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Impact of an abandoned mining site on the sediments of the Loutété River, south of Congo, Brazzaville

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Abstract

In order of the study is to assess the intensity of metallic pollution of metals and their spatial variation in surface sediments of the Loutété River. Physico-chemical analyzes (pH, organic matter, particle size) and heavy metal contents were determined using ICP-OES on sediment samples collected at 6 stations. The concentrations (mg.kg^{-1}) found varied from: As 16.7-2107.7, Pb 351-27300, Cr 16.6-82.9, Fe 15200-37000, Cu 18.9-653, Zn 101-9090, Mn 669-5190. The pollution of sediment samples was evaluated using the geo-accumulation index (Igeo), the contamination factor (CF) and the pollution load index (PLI). This study shows that the sediments are polluted in all the stations. The order of pollution intensity is the following, taking into account the Igeo values: Pb > As > Zn > Cu > Fe > Mn.

Keywords: Sediments, geo-accumulation index (Igeo), heavy metals, ICP-OES.

Introduction

In aquatic environment the pollution by heavy metals is a serious global problem[1]. They can migrate from the mining site and its waste to the different compartments of the environment, water, air, via several physico- chemistry mechanisms and found in sediments[2-4]. The sediment is an assembly consisting of more or less large particles or precipitated matter having separately undergone some transport[5]. They are heavy metal discharges and form an integral part of the cycle of these elements. The heavy metal contents in the sediments vary in the same direction as those of the source rock which represents the source and the reserve[6]. Under certain environmental conditions, pH can be modified by the contribution of plant debris and release heavy metals at the water-sediment interface and cause problems in the aquatic environment[7]. The Loutété river, located in the department of Bouenza (south of Congo Brazzaville), is a tributary of the Niari river. It flows in the districts of Mfouati and Loutété. For several years it has been influenced by the activities of a plant processing a sulphide-rich mineral of polymers. Currently this plant is abandoned. The phenomenon of transport of particles through runoff deposits contaminated particles over distant distances from the site, water runoff during the rainy season, contributes to the gradual accumulation of metal pollutants in the sediments at the plant site disused[8]. Studies on heavy metals in the vicinity of the abandoned plant and on Mfouati sediments have shown high concentrations of Pb, Zn, Cu, Mn and As[9]. At present, no studies have been carried out on the spread of metals in the sediments of the Mfouati River to the Loutété River. In this context, we propose to study the spatial evolution of the concentrations of heavy metals Pb, Cr, As, Cu, Zn, Fe in the sediments of the Loutété river from the district of Mfouati to that of Loutété and to assess the degree of the contamination using the geochemical indices such as the contamination factor, the geo-accumulation index and the pollution load index.

Materials and methods

Study area: The Loutété River is located between the south latitude of 367178.59 to 370507.20 UTM and longitude East of 9512957.94 to 9515800.06 UTM. The zone is characterized by an equatorial climate, savanna-type vegetation and a ferralitic soil. The temperature varies between 25 and 36°C during the rainy season against 18 and 24°C in dry season. Annual precipitation ranges from 1050 to 1650 millimeters[7].

Sampling and analysis: During the sampling campaign carried out in October 2014 (dry season), sediment samples were collected at six stations which were geo-referenced using a Garmin Etrex. The sediments were carried out with a polyethylene bucket and placed in plastic bags. For the analysis of heavy metals, the collected sediments were homogenized and dried in the open air of the laboratory and then sieved using a 2 mm sieve. After grinding and sieving at 53 µm, 0.5 g of each sample is placed in a glass tube by adding 5 ml of nitric acid (65% HNO3) added to the mixture. The glass tube is heated for 30 min in a digestion block. Then 2.5 ml of hydrochloric acid (HCl 38%) are added. After evaporation to dryness, the residue of the total attack is diluted in 50 ml with deionized water. The sample is filtered by means of a micropipette and analyzed by optical emission spectroscopy (ICP-OES) at the SGS laboratory in Pointe Noire. The granulometric analysis carried out made it possible to separate the particles according to their size, the

method applied is that of the Robinson pipette based on the Stokes Law according to the AFNOR standard[10]. Walkley and Black method was used to determine the organic matter content[11]. The pollution level of each metal in the sediment samples was characterized using the contamination factor (CF)[12], geo-accumulation Index (Igeo) and Pollution Load Index (PLI)[13].

$$CF = Cm / C_{réf} \quad (1)$$

CF: contamination factor, Cm: Concentration of the element measured in the sample, C_{ref} : reference concentration of the element (usually the content of the local geochemical background).

The contamination factor scale consists of four classes as: CF < 1 low contamination, 1 < CF <3 moderate contamination, 3 < CF < 6 considerable contamination, CF > 6 very high contamination.

The Pollution Load Index (PLI) of each sediment sample was also calculated. This index gives a quantitative estimate of the level of pollution of the chemical elements in a given sample[13]. It is expressed as:

$$PLI = (CF1 \times CF2 \times CF3 \ldots\ldots \times CFn)^{1/n} \quad (2)$$

Where, CF: contamination factor, n: number of metals.

The criterion[14] used on PLI is: PLI < 1: no pollution and for PLI > 1: presence of pollution.

The geo-accumulation index (Igeo) was determined from the base level of the metal content in the sediment according to the following equation[12]:

$$Igeo = \log_2 (Cn / 1.5\ Bn) \quad (3)$$

Where Cn: measured concentration of metal n in the sediments, Bn: geochemical background in the earth crust of the metal n[15] 1.5 is used in taking account natural fluctuations of background data.

The classification of Igeo is shown in Table-1.

Table-1: Müller classification[12].

Class	Igeo value	Sediment quality
0		Unpolluted
1	0 – 1	unpolluted to moderately polluted
2	1 – 2	moderately polluted
3	2 – 3	moderately polluted to severely polluted
4	3 – 4	severely polluted
5	4 - 5	severely polluted to very severely polluted
6	5 - 6	Very severely polluted

In our study, the reference concentrations of metals used are those of Wedepohl for earth crust[15].

Results and discussion

The physico-chemical characteristics of the sediment samples are reported in Table-2.

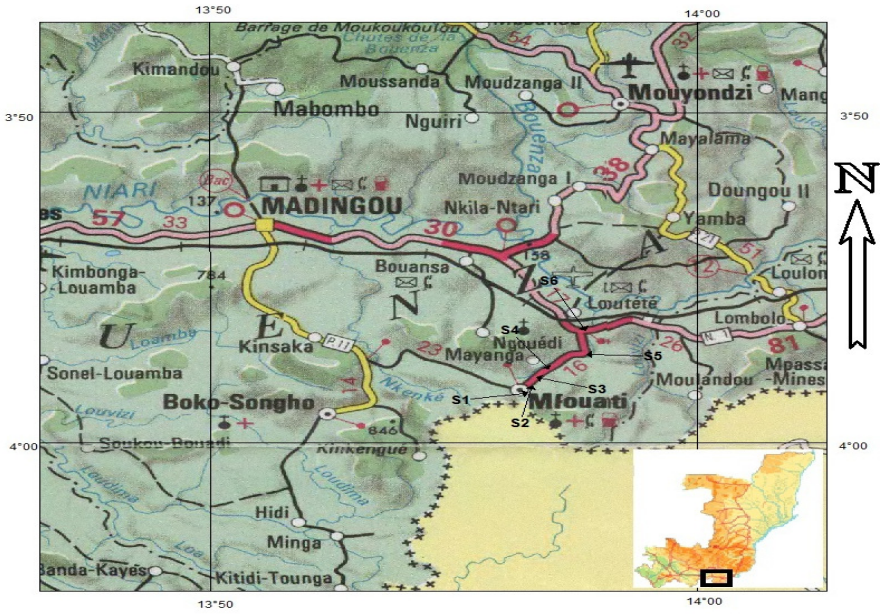

Figure-1: Location map of the study area.

The results of the particle size analysis presented show a predominance of coarse sand ranging from 30.11% (S1) to 91.69% (S6), fine sand varying from 11.29% (S6) to 34, 82% (S3) versus a small percentage of the clay fraction varying from 0.019% (S5) to 13.49% (S3), and fine silt from 1.49 % (S5) to 20.99% (S3). During the dry season, the low flow rate deposits the coarse particles first and the fine particles are transported at long distances. The abundance of coarse particles (sand) on a long distance is due to the constant renewal of the river bed and the nature of the terrain. In most aquatic environments where the flow rate is regulated, the mean velocity of the current is sufficient to transport the sediments downstream, without, however, preventing the fine particles from settling[16]. The specificity at the station S3, as can be seen in Figure-2, is due to the fact that the displacement increases the velocity of the water mass, so that the particles of coarse size are deposited first, followed by fine particles.

The contents of organic matter (Table-1) ranged from 0.15% (S5) to 2.29% (S3), and in the four other stations (S1, S2, S4 and S6) these contents remain sensibly constant. The Anova test between the four stations for one factor gives the following result: $F(1, 4) = 22.2$ $p<0,0092$. The small variations in organic matter content in these four stations can be explained by an important oxidation which causes the degradation of the organic matter [17]. The high content of organic matter in station 3 can be explained by the fact that this station is located in a marshy zone covered by strong vegetation. In this station, an enrichment of the fine particles smaller than 63 µm is also observed.

The pH value is weakly acidic for the sediment samples of stations S1, S4 and S6. The value is near neutral for the stations S2, S3 and S5.

Heavy Metal Distribution: The concentrations of heavy metals (As, Cr, Cu, Pb, Zn, Fe and Mn) in the sediments of the Loutété River are shown in Table-3.

Table-2: Characterization of surface sediments of the Loutété River.

Station	S1	S2	S3	S4	S5	S6
pH	5.42	6.48	6.97	5.42	6.67	5.17
% clay	3.4	3.99	13.49	1.99	0.019	1.49
% silt fine	8	13.49	20.99	6	1.49	1.99
% coarse silt	6.22	7.82	7.12	3.09	2.28	0.98
% coarse sand	58.6	58.05	30.11	74.42	80.01	91.69
% fine sand	20.94	18.33	34.82	15.22	11.29	29.2
OM %	0.21	0.29	2.29	0.25	0.15	0.26

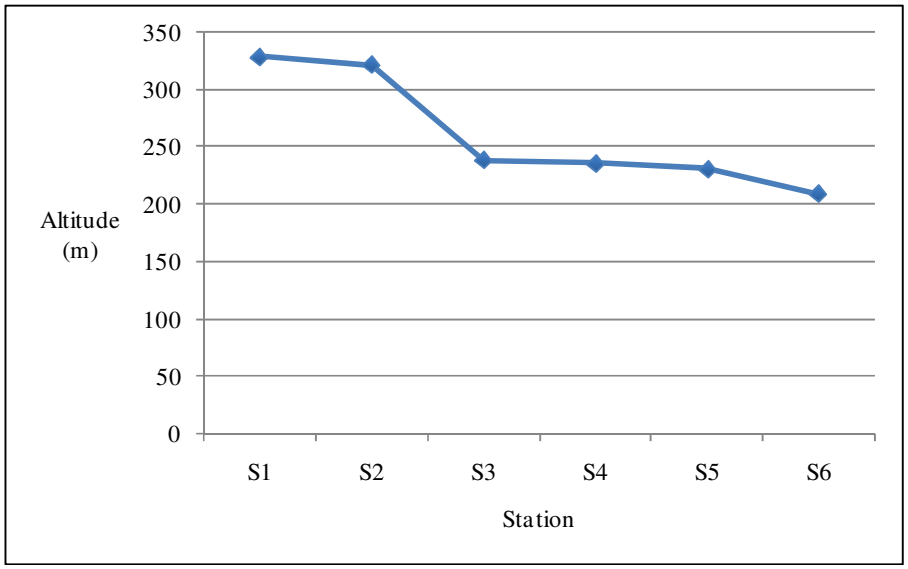

Figure-2: Elevation of stations on the Loutété River.

Chromium: The distribution of chromium content in the sediments is shown in Figure-3. The concentrations ranged from 16.6 - 82.9 mg/kg with a mean of 44.1 mg/kg. These concentrations are lower than that of unpolluted sediments[18] (Table-3) in the sample sediment S3. The concentration is elevated in stations S5 and S6 which is due to the transport of contaminated particles.

Copper: The highest concentration was observed at the station S4 and the lowest at S3 (Figure-4). Moreover, these concentrations are higher than those of the unpolluted sediments[18], except in S3. The main source of copper pollution is the mineralogical nature of the mining waste coming from the abandoned plant by runoff rain water. The high value of copper content in S4, S5 and S6 can be explained by the high mobility of copper ions as suggested by the scale of ion mobility[19] which is Cu> Cd> Zn> Pb. Copper with the highest mobility potential justifies its presence in large quantities in the stations S4, S5 and S6.

Table-3: Heavy metal concentration in the sediment samples (mg/kg).

Station	Cr	Cu	Fe	Pb	Zn	As	Mn
S1	39.6	286	33200	27300	1190	479	3270
S2	26.3	357	26600	8380	1780	251	2330
S3	16.6	18.9	15200	351	101	16,7	669
S4	35.2	653	31100	13300	9090	497	3460
S5	67.1	584	45300	9520	6550	590	5190
S6	82.9	342	37000	5680	2920	274	3670
Minimum	16.6	18.9	15200	351	101	16.7	669
Maximum	82.9	653	45300	27300	9090	590	5190
Average	44.61	373.48	31400	7446.2	3605.16	351.28	3098.16
S.D	25.31	226.75	10132.91	9180.18	3483.34	210.95	1506.92

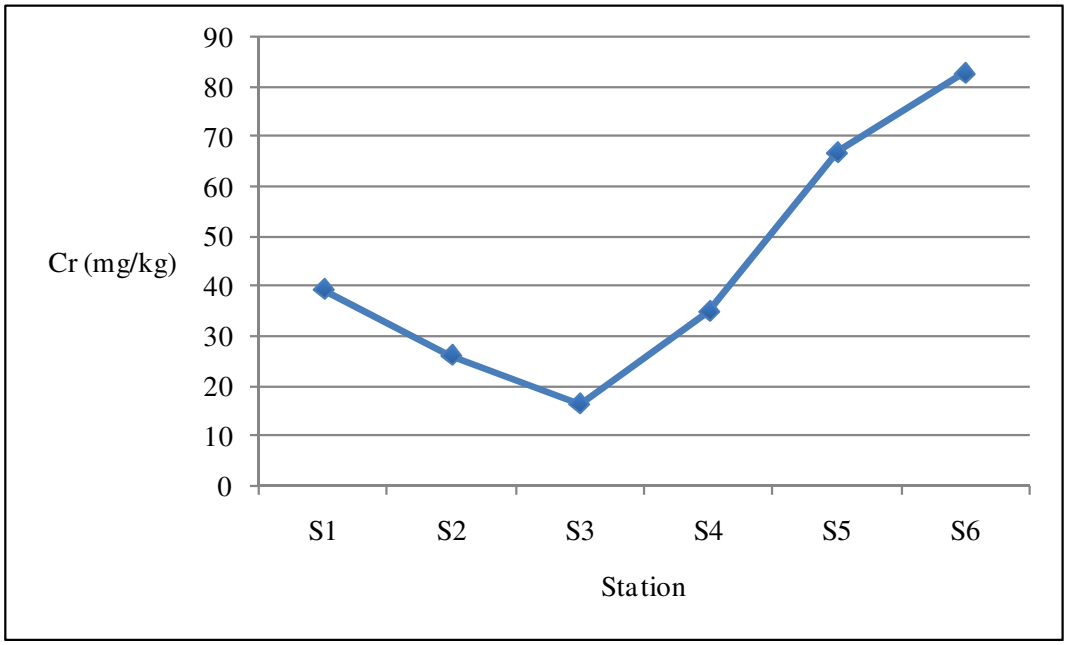

Figure-3: Distribution of chromium concentration in the sediments.

Iron: The concentration varied between 15200 and 45300 mg.kg^{-1}. High iron concentrations were observed at all the stations (Figure-5) and are due to the nature of the geochemical background of the region[20]. The concentrations are higher than those of unpolluted sediments in all the stations. According to some studies, these high levels of iron are not necessarily a sign of pollution, but may be related to the hydrodynamic and physico-chemical conditions of the medium[21,22].

Lead: The concentrations ranged from 351 - 27300 mg.kg^{-1}. The high values of Lead content were observed at S1, S4 and S5 (Figure-6), which are higher than the concentration in unpolluted sediments[18]. The high lead content in the station S1 may be due to on-site accumulation of the particles. In fact, leaching drains soil particles and mining slags which are mostly rich in iron sulphides and other sulphides metal[7] and deposits them on the river bed causing the gradual accumulation of metals. The metals were classified according to their adsorption potential[19]: Pb> Zn> Cd> Cu. Since Pb is the least mobile possessing the High potential adsorption and a low transfer power. Moreover, the observed concentrations of S4, S5 and S6 are explained by the phenomenon of particle transport by water runoff.

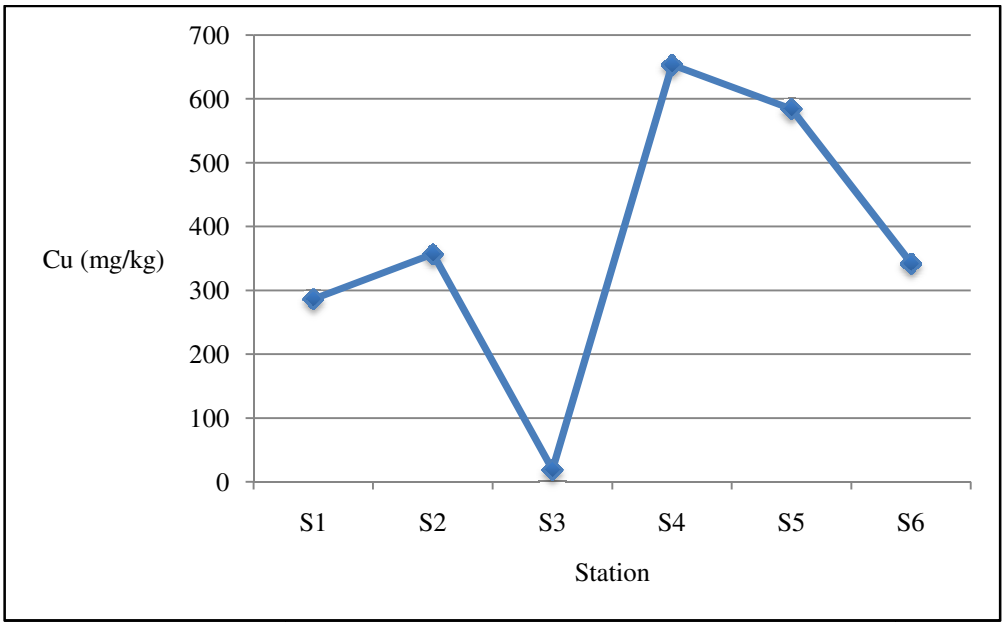

Figure-4: Distribution of copper concentrations in the sediments.

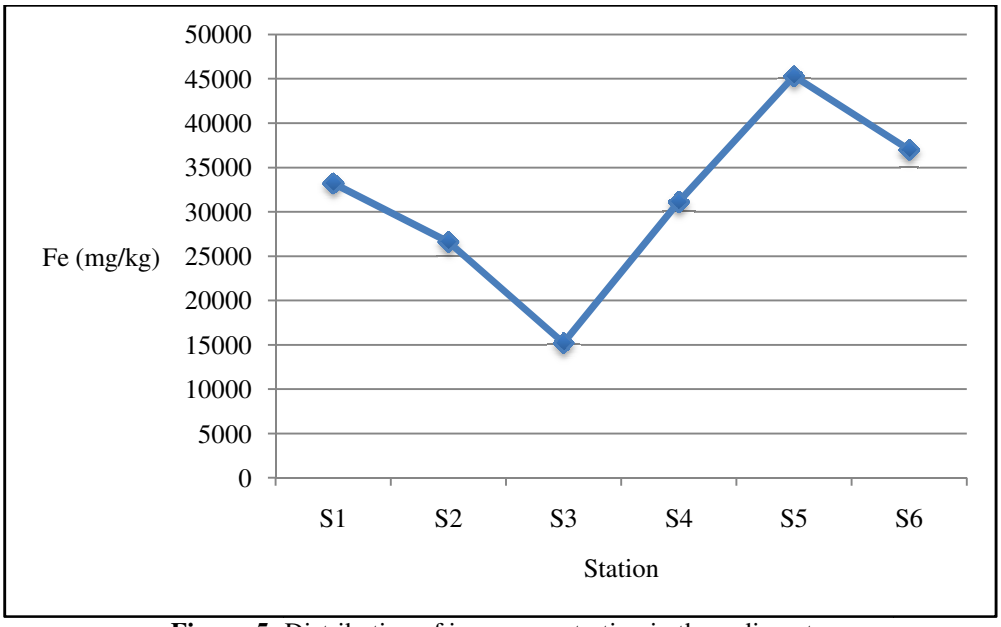

Figure-5: Distribution of iron concentration in the sediments.

Zinc: The concentrations of Zn ranged from 1101 - 9090mg/kg and are above the unpolluted sediment guideline[18]. The high levels of the concentration may be due to the hydrodynamic of the water mass. Indeed, the particles contaminated are transported at long distances due to the intensity of the water current. The distribution of zinc content is shown in Figure-7.

Arsenic: The concentrations varied between 16.7 and 590 mg.kg-1. The high contents were observed at S1, S2, S4, S5 and S6 (Figure-8). The runoff of rain water contributes to the accumulation of metals in the sediments. The runoff of rain water contributes to the accumulation of metals in the sediments. Arsenic concentrations in these sediments are very higher than the concentration in earth crust[15].

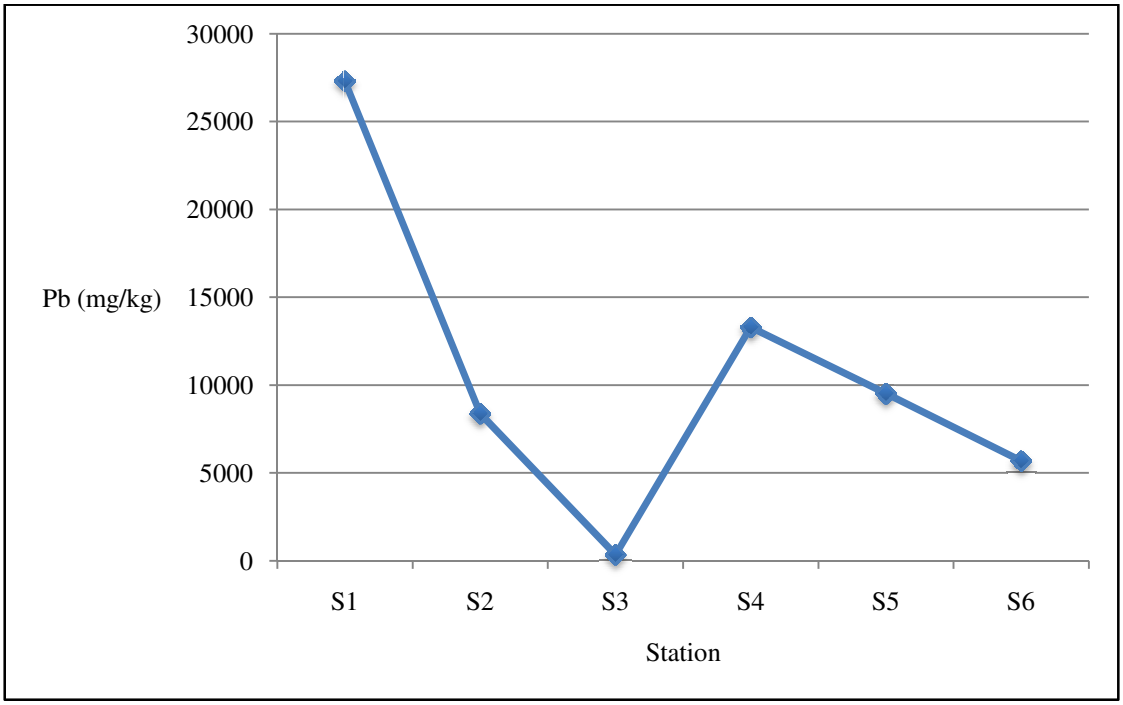

Figure-6: Distribution of lead concentrations in the sediments.

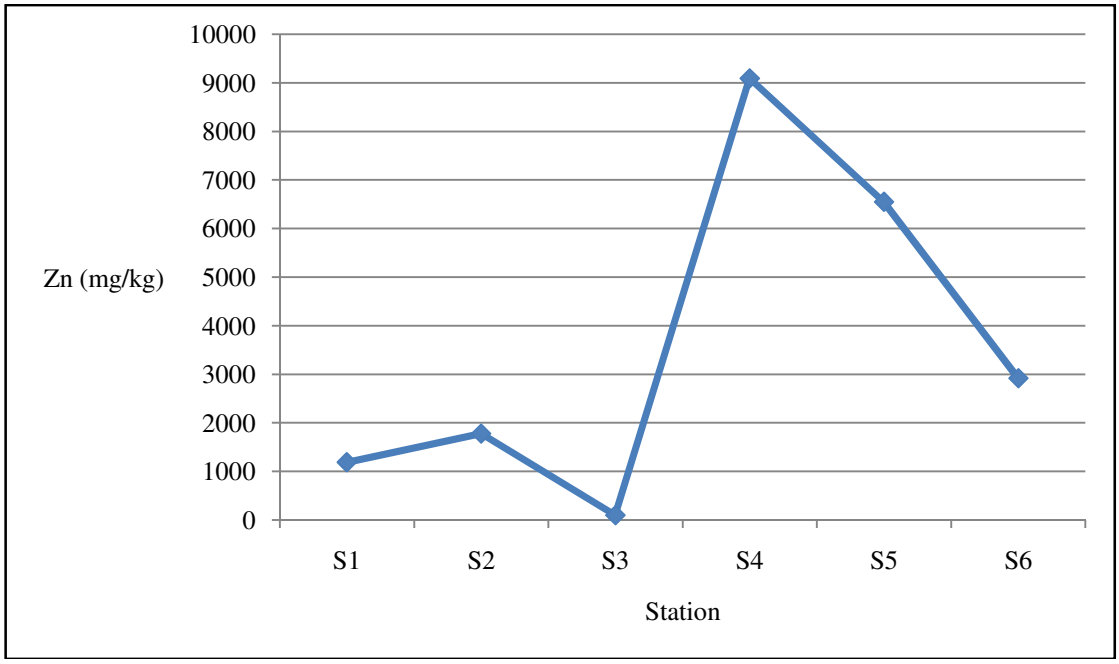

Figure-7: Distribution of in zinc concentrations in the sediments.

Manganese: The concentration oscillates between 669-5190 $mg.kg^{-1}$. In all the sediment samples, the concentrations are higher than that of the terrestrial crust[15] ($527mg.kg^{-1}$). As for all other metals, the accumulation of manganese in the sediment is linked to the leaching of mining waste in the plant. The distribution of manganese concentrations is shown in Figure-9. The average concentration of Cr, Pb, Zn, Cu, Fe and Mn in sediment samples of the Loutété river greatly exceeded the average in unpolluted sediments and earth crust value (Table-3).

Assessment of contamination: The pollution of sediments was characterized using geo-accumulation index, pollution load index and contamination factor. The geo-accumulation index values of the seven heavy metals are given in Table-4.

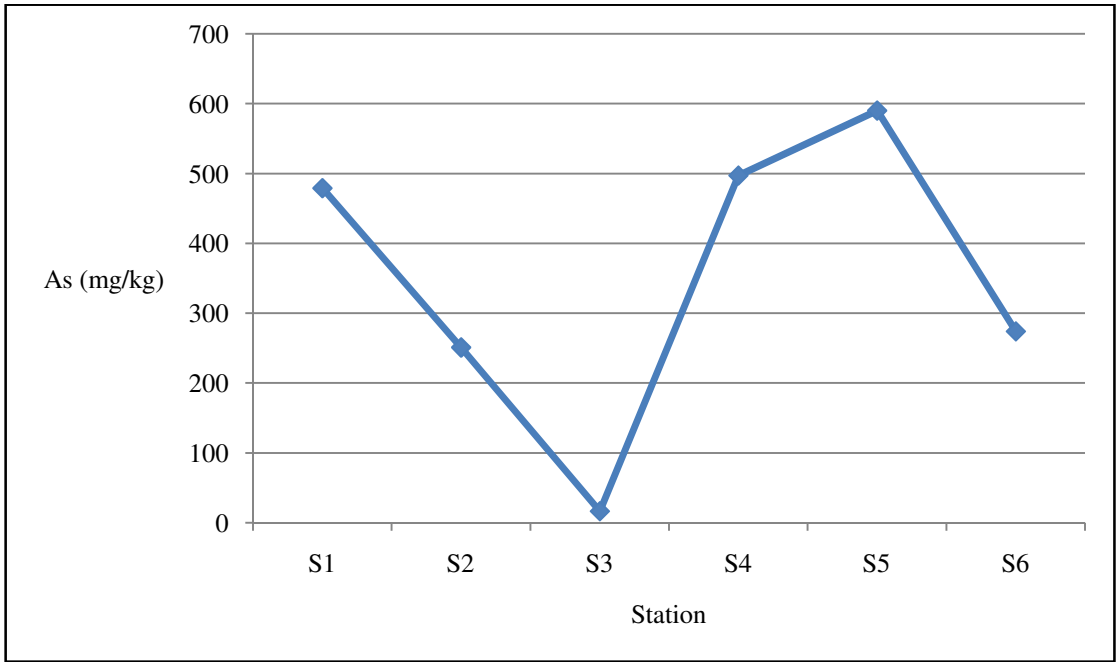

Figure-8: Variations of Arsenic concentrations in sediments.

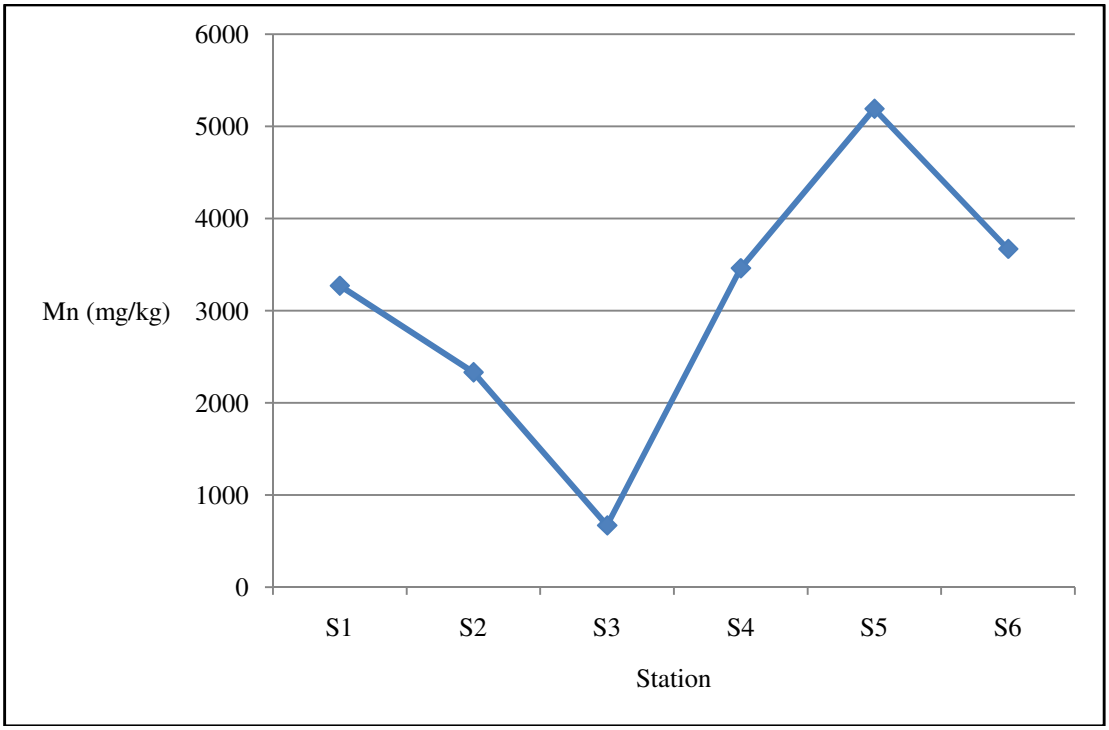

Figure-9: Distribution of manganese concentrations in the sediments.

Table-4: Concentration of metals (mg/kg) in sediments from different regions of the world.

Rivière	Pb (mg /kg)	Zn (mg /kg)	As (mg /kg)	Cu (mg /kg)	Cr (mg /kg)	Mn (mg /kg)	Fe (mg /kg)
Loutété	7446.2	3605.16	351.28	373.48	44.61	3098.16	31400
Mfouati	11800	2400		270		6900	53130
Deùle	19900	19600		507	139	594	
Day river				740.75	311.69		36010
Han River							51200
Estuary of comoé River					85.15		
Nakivubo stream						2603.20	98928.00
Annaba coastline	68.2	284.4			420		17790
Ebrie Lagoon		1081.7			1618.6		
El Kala, Algérie		114			157		16900
Ahémé Lake	26.25	170					
Oued Essouk	22140	1802		50			
Unpolluted sediment	20	75		20	25		10000
Earth crust	17	52	2	14	35	527	3034

Table-5: Geo-accumulation index of the metals in the sediments.

Station	Igeo						
	As	Cr	Fe	Cu	Zn	Pb	Mn
S1	7.35	-0.42	2.88	3.78	3.95	10.11	2.05
S2	6.41	-1.01	2.56	4.10	4.53	8.40	1.56
S3	2.49	-1.65	1.75	-0.16	0.37	3.80	-0.24
S4	7.40	-0.56	2.79	4.98	6.90	9.07	2.14
S5	7.65	0.36	3.33	4.82	6.42	8.58	2.72
S6	6.54	0.67	3.04	4.04	5.25	7.83	0.66
Mean	6.31	-0.44	2.73	3.59	4.57	7.97	1.48
SD	1.77	0.78	0.50	1.73	2.13	1.99	0.99

The order of metal accumulation in the sediment samples, in terms of mean concentration was as: Pb > As > Zn > Cu > Fe > Mn > Cr. The Igeo values of the metals was as As: 2.49 – 7.65; Cr: -1.65 – 0.67; Fe: 1.75 – 3.33; Cu: -0.16 - 4.98; Zn: 0.37 - 6.90; Pb: 3.80 – 10.11; Mn: -0.24 - 2.72. The sample sediments were moderatelely polluted to severely polluted with As at S3 and very severely polluted at the stations S1, S2, S4, S5 and S6. Cr: no pollution was observed at the stations S1 – S4 except the stations S5 and S6 which are in the class unpolluted to moderately polluted.

In all the stations the sediments are moderately polluted to strongly polluted with Fe except at the station S3. For Cu the sediments are strongly polluted in all the stations except station S3. Igeo values of Zn of the sediments of the stations S4 – S6 show that the sediments are severely polluted to very severely polluted.

At the stations S1 and S2, the sediments are severely polluted and moderately polluted at the station S3. For Pb, the sediments are very severely polluted in stations S1, S2, S4 – S6 and severely polluted at the station S3. For Mn the sediments are moderately polluted in all the stations, except station S3 in which they are unpolluted.

Contamination factor and Pollution load index: Table-5 shows the results of contamination factor and pollution load index of the various metallic elements in the sediments of various stations. The contamination factor of the heavy metals was as: As 8.35 - 295, Zn 1.94 - 125.96, Cu 1.35 - 46.64, Fe 5 - 14.93, Pb 3.8 - 10.11 and Mn 1.26 - 9.84.

These values reflect a very high metal contamination of the sediments because CF > 6. The sediments in all the stations are in the class of moderate contamination in Cr, except in the stations S2 and S3 where the class is of low contamination. The pollution load index calculated shows that the sediments of Loutété River are polluted because PLI> 1.

Conclusion

The general objective of this work was to evaluate the influence of an abandoned mining site on the sediments of the Loutété River. The results of the particle size analysis showed that the predominant fraction in the sediment of Loutété River is coarse sand. The content of organic matter in the sediments is very low. The sediments are slightly acidic and near neutral in the particular station S3. The concentrations of As, Cr, Pb, Zn, Cu, Fe, Mn found in sediments are higher than those of unpolluted sediments and earth crust.

The calculation of geochemical indices, such as the geo-accumulation index (Igeo), the contamination factor (FC) and pollution load index show that the sediments are polluted.

Table-6: Contamination factor of the metals and Pollution load index of sediments

Station	CF	CF	CF	CF	CF	CF	CF	PLI
	As	Cr	Fe	Cu	Zn	Pb	Mn	
S1	239.50	1.13	10.94	20.42	22.88	10.11	6.20	13.61
S2	125.50	0.75	8.76	25.50	34.23	8.40	4.42	11.5
S3	8.35	0.47	5.00	1.35	1.94	3.80	1.26	2.19
S4	248.50	1.00	10.25	46.64	174.8	9.07	6.56	19.89
S5	295.00	1.91	14.93	41.71	125.96	8.58	9.84	23.3
S6	137.00	2.36	12.19	24.42	56.15	7.83	6.96	16.21
mean	175.64	1.27	10.35	26.67	69.33	7.965	5.87	14.45
SD	96.29	0.66	3.05	14.79	61.15	1.99	2.61	6.72

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