0.96	3.51	0.50	0.31	1.46	1.41	0.00	0.01
Mean	0.03	1.34	2.92	0.79	0.51	1.72	1.93	0.00	0.02

Cobalt EF values ranged from 0.88 at KC-GS-TP/SD2 to 1.82 at KC-GS/SD1, table 7. Most sampling sites have EF for Co less than 2 which reveal that Asa River sediment is classified as deficient to minimal enrichment. Cobalt CF values ranged from 1.96 at KC-GS-TP/SD2 to 4.06 at KC-GS/SD1, with a mean value of 2.92. At all sampling sites, the CF values for Co were more 1 and less than 3. According to [17] all sampling sites were moderately contaminated by Co. Cobalt I_{geo} values ranged from 0.46 to 1.44. All sampling sites has I_{geo} for Co more than 0 but less than 2 ($0<I_{geo}<2$). I_{geo} values for Co indicate that Asa River sediments are unpolluted to moderately polluted for all sampling sites [9]. Chromium concentration varied from 53.05 to 55.64 mg/kg. GS/SD1, which is detergent company point one had the highest mean concentration of Cr of all the sampling sites. In comparison with sediment quality guidelines (SOG), Chromium mean values exceeded the limits for WHO, USEPA and CCME guidelines.

Table 9. *Geoaccumulation Indices (I_{geo}) values of heavy metals in Asa River Sediments.*

Sampling sites	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn	Itot
GS/SD1	-5.64	0.30	1.08	-0.47	-1.74	0.20	-0.23	-11.25	-7.38	-25.73
GS/SD2	-6.64	0.28	0.89	-0.62	-1.47	-0.01	-0.01	-11.57	-6.97	-26.12
GS/SD3	-5.97	0.12	0.91	-0.58	-1.32	0.23	-0.17	-11.02	-6.97	-24.77
KC/SD1	-5.64	0.33	0.99	-1.12	-2.25	0.14	0.45	-11.61	-6.97	-26.32
KC/SD2	-5.44	0.20	0.90	-0.67	-1.43	0.24	-0.01	-11.44	-6.64	-26.13
KC/SD3	-5.80	0.01	1.12	-0.89	-1.29	0.11	0.00	-11.57	-6.84	-26.99
KC-GS/SD1	-3.64	-0.18	1.44	-1.60	-1.18	-0.09	0.31	-11.32	-6.64	-28.78
KC-GS/SD2	-8.97	-0.97	1.23	-0.76	-1.40	0.08	0.28	-11.75	-6.67	-32.71
KC-GS/SD3	-7.97	-0.64	1.09	-0.71	-1.32	0.01	0.50	-11.05	-6.27	-26.36
KC-GS/SD4	-8.38	-0.84	1.32	-0.94	-1.22	0.24	0.59	-11.29	-6.38	-26.90
KC-GS-TP/SD1	-6.06	0.11	1.02	-0.76	-1.89	-0.23	0.62	-10.85	-6.95	-24.99
KC-GS-TP/SD2	-6.06	-0.67	0.39	-1.15	-1.36	0.01	0.77	-11.15	-6.98	-26.20
KC-GS-TP/SD3	-6.27	-0.76	1.32	-1.00	-1.47	0.06	0.54	-11.05	-6.69	-25.32
KC-GS-TP-AS/SD	-5.32	-0.32	0.56	-1.09	-1.47	0.15	0.67	-10.59	-6.24	-23.65
FB/SD1	-3.29	0.49	0.97	-1.03	-1.47	0.14	0.15	-11.05	-6.73	-21.82
FB/SD2	-3.44	0.57	1.12	-0.97	-1.09	0.32	0.25	-10.88	-6.80	-20.92
FB/SD3	-5.80	-0.30	0.73	-0.92	-1.84	0.23	0.29	-11.12	-6.24	-24.97
FB-AS/SD	-7.38	-0.71	0.70	-1.09	-1.64	0.45	0.37	-10.94	-6.16	-26.40
AS1/SD1	-6.06	-0.86	0.82	-1.15	-1.79	0.15	0.16	-10.88	-6.86	-26.47
AS2/SD2	-6.06	-0.18	1.34	-0.74	-1.84	0.00	0.10	-10.94	-6.51	-24.83
AS3/SD3	-6.06	-0.12	0.82	-0.79	-2.25	0.14	0.33	-10.75	-6.51	-25.19
AS4/SD4	-6.51	0.03	0.46	-0.97	-1.36	0.58	0.61	-10.80	-6.38	-24.34
AS5/SD5	-6.38	-0.32	0.58	-0.97	-1.56	0.77	0.97	-10.63	-5.88	-23.42
AS6/SD6	-6.27	-0.71	0.74	-1.25	-1.29	0.86	1.09	-10.40	-5.64	-22.87
CTRL1/SD	-5.44	-0.16	0.52	-1.03	-2.12	-0.18	-0.18	-11.61	-7.16	-27.36
CTRL2/SD	-7.16	-0.64	1.23	-1.56	-2.25	-0.03	-0.09	-11.32	-6.97	-28.79

Table 10. *Asa River Sediments heavymetals Pollution Load Index (PLI) values.*

Sampling sites	PLI
GS/SD1	0.39
GS/SD2	0.22
GS/SD3	0.33
KC/SD1	0.32
KC/SD2	0.40
KC/SD3	0.38
KC-GS/SD1	0.39
KC-GS/SD2	1.79
KC-GS/SD3	0.30
KC-GS/SD4	3.20
KC-GS-TP/SD1	0.29
KC-GS-TP/SD2	0.21
KC-GS-TP/SD3	0.38
KC-GS-TP-AS/SD	0.51
FB/SD1	0.92
FB/SD2	1.23
FB/SD3	0.40
FB-AS/SD	2.31
AS1/SD1	0.17
AS2/SD2	0.39
AS3/SD3	0.32
AS4/SD4	0.49
AS5/SD5	0.63
AS6/SD6	0.62
CTRL1/SD	0.20
CTRL2/SD	0.12
Mean	0.65

Chromium EF values ranged from 0.39 at (KC-GS/SD1 and CONTROL 2/SD) to 0.85 at GS/SD1. All sampling sites have EF less than 2, table 7. Sampling sites are classified as deficient to minimal enrichment. Chromium CF values varied from 0.50 at (KC-GS/SD1 and CTRL 2/SD) to 1.07 at GS/SD1, with a mean value of 0.79, table 8. At all sampling sites, the CF value is greater than 1 but less than 3, suggesting that sediments were moderately contaminated. Chromium I_{geo} values were negative. It is classified as unpolluted by Cr [17]. Nickel concentration varied from 24.15 to 25.97 mg/kg. Battery company point 2 (FB/SD2) had the highest Ni mean concentration and pharmaceutical company B point 1 (KC/SD1) had the least of all the sediments. The mean value is less than world surface rock average and mean shale concentration as background level. According to WHO and USEPA guidelines, Ni concentrations mean exceeded the guidelines suggesting that Asa River sediments are polluted by Ni. Nickel enrichment factor (EF) valuesrange from 0.22 at control 2/SD and KC/SD1 to 0.51 at FB/SD2. All sampling sites have EF<2, these revealed deficiency to minimal enrichment. Nickel CF values ranged from 0.31 at control 2/SD, AS3/SD3 and KC/SD1 sites to 0.66 at KC-GS/SD1 with mean value of 0.51.

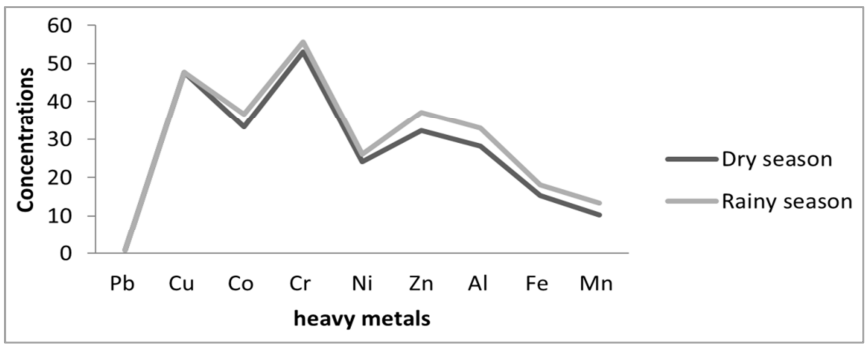

Figure 3. *Asa River sediments heavy metals parameters seasonal and spatial variations.*

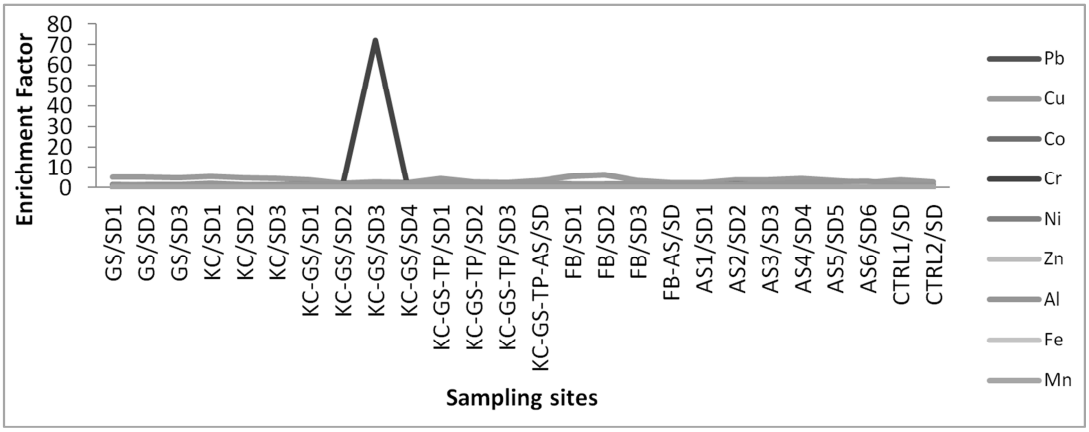

Figure 4. *Asa River Sediments heavy metals for Enrichment Factor (EF).*

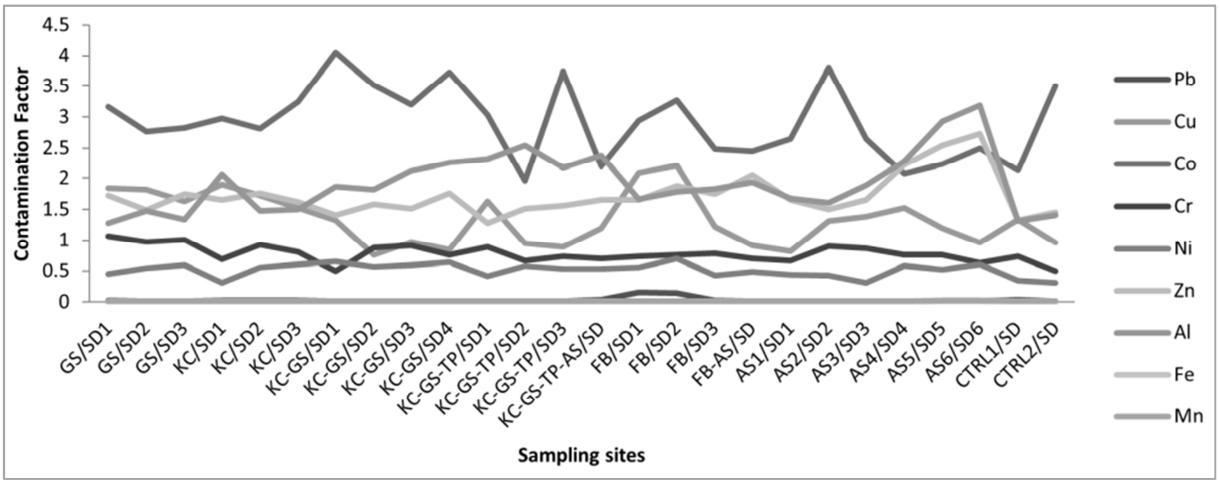

Figure 5. *Asa River sediments heavy metals for Contamination Factor (CF) values.*

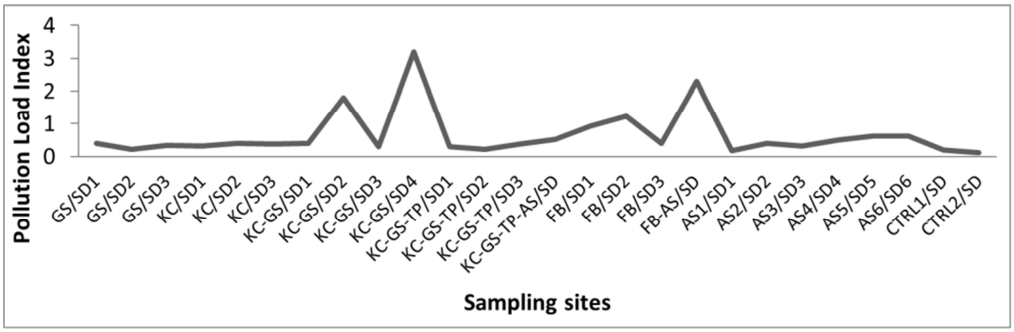

Figure 6. *Asa River sediments sampling sites for Pollution Load Index (PLI) values.*

All sampling sites have CF<1 which face low contamination by Ni. Nickel Igeo values were negative at all the sites. It implies that Asa River sediments were unpolluted at all the sites. This result was in good agreement with that of [9].

Zinc concentration varied from 32.29 to 37.11 mg/kg. Asa River point 6 at Amilegbe bridge (AS6/SD6) had the highest Zn mean concentration and meeting point 1 of pharmaceutical company B-detergent company – pharmaceutical company A (KC-GS-TP/SD1) had the least of all the sediments. Zn concentrations mean did not exceed the guidelines suggesting that Asa River sediments are not polluted by Zn. Zinc EF values range from 0.27 at KC-GS-TP/SD1 to 0.58 at AS6/SD6. All sampling sites have EF<2, these revealed deficiency to minimal enrichment. Zinc CF values ranged from 1.28 at KC-GS-TP/SD1 to 2.73 at AS6/SD6 with mean value of 1.72. All sampling sites have 1≤CF<3 which faces moderate contamination by Zn. Zinc Igeo values were positive except for sites GS/SD2, KC-GS/SD1, KC-GS-TP/SD1, CTRL 1/SD and CTRL 2/SD respectively. Most sampling sites are in class 1, which indicates, unpolluted to moderately polluted except for sites GS/SD2, KC-GS/SD1, KC-GS-TP/SD1, CTRL1/SD and CTRL 2/SD, which are in class 0, indicates unpolluted. This result was in agreement with that of [17].

Aluminum concentration varies from 28.15 to 32.90 mg/kg. Asa River Amilegbe bridge point 6 (AS6/SD6) had the highest Al mean concentration and detergent company point 1 (GS/SD1) had the least of all the sediments. Aluminum EF values range from 1.29 at GS/SD1 to 3.20 at AS6/SD6. Most sampling sites have EF<2, except sites KC-GS-TP/SD2, AS5/SD5 and AS6/SD6 which has 2≤EF<5 indicative of moderate enrichment. Aluminum CF values ranged from 1.28 at GS/SD1 to 3.19 at AS6/SD6 with mean value of 1.93. Most sampling sites face moderate contamination with 1≤CF<3 except site AS6/SD6 which face considerable contamination with 3≤CF<6. Aluminum Igeo values at most sampling sites were positive. According to Muller's classification, Asa River sediments observed unpolluted to moderately polluted.

Iron concentration varied from 15.33 to 18.14 mg/kg. Amilegbe bridge Asa River point 6 (AS6/SD6) had the highest Fe mean concentration and pharmaceutical company B – detergent company meeting point 2 (KC-GS/SD2) had the least of all the sediments. According to USEPA guidelines, Fe concentrations did not exceed the guidelines suggesting that Asa River sediments are not polluted by Fe. Iron EF values are 0.00 for all sampling sites which reveals EF<2 and it confirms deficiency to minimal enrichment. Iron CF valueis 0.00 for all sites. All sampling sites have CF<1 which face low contamination by Fe. Iron Igeo values at all sampling sites were negative. It was observed that all the sites wereunpolluted.

Manganese concentration varied from 10.32 to 13.36 mg/kg. Asa River Amilegbe bridge point 6 (AS6/SD6) had the highest Mn mean concentration and detergent company point 1 had the least of all the sediments. According to USEPA guidelines, Mn concentrations did not exceed the guidelines suggesting that Asa River sediments are not polluted by Mn. Manganese EF values range from 0.01 at most sampling sites to 0.03 at AS6/SD6. All sampling sites have EF<2, these indicated minimal enrichment. Maganese CF values ranged from 0.01 at most sampling sites to 0.03 at AS5/SD5 and AS6/SD6 respectively. All sampling sites have CF<1 which face low contamination by Mn. Maganese Igeo values at all sampling sites reveal 0 (≤0) that is negative. It was observed that all the sites are unpolluted. This result was in good agreement with that of [25].

Pollution Load Index was used to effectively compare whether the sampling sites suffer contamination or not. PLI values ranged from 0.12 to 3.20 with a mean of 0.65 as displayed in figure 6 and table 10. PLI were less than 1 at most sites except KC-GS/SD2, KC-GS/SD4, FB/SD2 and FB-AS/SD were greater than 1. According to [19], all sampling sites suggest perfection (or no overall pollution), where as KC-GS/SD2, KC-GS/SD4, FB/SD2 and FB-AS/SD shows sign of pollution or deterioration of site quality. Relatively higher PLI value at those sites KC-GS/SD2, KC-GS/SD4 (meeting points 2 and 4 of pharmaceutical company B and detergent company) with FB/SD2 and FB-AS/SD (battery company point 2 and point of entry of battery company into Asa River) suggest inputs from effluent discharge and anthropogenic sources.

4. Conclusions

Metal contamination status was investigated in Asa River sediments. Pb, Cu, Co, Cr, Ni, Zn, Al, Fe and Mn concentrations were estimated in twenty-six sampling sites. The mean concentrations order of tested heavy metals: Cr>Cu>Co>Zn>Al>Ni>Fe>Mn>Pb. The mean

concentrations correlation analysis show good to strong positive correlations among Pb, Co, Ni, Zn, Al, Fe and Mn suggesting that these metals have common sources. The EF values suggests that Asa sediments were deficient to minimal enrichment for Pb, Co, Cr, Ni, Zn, Fe and Mn while moderate enrichment for Cu and Al. According to CF, Pb, Ni, Fe and Mn shows low contamination while Cu, Co, Cr, Zn and Al face moderate contamination. According to PLI most sites suggest no overall pollution of site quality.

In general, the overall total geo-accumulation indexes (I_{tot}) of the entire study area for different metals were found to be negative as reveal in table 9. This suggests that concentration mean of most heavy metals in Asa sediments are lower than world surface rock average. Considering all assessing criteria, Cu and Co are responsible for significant amount of heavy metal contamination while Pb, Cr, Ni, Zn, Al, Fe and Mn are responsible for low contamination.

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