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Assessment of the Quality of Sediments and Agricultural Soils: Case of the Ity-Floleu Area in the Prefecture of Zouan-Hounien, Western Côte d'Ivoire

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Abstract

The objective of this study is to assess the level of metal contamination of sediments and agricultural soils in the Ity-Floleu zone. The concentrations of trace elements (Fe, Mn, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) were measured in different seasons over two successive years. The sediment pollution index made it possible to note that the sediments and agricultural soils of the various stations studied are highly polluted in all seasons. The calculation of the geoaccumulation index indicates that surface water sediments most often experience extreme or moderate pollution in As, Cd, Cu, Hg and Zn in the dry or rainy season except in Pb in some cases. We observed that the sediments of the Cavally river present a serious pollution due to extreme anthropic activities carried out along the river. Over the entire region, the results of the potential ecological risk index (RI) indicate that all the sediments and agricultural soils analysed present a moderate ecological risk in terms of Pb and Zn in certain cases and an ecological risk is observed low bound to other metals in all seasons. This metallic pollution generated by human activities in this region can have consequences for the environment and biodiversity.

Keywords

Anthropogenic Activities, Cavally River, Contamination Factors, Contamination Indices, Metallic Trace Elements, Sediments and Agricultural Soils

1. Introduction

Soil plays and continues to play an eminent role in the major biogeochemical cycles and the fate of polluting substances, it accumulates and makes available to plants and animals most of the elements essential for life (air, water, nutrients, etc). In addition to its role as a nutrient reserve, the soil can also constitute an effective environmental filter by purifying the water which passes through it of various pollutants which can contaminate the food chain and the groundwater tables. This complex environment raises important questions about its ability to conserve elements such as heavy metals (Kebir, 2012). For a long time, people paid little attention to their natural environment. The situation today is dramatic, in particular for aquatic ecosystems.

The contaminants that reach these media are still a major environmental problem. Indeed, the concentration of most of these contaminants sometimes rises to levels that are toxic to aquatic life in both water and sediments (Sahli et al., 2014). The environmental impacts linked to human activities in Côte d'Ivoire are progressing worryingly. The results in environmental degradation, the most visible of which are: deforestation, loss of biodiversity, pollution and also by consequences on hygiene and health at community and domestic levels (Akther et al., 2019). This concern affects the sub-prefecture of Zouan Hounien where human activities such as mining, wastewater, domestic waste or agriculture are among the most polluting (Serge et al., 2020). Among the many compounds emitted by human activities, trace metal elements (MTE) constitute one of the major sources of contamination. These MTE enter aquatic systems, through point sources (industrial and urban effluents) diffuse sources (runoff, dry and wet atmospheric deposition), in the form particulate, dissolved and colloidal forms (Shohel et al., 2017). Some of these MTEs are essential to the life of organisms, both micro and macroscopic (Sigg et al., 1992); thus a too low concentration could lead to deficiency phenomena, however present in too high quantities, they will generate risks of toxicity. However, other MTEs are not essential, and cause, even in very small amounts, proven toxicity (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) (Chassin et al., 1996).

2. Material and Method

2.1. Study Area

Ity is a village located 15 km south-east of Zouan-Hounien (Côte d'Ivoire), the chief town of the department. The Ity sector is moderately rugged with altitudes varying between 255 m along the Cavally River and 450 m. The region is part of a vast forest area that covers both Côte d'Ivoire and Liberia (Ettien, 2010). Located in the west of the Côte d'Ivoire, the Cavally watershed is between 6˚47' and 6˚52' North latitude, and between 8˚5' and 8˚6' West longitude. This watershed covers an area of 3647.53 km^2 with the Floleu hydrometric station as an outlet (**Figure 1**). With a length of 700 km, the Cavally River is shared by three countries: Côte d'Ivoire, Guinea and Liberia. The Cavally River is very meandering and the bed of the stream is disturbed by gold mining activities (Naho, 1988). The basic agricultural products of the Ity sector are mainly coffee, cocoa, palm

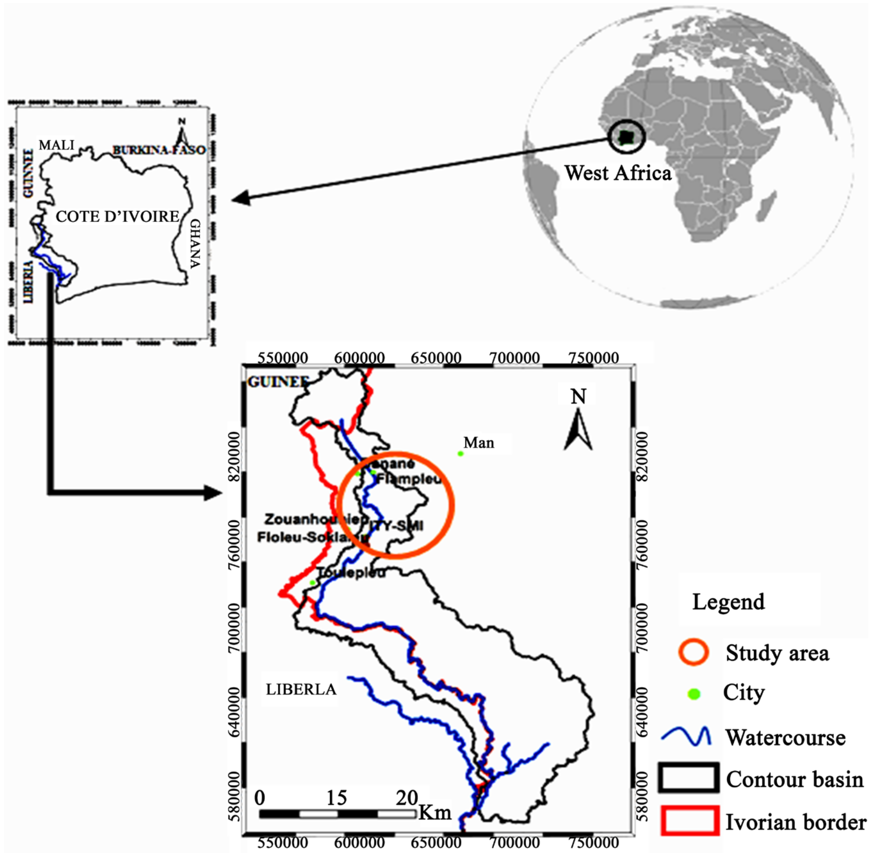

Figure 1. Map of the Cavally watershed study area.

oil, cassava, rice and bananas.

The Zouan-Hounien region belongs to a mountain climate with alternating two rainy seasons: long dry season from November to February, short rainy season from March to July, short dry season from late July to end of August, heavy rainy season from September to November. The driest month is January, with 15 mm of rainfall. The most significant rainfall is recorded in September, with an average of 237 mm. The average annual rainfall is 1866 mm and the average annual temperature in Zouan-Hounien is 25.6˚C (Brou, 2019).

The local geology is difficult to define, as there is no outcrop in the area. In addition to this difficulty, there is the presence of a dense vegetation cover. The Ity gold deposit is located in the Toulépleu-Ity Birimian unit located west of the Sassandra fault, in the Kénema-Man domain. This set is oriented in a NE-SW direction (Ettien, 2005). SODEMI's exploration work between 1962 and 1968 revealed strong gold mineralisation in the Ity sector where, in the 1940s and 1950s, there was already intense gold mining activities (Papon, 1973). These gold mining activities are greatly increased. In the North, the basin is dominated by schist, rhyolite, and migmatite, while in the South, it is characterized by intrusions of metamorphic rocks, gneisses and mesozonal formations. The strong erosion is a character of rejuvenation of these soils (Vo Quang & de Guyon, 1966).

2.2. Sample Collection

The sediment samples were taken from the waterbeds of the Cavally River, the paddy field and the river. In the paddy fields, there are rice, corn and market gardening farms (okra, salad, cabbage). Agricultural soils have also been sampled where mining activities (around mining company and gold washing) are practiced. The measurements were carried out twice during the dry season (low water season) and twice during the rainy season (flood season) over a period of an annual cycle for two consecutive years on the study site during four campaigns (from January 04, 2017 to October 20, 2018). Sampling points were located using a Garmin eTrex 20 type Global Positioning System (GPS) receiver (**Figure 2**).

Sediment and agricultural soil samples were collected using an American stainless steel shovel at the surface layer. The depth of each sample will be limited by the highly indurated levels encountered in this environment. The collected samples were then stored in hermetically sealed PET bags for analysis. The samples were taken to the laboratory, left to dry at room temperature in the laboratory.

2.3. Sample Analysis

The measurements of the mineral trace elements (Fe, Mn, As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) were analysed by the spectrophotometric method (precision ± 1

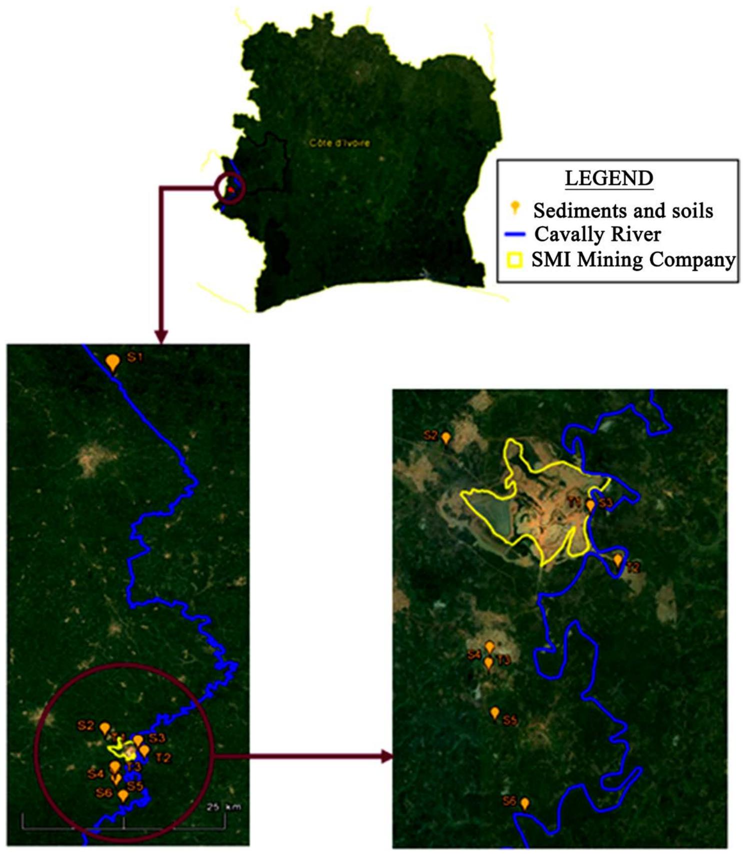

Figure 2. Map of the different sampling stations in the Ity-Floleu study area (Google Earth).

nm) using the ICP-AES. This spectrometer operates in simultaneous mode that is to say that all the elements are analysed at the same time under the same operating conditions. The analyses were carried out at the Center for Research in Oceanology (CRO) in Abidjan (Côte d'Ivoire).

A total of 24 surface water sediment samples and 12 agricultural soil samples were analysed.

Mineralisation of sediment and agricultural soil samples

Destruction of organic material is obtained by treating the sample at 450˚C in the presence of ammonium nitrate. The dry sediments were ground in a mortar, then sieved through a 250 µm mesh sieve.

The acid used for the mineralisation of the solids from the preparation of the sediment is a solution of aqua regia. The latter consists of three volumes of hydrochloric acid (37% hydrochloric acid solution) and one volume of nitric acid (65% nitric acid solution). Aqua regia, also called royal water, can dissolve all metals. The application standard for solids mineralisation is NF EN ISO 15587-1. The operating protocol followed is as follows. First, 0.5 grams of the dry solid sample is weighed and placed in a "Digitube" digestion tube. Then 6 mL of hydrochloric acid solution and 2 mL of nitric acid are added to the tube. Then, the sample is heated at 95˚C for 75 minutes in the hot block mineralizer. The mineralized product obtained is cooled to room temperature and subsequently calibrated to 50 mL with deionized water and centrifuged at 2000 revolutions/minute for three minutes.

The detection limits are recorded in Table 1.

2.4. Data and Methods

The results are expressed as means calculated with the Excel 2007 software. The comparison of the means, the correlation matrix and the principal component analysis (PCA) were carried out using the XLSTAT statistical software version 2016.02.27444.

Calculation of factors and indices of metallic contamination of sediments

In order to assess the state of metallic contamination of the sediments studied, calculations of various factors and indices were carried out. To estimate the intensity of the contamination, the enrichment factor and the geo-accumulation index were calculated (Samiha et al., 2018). Their principle is based on the comparison of the measured values compared to reference values such as the average of the element contents of the upper continental crust (UC) (Wedepohl, 1995).

Calculation of the contamination factor (CF)

The contamination factor or CF is one of the factors used to assess the

Table 1. Detection limit for solutions acidified with nitric acid.

Elements	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Detection limit (mg/L)	0.005	0.0005	0.005	0.050	0.010	0.0001	0.005	0.005	0.005	0.010

contamination of a metal analysed in a sediment. It is expressed by the ratio between the content of the metal in the sediment (C_s) and the content of the same metal in the geochemical background of the watershed of the study area concerned (C_g) (Pekey et al. 2004; Raj & Jayaprakash, 2008). In our case, the mean values of the continental crust (Wedepohl, 1995) (**Table 2**) had to be used as a reference due to the lack of baseline geochemical background data in the geographical area studied.

The CF is calculated according to the following formula:

$$\mathrm{CF} = \frac{C_s}{C_g} \tag{1}$$

The CF value makes it possible to classify the sediment according to contamination into 4 groups (Hakanson, 1980; Pekey et al., 2004): CF ≤ 1: there is no contamination resulting from natural or anthropogenic inputs; 1 < CF ≤ 3: the sediment is moderately contaminated; 3 < CF ≤ 6: the contamination is considerable and CF > 6: very strong contamination.

Calculation the enrichment factor (EF)

According to the study by Hernandez et al. (2003), the enrichment factor (EF) is defined as the relative abundance of a chemical element in a soil compared to that found in the bedrock. In this work, EF is determined by comparing elemental concentrations with those in the upper continental crust (UC) (Wedepohl, 1995) (**Table 2**). We chose aluminum as a reference element because it is considered to be a marker of the clay fraction, a fraction for which trace metals (Me) have a strong affinity (Hamzeh, 2012). This element has been used as a reference in many studies similar to ours (Huang & Lin, 2003; Neto et al., 2006; Praveena et al., 2010; Strady et al., 2017).

The enrichment factors were calculated according to the following formula:

$$\mathrm{EF} = \frac{[\mathrm{Me}/\mathrm{Al}]\ \text{sediment}}{[\mathrm{Me}/\mathrm{Al}]\ \text{reference}} \tag{2}$$

EF values ranging from 0.5 to 1.5 show natural weathering (Zhang & Liu, 2002). However, values above 1.5 suggest sources of anthropogenic contamination. Values between 1.5 and 3 indicate minor enrichment, between 3 and 5 indicate moderate enrichment, and between 5 and 10 indicate severe enrichment. Above 10 is considered extremely severe enrichment.

Calculation of the sediment pollution index (SPI)

The calculation of the enrichment factors (EF) made it possible to establish a classification of sediments according to their metallic contamination. This weighting factor varies depending on the toxicity of the element. Thus, Rubio et al. (2000)

Table 2. Concentrations of metallic elements in the upper continental crust (Wedepohl, 1995).

Elements (mg/kg)	Fe	Mn	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Al
Wedepohl, 1995	30,890	527	2	0.102	35	14.3	0.056	18.6	17	52	77,440

introduced the sediment pollution index (SPI) which is the linear sum of EF taking into account the relative toxicity of each metal by assigning a weighting factor to it. Arsenic and Pb are assigned a weight of 5300 to Cd, 1 to Cr and Zn, 50 to Hg and 2 to Ni (Rubio et al., 2000; Singh et al., 2002). Thus, the SPI can be expressed by the following formula:

$$\text{SPI} = \frac{\sum(\text{EFm}) \times \text{Wm}}{\sum \text{Wm}} \tag{3}$$

With FEm: Enrichment factor of the metal considered.

Wm: Toxicity weight or weighting factor.

The SPI values are accompanied by five pollution classes (Singh et al., 2002) which are distributed as follows: 0 ≤ SPI < 2, healthy sediment; 2 ≤ SPI < 5, slightly polluted sediment; 5 ≤ SPI < 10, moderately polluted sediment; 10 ≤ SPI < 20, heavily polluted sediment and 20 ≤ SPI, dangerous sediment.

Calculation of the geoaccumulation index (Igeo)

Another factor for evaluating the metallic contamination of sediments can be calculated, this is the geoaccumulation index (Igeo). The Igeo index was introduced by Muller (1979) with the aim of determining the degree of metallic contamination in sediments. It is calculated using the following equation:

$$\text{Igeo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \tag{4}$$

where:

C_n is the measured concentration of a metal (n) in the sediment;

B_n is the concentration of metal (n) in the geochemical background of the watershed;

1.5 is the matrix correction factor for the geochemical background related to lithology.

In our case, we used Al as a reference the elemental composition of the continental crust (Wedepohl, 1995) as explained previously for the calculations of FE and CF. According to the work of Muller (1981) the sediments can be classified into 6 groups according to the value of Igeo. This pollution states that: Igeo ≤ 0, unpolluted; 0 ≤ Igeo < 1, from unpolluted to moderately polluted; 1 ≤ Igeo < 2, moderately polluted; 2 ≤ Igeo < 3, from moderately polluted to heavily polluted; 3 ≤ Igeo < 4, heavily polluted and 4 ≤ Igeo < 5, from highly polluted to extremely polluted.

Calculation of the potential ecological risk index (RI)

A final factor can be used to estimate the ecological risk due to the metallic elements contained in the sediments (Xu et al., 2008; Cui et al., 2014): the ecological risk index (RI). This index was adopted for the first time by Hakanson (1980), it takes into account the concentration of the pollutant, the type of pollutant, its degree of toxicity and the environmental response to this toxicity. The RI is calculated from the following equation:

$$\text{RI} = \sum E_r^i = \sum\left(T_r^i \times C_r^i\right) = \sum\left(T_r^i \times \frac{C^i}{Cu^i}\right) \tag{5}$$

Hence, E_r^i is the potential ecological risk coefficient of an element; T_r^i is the coefficient of toxicity of a particular metallic element; C_r^i is the pollution factor; C^i is the concentration of an element in the sediment analysed; and Cu^i is the concentration of the same element in the reference.

The reference in our case is the one used to calculate the other factors (Wedepohl, 1995). The toxicity coefficients are 5 for Pb, Ni, Cd, Cu, Zn and 2 for Cr; these values are based on similar studies found in the literature (Xu et al., 2008).

The values of E_r^i and RI qualify the sediments in several classes in order to assess the ecological risk that their contamination can generate. The classification of sediment quality according to the potential E_r^i ecological risk coefficient of an element *i* is: $E_r^i \le 40$, low ecological risk; $40 < E_r^i \le 80$, moderate ecological risk; $80 < E_r^i \le 160$, moderate ecological risk; $160 < E_r^i \le 320$, very high ecological risk and $E_r^i > 320$, severe ecological risk. When classifying the quality of sediments according to the RI ecological risk index, we have: RI ≤ 150, low ecological potential; 150 < RI ≤ 300, moderate ecological potential; 300 < RI ≤ 600, high ecological potential and RI > 600, severe ecological potential.

3. Results

3.1. Concentration of Minerals in Agricultural Sediments and Soils

Table 3 indicates that the seasonal average Fe contents vary from 7623.99 mg/kg at station S_5 and 20,996.6 mg/kg at station S_3 in the dry season, in the rainy season from the detection limit at station S_3 and 705.56 mg/kg at station S_6. Mn concentrations are between the detection limit at station S_4 at 27.12 mg/kg at station T_2 in the dry season, in the rainy season between the detection limit at stations S_4, S_5, S_6, T_3 at 0, 33 mg/kg at station T_1. The As contents range from 0.49 mg/kg at station S_2 to 779.90 mg/kg at station S_6 in the dry season, in the rainy season they are at the limit of detection in all stations except S_3 stations (58.50 mg/kg) and T_1 (0.016 mg/kg). The Cd contents are between the limit of detection in almost all stations at 19.54 mg/kg at station S_3 in the dry season, in the rainy season at 5.84 mg/kg at station T_1. The Cr concentrations are between 0.29 mg/kg at station S_4 and 6.79 mg/kg at station S_3 in the dry season, in the rainy season between 0.61 mg/kg at station S_5 and 1.13 mg/kg at station T_2. Cu concentrations vary between 1.75 mg/kg at station S_4 to 76.61 mg/kg at station S_3 in the dry season, in the rainy season between 0.17 mg/kg at station T_1 to 90.74 mg/kg at station S_2. The Hg contents oscillate between the detection limit in several stations and 5.93 mg/kg at station S_1 in the dry season, in the rainy season and 3.33 mg/kg at station S_4. Ni concentrations are at the limit of detection in all stations except the T_2 (7.21 mg/kg) and S_3 (18.64 mg/kg) stations. The Pb contents range from the limit of detection at stations S_3, T_3 to 118.89 mg/kg at station S_1 in the dry season, in the rainy season from 0 mg/kg at station S_1 to 213.50 mg/kg at S_2 station. The Zn concentrations vary from 25.84 mg/kg at station S_4 and 476.00 mg/kg at station S_6 in the dry season, in the rainy season they are at the limit of detection in all the stations.

Table 3. Seasonal variation of minerals in sediments and agricultural soils (mg/kg) from January 2017 to October 2018.

Stations	Seasons	Fe	Mn	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S_1	DS	13,504.65	5.63	614.27	0.00	6.74	7.05	5.93	<0.005	118.89	58.41
	RS	4.41	0.02	<0.005	<0.0005	1.12	24.70	1.59	<0.005	0.00	<0.010
S_2	DS	7523.82	13.78	0.49	<0.0005	3.93	1.32	0.15	<0.005	19.67	61.10
	RS	4175.00	0.01	<0.005	<0.0005	0.98	90.74	0.59	<0.005	213.50	<0.010
S_3	DS	20,996.60	12.23	12.58	19.54	6.79	76.61	0.13	<0.005	<0.005	59.16
	RS	9500.00	0.01	58.50	<0.0005	0.87	90.00	<0.0001	18.64	1.44	<0.010
S_4	DS	8404.31	<0.005	1.36	0.02	0.29	1.75	<0.0001	<0.005	0.44	25.84
	RS	3.31	<0.005	<0.005	<0.0005	0.62	44.25	3.33	<0.005	0.01	<0.010
S_5	DS	7623.99	10.25	40.37	0.01	5.30	2.88	0.18	<0.005	3.24	33.06
	RS	635.00	<0.005	<0.005	<0.0005	0.61	41.20	<0.0001	<0.005	2.26	<0.010
S_6	DS	8327.97	23.68	779.90	<0.0005	6.63	12.49	0.13	<0.005	21.50	476.00
	RS	705.56	<0.005	<0.005	<0.0005	1.06	50.17	<0.0001	<0.005	2.36	<0.010
T_1	DS	16,021.44	15.96	463.73	6.39	5.21	16.62	2.30	<0.005	15.76	49.63
	RS	5160.10	0.33	0.16	5.84	0.74	0.17	0.22	<0.005	5.25	<0.010
T_2	DS	14,988.07	27.12	2.14	0.05	4.78	39.14	<0.0001	7.21	1.71	49.11
	RS	8116.00	0.12	<0.005	2.53	1.13	7.86	0.18	<0.005	38.57	<0.010
T_3	DS	11,581.13	17.26	3.11	<0.0005	3.91	5.09	<0.0001	<0.005	<0.005	91.71
	RS	4130.00	<0.005	<0.005	<0.0005	0.78	70.10	0.19	<0.005	1.00	<0.010
Sediment standards		-	-	**50**	**10**	**1000**	**1000**	**10**	**200**	**800**	**3000**
Soil standards		-	-	**10**	**2**	**150**	**100**	**1**	**50**	**100**	**300**

DS: Dry season; RS: Rainy season; S_1 to S_4: Sediments and T_1 to T_3: agricultural soils.

3.2. Contamination Factor (CF)

The following table (Table 4) shows the CF values calculated according to the two seasons (wet and dry) at the level of the sampling stations of the present study.

The calculated CF values obtained for all stations can be classified into three groups. The stations with very high As contamination are at stations S_1 (CF = 307.13), S_3 (CF = 6.29), S_5 (CF = 20.19), S_6 (CF = 389.95) and T_1 (CF = 231.86) in dry period with a maximum value in S_1, S_6, T_1 and at station S_3 (CF = 29.25) in rainy period; in Cd at stations S_3 (CF = 191.57) and T_1 (CF = 62.60) in the dry period with a maximum value in S_3 and at stations T_1 (CF = 57.27) and T_2 (CF = 24, 83) in rainy season; in Cu at stations S_2 (CF = 6.35) and S_3 (CF = 6.29) during rainy periods; in Hg at stations S_1 (CF = 105.91) and T_1 (CF = 41.05) in dry periods and at stations S_1 (CF = 28.45), S_2 (CF = 10.45) and S_4 (CF = 59.55) in the rainy period; in Pb at stations S_1 (CF = 6.99) in the dry period and S_2 (CF = 12.56) in the rainy period and in Zn at station S_6 (CF = 9.15) in the dry period. The stations of considerable Cu contamination are located at station S_3 (CF =

Table 4. Values of the contamination factors (CF) in each station from January 2017 to October 2018.

Stations	Seasons	Fe	Mn	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S_1	DS	0.44	0.01	307.13	0.02	0.19	0.49	105.91	0.00	6.99	1.12
	RS	0.00	0.00	0.00	0.00	0.03	1.73	28.45	0.00	0.00	0.00
S_2	DS	0.24	0.03	0.25	0.00	0.11	0.09	2.63	0.00	1.16	1.17
	RS	0.14	0.00	0.00	0.00	0.03	6.35	10.45	0.00	12.56	0.00
S_3	DS	0.68	0.02	6.29	191.57	0.19	5.36	2.26	0.00	0.00	1.14
	RS	0.31	0.00	29.25	0.00	0.02	6.29	0.00	1.00	0.08	0.00
S_4	DS	0.27	0.00	0.68	0.17	0.01	0.12	0.00	0.00	0.03	0.50
	RS	0.00	0.00	0.00	0.00	0.02	3.09	59.55	0.00	0.00	0.00
S_5	DS	0.25	0.02	20.19	0.06	0.15	0.20	3.24	0.00	0.19	0.64
	RS	0.02	0.00	0.00	0.00	0.02	2.88	0.00	0.00	0.13	0.00
S_6	DS	0.27	0.04	389.95	0.00	0.19	0.87	2.28	0.00	1.26	9.15
	RS	0.02	0.00	0.00	0.00	0.03	3.51	0.00	0.00	0.14	0.00
T_1	DS	0.52	0.03	231.86	62.60	0.15	1.16	41.05	0.00	0.93	0.95
	RS	0.17	0.00	0.08	57.27	0.02	0.01	3.95	0.00	0.31	0.00
T_2	DS	0.49	0.05	1.07	0.45	0.14	2.74	0.00	0.39	0.10	0.94
	RS	0.26	0.00	0.00	24.83	0.03	0.55	3.22	0.00	2.27	0.00
T_3	DS	0.37	0.03	1.55	0.00	0.11	0.36	0.00	0.00	0.00	1.76
	RS	0.13	0.00	0.00	0.00	0.02	4.90	3.32	0.00	0.06	0.00

5.36) in the dry period and at stations S_6 (CF = 3.51) and T_3 (CF = 4.90) in rainy period and in Hg at stations S_5 (CF = 3.24) in the dry period and T_2 (CF = 3.22) in the wet period. The stations of moderate As contamination are located at stations T_2 (CF = 1.07) and T_3 (CF = 1.55) in the dry period; in Cu at station T_1 (CF = 1.16) in the dry period and at stations S_1 (CF = 1.73) and S_5 (CF = 2.88) in the rainy period; in Hg at stations S_2 (CF = 2.63), S_3 (CF = 2.26) and S_6 (CF = 2.28) in the dry period; in Pb stations S_2 (CF = 1.16) and S_6 (CF = 1.26) in the dry period and at station T_2 (CF = 2.27) in the rainy period and in Zn at stations S_1 (CF = 1.12)), S_2 (CF = 1.17), S_3 (CF = 1.14) and T_3 (CF = 1.76) in the dry period.

3.3. Enrichment Factor (EF)

Table 5 shows the enrichment factors calculated at each sampling site according to the two characteristic seasons (dry season and rainy season). Overall, the stations are characterized by variable enrichment most often of human origin (EF > 1.5). All the stations studied present an extremely severe enrichment in chromium (11.30 < EF < 320.12) and in copper (19.45 < EF < 22 475.74) in all seasons except station S_2 which experiences severe enrichment in Cr (EF = 8.56) in the rainy season. The great majority of sediments and agricultural soils present an extremely severe enrichment in Fe, Mn, As, Hg, Pb and Zn in the dry season as in the rainy season except in Mn, Cd and Ni at certain stations. During this

Table 5. Values of enrichment factors (EF) in each station from January 2017 to October 2018.

Stations	Seasons	Fe	Mn	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S_1	DS	726.55	17.75	510,416.19	40.98	320.12	819.07	176,008.37	0.00	11,622.38	1866.59
	RS	0.70	0.18	0.00	0.00	155.21	8408.87	138,511.45	0.00	1.29	0.00
S_2	DS	51.51	5.53	52.08	0.00	23.74	19.45	556.37	0.00	244.71	248.46
	RS	41.26	0.00	0.00	0.00	8.56	1937.21	3191.35	0.00	3834.15	0.00
S_3	DS	242.88	8.29	2248.06	68,452.20	69.32	1914.32	808.23	0.00	0.00	406.53
	RS	139.62	0.01	13,279.33	0.00	11.30	2857.31	0.00	455.08	38.46	0.00
S_4	DS	910.66	0.00	2276.07	584.61	27.71	410.71	0.00	0.00	87.41	1663.06
	RS	0.30	0.00	0.00	0.00	49.51	8696.19	167,352.49	0.00	0.99	0.00
S_5	DS	182.64	14.39	14,937.37	44.86	111.98	148.95	2397.39	0.00	141.20	470.49
	RS	93.86	0.00	0.00	0.00	80.09	13,154.89	0.00	0.00	607.00	0.00
S_6	DS	186.70	31.11	270,047.13	0.00	131.10	604.73	1578.37	0.00	875.84	6339.19
	RS	48.83	0.00	0.00	0.00	65.01	7500.54	0.00	0.00	296.41	0.00
T_1	DS	265.80	15.52	118,825.81	32,083.41	76.34	595.46	21,038.68	0.00	474.99	489.07
	RS	172.83	0.65	81.22	59,256.92	21.94	12.30	4081.91	0.00	319.51	0.00
T_2	DS	453.45	48.09	998.36	416.79	127.64	2557.92	0.00	362.26	94.24	882.69
	RS	352.84	0.30	0.00	33,349.53	43.32	738.14	4330.16	0.00	3046.75	0.00
T_3	DS	850.47	74.30	3522.80	0.00	253.72	806.82	0.00	0.00	0.00	4000.92
	RS	613.01	0.00	0.00	0.00	102.68	22,475.74	15,215.88	0.00	269.70	0.00

same dry season there is no enrichment in Cd at stations S_2, S_6 and T_3, in Hg at stations S_4, T_2 and T_3 and in Pb at stations S_3 and T_3. During the rainy season, there is no enrichment in metals and MTE for some stations, especially in Zn for all stations. The results indicate that there is an extremely severe enrichment in Hg ($3191.35 < EF < 167,352.49$) and in Pb ($38.46 < EF < 3834.15$) for most stations, in Fe at the level of stations S_2, S_5 and S_6, in As for stations S_3 and T_1 and in Cd at stations T_1 and T_2. EF calculations showed a natural alteration in Fe at station S_1 (EF = 0.70) and in Pb at stations S_1 (EF = 1.29) and S_4 (FE = 0.99). The order of average enrichment per season in metals and MTE in sediments and agricultural soils in the Ity-Floleu zone is established during the dry season as follows: As > Hg > Cd > Zn > Pb > Cu > Fe > Cr > Ni > Mn and during the rainy season as follows: Hg > Cd > Cu > As > Pb > Fe > Cr > Ni > Mn > Zn.

3.4. Sediment Pollution Index (SPI)

The results of the sediment pollution index (SPI) calculation contained in Table 6 show that the sediment stations can be classified in descending order of pollution by season according to the values of the SPI. During the dry season, the most polluted and least polluted stations are the following: $S_3 > S_1 > T_1 > S_6 > S_5 > S_4 > T_2 > S_2 > T_3$ and during the rainy season, we have the stations: $T_1 > T_2 > S_4 > S_1 > T_3 > S_2 > S_3 > S_5 > S_6$. In addition, the S_3 station, which is a sediment of

Table 6. Values of the sediment pollution index (SPI) in each station from January 2017 to October 2018.

Stations	Seasons	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	SPI
S_1	DS	6972.90	33.59	0.87	4.48	24,044.86	0.00	158.78	5.10	31,220.58
	RS	0.00	0.00	0.42	45.95	18,922.33	0.00	0.02	0.00	18,968.72
S_2	DS	0.71	0.00	0.06	0.11	76.01	0.00	3.34	0.68	80.91
	RS	0.00	0.00	0.02	10.59	435.98	0.00	52.38	0.00	498.96
S_3	DS	30.71	56,108.36	0.19	10.46	110.41	0.00	0.00	1.11	56,261.24
	RS	181.41	0.00	0.03	15.61	0.00	2.49	0.53	0.00	200.07
S_4	DS	31.09	479.19	0.08	2.24	0.00	0.00	1.19	4.54	518.34
	RS	0.00	0.00	0.14	47.52	22,862.36	0.00	0.01	0.00	22,910.03
S_5	DS	204.06	36.77	0.31	0.81	327.51	0.00	1.93	1.29	572.68
	RS	0.00	0.00	0.22	71.88	0.00	0.00	8.29	0.00	80.40
S_6	DS	3689.17	0.00	0.36	3.30	215.62	0.00	11.96	17.32	3937.74
	RS	0.00	0.00	0.18	40.99	0.00	0.00	4.05	0.00	45.21
T_1	DS	1623.30	26,297.87	0.21	3.25	2874.14	0.00	6.49	1.34	30,806.60
	RS	1.11	48,571.24	0.06	0.07	557.64	0.00	4.36	0.00	49,134.48
T_2	DS	13.64	341.63	0.35	13.98	0.00	1.98	1.29	2.41	375.27
	RS	0.00	27,335.68	0.12	4.03	591.55	0.00	41.62	0.00	27,973.00
T_3	DS	48.13	0.00	0.69	4.41	0.00	0.00	0.00	10.93	64.16
	RS	0.00	0.00	0.28	122.82	2078.67	0.00	3.68	0.00	2205.46

the river where effluents from the mining company SMI are discharged and the intense gold mining activities carried out around and on the river bed, is the most polluted in the dry season. The T_1 and T_2 stations, which are former farms, both located on the periphery of the SMI mining company where intense gold mining activities are carried out, are the most polluted during the rainy season. The heavy pollution noted in the various stations can be explained by anthropogenic inputs (mining extractions, agricultural activities and domestic garbage) due to drainage during the rainy season and mining effluents due to gold extraction. On the other hand, station S_1 which is a sediment of the Cavally river located upstream about 60 km is also heavily polluted.

3.5. Geoaccumulation Index (Igeo)

The Igeo values calculated at the station level are presented in Table 7. According to the results table, the Igeo values obtained indicate that the sediments are extremely polluted in As at the stations S_1 (Igeo = 7.68), S_6 (Igeo = 8.02) and T_1 (Igeo = 7.27) during the dry season. Stations S_3 (Igeo = 7.00) and T_1 (Igeo = 5.38) are also extremely polluted with Cd during the dry season and at station T_1 (Igeo = 5.25) during the rainy season. Likewise the sediments are extremely polluted in Hg at station S1 (Igeo = 6.14) during the dry season and at station S_4 (Igeo = 5.31) during the rainy season. Sediments and agricultural soils from highly

Table 7. Values of geoaccumulation indices (Igeo) in each station from January 2017 to October 2018.

Stations	Seasons	Fe	Mn	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S_1	DS	−1.78	−7.13	7.68	−5.93	−2.96	−1.61	6.14	*	2.22	−0.42
	RS	−13.36	−15.27	*	*	−5.56	0.20	4.25	*	−12.47	*
S_2	DS	−2.62	−5.84	−2.61	*	−3.74	−4.03	0.81	*	−0.37	−0.35
	RS	−3.47	−16.59	*	*	−5.74	2.08	2.80	*	3.07	*
S_3	DS	−1.14	−6.01	2.07	7.00	−2.95	1.84	0.59	*	*	−0.40
	RS	−2.29	−16.59	4.29	*	−5.91	2.07	*	−0.58	−4.15	*
S_4	DS	−2.46	*	−1.14	−3.10	−7.50	−3.61	*	*	−5.84	−1.59
	RS	−13.77	*	*	*	−6.41	1.04	5.31	*	−12.05	*
S_5	DS	−2.60	−6.27	3.75	−4.63	−3.31	−2.90	1.11	*	−2.97	−1.24
	RS	−6.19	*	*	*	−6.42	0.94	*	*	−3.50	*
S_6	DS	−2.48	−5.06	8.02	*	−2.99	−0.78	0.60	*	−0.25	2.61
	RS	−6.04	*	*	*	−5.62	1.23	*	*	−3.44	*
T_1	DS	−1.53	−5.63	7.27	5.38	−3.33	−0.37	4.77	*	−0.69	−0.65
	RS	−3.17	−11.23	−4.26	5.25	−6.14	−6.98	1.40	*	−2.28	
T_2	DS	−1.63	−4.87	−0.49	−1.75	−3.46	0.87	*	−1.95	−3.89	−0.67
	RS	−2.51	−12.69	*	4.05	−5.54	−1.45	1.10	*	0.60	*
T_3	DS	−2.00	−5.52	0.05	*	−3.75	−2.08	*	*	*	0.23
	RS	−3.49	*	*	*	−6.07	1.71	1.15	*	−4.67	*

*: impossible to determine.

polluted to extremely polluted in Hg are observed at station T_1 (Igeo = 4.77) during the dry season and during the rainy season in As at station S_3 (Igeo = 4.29), in Cd at station T_2 (Igeo = 4.05) and in Hg at station S_1 (Igeo = 4.25). Station S_5 is heavily polluted with As (Igeo = 3.75) during the dry season and station S_2 with Pb (Igeo = 3.07) during the rainy season. Moderately polluted to highly polluted sediments in As are located at station S_3 (Igeo = 2.07), in Pb at station S_1 (Igeo = 2.22) and in Zn at station S_6 (Igeo = 2.61) during the dry season and during the rainy season in Cu at stations S_2 (Igeo = 2.08) and S_3 (Igeo = 2.07), in Hg at station S_2 (Igeo = 2.80). Sediments and agricultural soils are moderately polluted in Cu at station S_3 (Igeo = 1.84) during the dry season and at stations S_4 (Igeo = 1.04), S_6 (Igeo = 1.23) and T_3 (Igeo = 1, 71) during the rainy season. Stations T_1 (Igeo = 1.40), T_2 (Igeo = 1.10) and T_3 (Igeo = 1.15) also show moderate pollution in Hg (Igeo = 1.39) during the rainy season.

3.6. Potential Ecological Risk Index (RI)

The results obtained in Table 8 show that the sediments present a severe ecological risk ($E_r^i > 320$) linked to As at stations S_1 ($E_r^{\text{As}} = 3071.33$) and S_6 ($E_r^{\text{As}} = 3899.50$) in the dry season, linked to to Cd at station S_3 ($E_r^{\text{Cd}} = 957.86$) in the dry season and linked to Hg at station S_1 ($E_r^{\text{Hg}} = 4236.38$) in the dry season

Table 8. Values of the ecological risk coefficient (E_r^i) for each element and the ecological risk index (RI) associated with each station in both seasons.

Stations	Saisons	E_r^i								RI
		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	
S_1	SS	3071.33	0.74	0.39	2.46	4236.38	0.00	34.97	1.12	7347.39
	SP	0.00	0.00	0.06	8.64	1138.07	0.00	0.00	0.00	1146.77
S_2	SS	2.46	0.00	0.22	0.46	105.24	0.00	5.79	1.17	115.35
	SP	0.00	0.00	0.06	31.73	418.14	0.00	62.79	0.00	512.72
S_3	SS	62.91	5747.17	0.39	26.79	90.48	0.00	0.00	1.14	5928.87
	SP	292.50	0.00	0.05	31.47	0.00	5.01	0.42	0.00	329.45
S_4	SS	6.80	5.24	0.02	0.61	0.00	0.00	0.13	0.50	13.30
	SP	0.00	0.00	0.04	15.47	2381.99	0.00	0.00	0.00	2397.50
S_5	SS	201.86	1.82	0.30	1.01	129.59	0.00	0.95	0.64	336.17
	SP	0.00	0.00	0.04	14.41	0.00	0.00	0.66	0.00	15.11
S_6	SS	3899.50	0.00	0.38	4.37	91.17	0.00	6.32	9.15	4010.89
	SP	0.00	0.00	0.06	17.54	0.00	0.00	0.69	0.00	18.30
T_1	SS	2318.65	1878.13	0.30	5.81	1642.11	0.00	4.63	0.95	5850.59
	SP	0.79	1718.24	0.04	0.06	157.81	0.00	1.54	0.00	1878.48
T_2	SS	10.68	13.38	0.27	13.69	0.00	1.94	0.50	0.94	41.41
	SP	0.00	745.00	0.06	2.75	128.98	0.00	11.34	0.00	888.13
T_3	SS	15.53	0.00	0.22	1.78	0.00	0.00	0.00	1.76	19.30
	SP	0.00	0.00	0.04	24.51	132.75	0.00	0.29	0.00	157.60

and at stations S_1 ($E_r^{Hg} = 1138.07$), S_2 ($E_r^{Hg} = 418.14$) and S_4 ($E_r^{Hg} = 2381.99$) in the rainy season. Sediments also present a very high ecological risk ($160 < E_r^i \le 320$) linked to As at station S_5 ($E_r^{As} = 201.86$) in the dry season and at station S_3 ($E_r^{As} = 292.50$) in the rainy season. Sediments also present a considerable ecological risk ($80 < E_r^i \le 160$) linked to Hg at stations S_2 ($E_r^{Hg} = 105.24$), S_3 ($E_r^{Hg} = 90.48$), S_5 ($E_r^{Hg} = 129.59$) and S_6 ($E_r^{Hg} = 91.17$) in the dry season. The sediments present a moderate ecological risk ($40 < E_r^i \le 80$) linked to As at station S_3 ($E_r^{As} = 105.24$) in the dry season and linked to Pb at station S_2 ($E_r^{Pb} = 105.24$) in season rainy.

The results indicate that agricultural soils present a severe ecological risk linked to As at station T_1 ($E_r^{As} = 2318.65$), linked to Cd at station T_1 ($E_r^{Cd} = 1878.13$) and linked to Hg at station T_1 ($E_r^{Hg} = 1642.11$) during the dry season and during the rainy season linked to Cd at stations T_1 ($E_r^{Cd} = 1718.24$) and T_2 ($E_r^{Cd} = 745.00$) in the rainy season. Agricultural soils show a considerable ecological risk linked to Hg at stations T_2 ($E_r^{Hg} = 128.98$) and T_3 ($E_r^{Hg} = 132.75$) in the rainy season. There is also a moderate ecological risk associated with Hg at station T_1 ($E_r^{Hg} = 157.81$) in the rainy season.

The results indicate that the vast majority of sediments and agricultural soils analyzed present a low ecological risk linked to metals (Cr, Cu, Ni, Pb, Zn), since the E_r^i values are less than 40 at all stations, that this is in the rainy and dry season except in Pb at station S_2 in the rainy season where there is a moderate ecological risk.

3.7. Relationship between TME in Sediments and Agricultural Soils

The correlation matrix between sediment variables and agricultural soils recorded in Table 9 reveals that iron is well positively correlated with Cadmium (r = 0.904) and copper (r = 0.795). Manganese is positively correlated with mercury (r = 0.690) and zinc (r = 0.753). Cadmium is positively correlated with copper (r = 0.846) and nickel (r = 0.746). Arsenic correlates positively with zinc (r = 0.737). Copper is positively correlated with nickel (r = 0.675).

The results of the PCA in the space of the variables of the factorial design (F1-F2) allow us to indicate that this design expresses 64.08% of the expressed variance (Figure 3). The factor F1 (36.62%) is determined by a first grouping of variables which takes into account Fe, Ni, Cd and Cu which is opposed to Hg and Pb. The second component (F2) represents 27.46% of the totality of the variance. It strongly associates Cr, Mn, As and Zn (2nd grouping).

4. Discussion

4.1. Contamination Factor (CF)

The calculation of the contamination factor (CF) showed a sensitive contamination was not noted for Fe, Mn, Cr and Ni in all the stations during the rainy season but we observe a low contamination during the dry season (CF < 1). The high values of CF > 3 concerning the elements As (6.29 to 389.95), Cd (24.83 to 191.57), Cu (3.09 to 6.29) and Hg (3.22 to 105.91) reveal a very strong contamination in several stations of the study area during certain dry or rainy seasons.

Table 9. Correlation matrix between ETM.

Variables	Fe	Mn	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Fe	1									
Mn	−0.067	1								
As	−0.270	0.338	1							
Cd	0.904	0.008	−0.139	1						
Cr	0.338	0.375	0.574	0.379	1					
Cu	0.795	0.004	−0.284	0.846	0.212	1				
Hg	−0.299	−0.690	0.261	−0.410	−0.304	−0.442	1			
Ni	0.630	−0.255	0.028	0.746	0.203	0.675	−0.009	1		
Pb	−0.241	−0.236	0.064	−0.160	0.094	0.032	0.108	−0.120	1	
Zn	−0.192	0.753	0.737	0.041	0.382	0.027	−0.281	0.018	−0.100	1

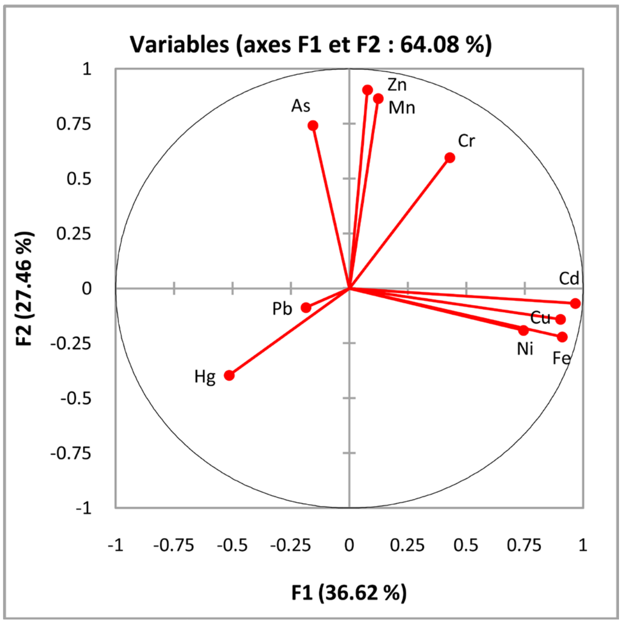

Figure 3. Representation of ETM contents in two dimensions according to factors F1 and F2 in a PCA.

This pollution is linked to the impact of human activities (mining and agricultural practices) along the rivers. These FCs are greater than those of the sediments in Oued Chéliff and Oued Rhiou in Algeria, which undergo the same types of contamination (Benkaddour, 2018).

4.2. Enrichment Factor (EF)

The results of the enrichment factor made it possible to understand the general way that the stations are characterized by enrichment variables most often of anthropogenic origin (EF > 1.5). The stations studied present an extremely severe enrichment in chromium (11.30 < EF < 320.12) and in copper (19.45 < EF < 22,475.74) in all seasons. Most sediments and agricultural soils present a severe enrichment in Fe, As, Cd, Hg, Pb and Zn in the dry season as in the rainy season except in Mn and Ni in certain cases. The main source of this severe enrichment is linked to mining and agricultural activities (the use of pesticides and fertilizers) located in the sampling area. These enrichments testify to a strong pollution of anthropogenic origin, hence the interest of coring to study the history of this pollution. According to Zhang & Lui (2002), an EF between 0.05 and 1.5 indicates that the metal is entirely crystallized in the sediment, while an EF greater than 1.5 is of anthropogenic origin. In this study, apart from Ni in some cases, the enrichment of the elements studied in sediments and agricultural soils is greater than 1.5, suggesting an anthropogenic origin.

4.3. Sediment Pollution Index (SPI)

The SPI made it possible to classify and note that the sediments and agricultural soils of the various stations studied are dangerous in all seasons. The strong pollution of the sediments can be explained by anthropogenic inputs due to the drainage emitted from the intense gold mining activities envisaged in the vicinity and even on the bed of the river and by effluents from the mining company SMI (stations S_2, S_3, T_1 and T_2). As for the pollution of agricultural soils, it is linked to agricultural practices and the pollutants can be found in the sediments by leaching. On the other hand, the sediment of the Cavally river from the S_1 station located upstream about 60 km is also heavily polluted. These SPI results compared to those carried out by Yapi (2015) in the gold mining environment in the sub-prefecture of Hiré (Côte d'Ivoire) show that the vast majority of sediments and agricultural soils in the area studied are the most dangerous whatever the season.

4.4. Geoaccumulation Index (Igeo)

The evaluation of the metal contamination of sediments and agricultural soils by the Igeo calculation indicates that the sediments of the surface water of the stations visited most often experience pollution (extreme or moderate) in As, Cd, Cu, Hg and Zn in dry or rainy season except in Pb in certain cases. Our results were compared with those of the Mediterranean Moulouya River (Morocco), whose research was based on the evaluation of the metallic contamination of sediments by the Igeo calculation. For all the other stations, the sediments are unpolluted in Fe, Mn, Cr and Ni. We found that the sediments of the Cavally River have a higher degree of pollution than those of the Moulouya River (Morocco) (Iavazzo et al., 2012) which also experiences strong anthropogenic pressure exerted along these rivers. Similarly, another comparison was made with one of the largest rivers in Morocco (Oued Sebou) subjected to strong anthropogenic pressure (Hayzoun, 2014), the pollution recorded in the sediments of the Floleu river is lower than that of the Oued Sebou but that of the Cavally river studied is still higher than that of the Oued Sebou in particular for the following elements: As and Cd.

4.5. Potential Ecological Risk Index (RI)

Over the entire region, the results of the potential ecological risk (RI) index indicate that all sediments and agricultural soils analysed present a low ecological risk linked to metals (Cr, Cu, Ni, Pb, Zn) in level of all stations, whether in wet and dry periods except in Pb at the level of station S_2 in rainy season where there is a moderate ecological risk. However, the results obtained show that the sediments and agricultural soils analysed present severe and very high ecological risks linked to As, Cd and Hg detected at certain stations of sediments and agricultural soils during the two seasons. All the sediments and agricultural soils in the present study indicate an index of potential ecological risk lower than that of the sediments of the Potou lagoon (Côte d'Ivoire) which has a value RI = 2713.9 impacted by human activities according to the work of Traoré (2016).

4.6. Origin of Pollution of Sediments and Agricultural Soils in Ity's Mining Environment

Analysis of the results of the PCA shows that the first principal component (F1) very largely dominates the second and represents about 64.08% of the total variance. It shows a 1st grouping composed of Fe, Cu, Cd and Ni which is opposed to Hg and Pb. The elements of this component can have a natural origin coming from the pedogeochemical background and from volcanic and anthropogenic eruptions from gold mining extractions, domestic and agricultural effluents (organic or mineral fertilizers, pesticides, etc.). We also notice a strong association of Fe, Cu, Cd and Ni with this F1 component, reflecting their great affinity. The presence of these elements would be of anthropogenic origin. The second component (F2) represents 27.46% of the total variance. It strongly associates As, Mn and Zn (2nd grouping). The relationship between these elements would show a strong influence of anthropogenic origin. From this analysis, we retain that the pollution of sediments and agricultural soils in the study area seems to reflect the mixture of anthropogenic and natural inputs but strongly dominated by anthropogenic inputs. These occasional or diffuse inputs of ETM in agricultural soils, which have existed for years, even centuries, in aquatic environments are stored in certain sediment compartments (Salomons, 1984; Tessier, 2012) after runoff following thunderstorms and are increasing due to the intensity of human activities (mining and agricultural).

5. Conclusion

The results obtained in this work allowed an assessment of the metallic pollution of sediments and agricultural soils in the Ity-Floleu zone. The calculation of several factors (contamination and enrichment factors) and indices (indices of sediment pollution, potential ecological risk and geoaccumulation) was used for the study of sediments and agricultural soils. The stations studied show an extremely severe enrichment in chromium and copper in all seasons. The evaluation of the metallic contamination of sediments and agricultural soils by the Igeo calculation shows that the sediments and agricultural soils of the stations visited most often experience pollution (extreme or moderate) in As, Cd, Cu, Hg and Zn in season dry or rainy except in Pb in certain cases. Across the region, the results obtained show that the sediments and agricultural soils analysed present ecological risks (very high and severe) linked to the metal Cd detected at several stations during the two seasons. The SPI made it possible to classify and note that the sediments and agricultural soils of the various stations studied are dangerous in all seasons. The dominant phenomenon in the acquisition of pollutants is linked to the intense gold mining activities carried out near and even on the river bed. This serious pollution due to human activities in this region can have consequences on agricultural products from these soils and fish from the Cavally River which could constitute risks of bioaccumulation and toxicity and generate negative impacts on the health of the population.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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