Assessment of Chemical Contamination of Sediments and Agricultural Soils by Gold Mining Activities: Case of the Ity-Floleu Zone, Zouan-Hounien Sub-Prefecture, West of Côte d'Ivoire

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Abstract: In this work, the concentrations of nutrients $(NO_3, NO_2, NH_4^+, PO_4^{3-}, SO_4^{2-})$, major (Ca, Fe, K, Mg, Mn and Na) and traces (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) were measured in different seasons over two successive years. The results show that the nutrient content in sediments and agricultural soils are generally higher in the rainy season than in the dry season. The levels of As in some stations of sediment and agricultural soils greatly exceed the standards set by the WHO during the two seasons, those of Cd in some stations of sediment and agricultural soils in the dry season and those of Hg in certain agricultural soils in the season. dried. The presence of other prohibited products present in certain soils demonstrates the fraudulent use of formulations containing these substances. Principal component analysis (PCA) and ascending hierarchical classification (AHC) have shown that pollution of these receiving environments is of natural origin but would be greatly intensified by human activities. This pollution could constitute risks of bioaccumulation and toxicity and generate negative impacts on the health of the population.

Keywords: anthropogenic activities, Cavally watershed, pollution, sediments, agricultural soils

1. Introduction

The pollution of the aquatic environment by toxic substances of anthropogenic origin, in particular metallic trace elements, is one of the major problems facing society today. These pollutants contaminate aquatic systems from point and diffusion sources (drainage, wastewater, industrial and agricultural wastewater) [1], [2]. In aquatic systems, sediments are studied for their role as indicators of environmental contamination, because sediments have the capacity to fix pollutants, in particular trace metal elements (TME), then to constitute a reservoir, then to become a potential source of water pollutants [3]. In fact, the pollution of aquatic ecosystems is not limited to one of the compartments (water, sediment or soil) and is not limited to the area close to the source of pollution. Unlike organic pollutants, TMEs hardly undergo biological or chemical degradation reactions and can accumulate in the food chain [4], [5]. Aquatic organisms can accumulate certain environmental pollutants at concentrations much higher than the concentration detected in the water column [5]. Numerous studies have shown the potential action of fish consumption in preventing cardiovascular disease and coronary heart disease [6], stroke [7], certain cancers [8], depression [9], and some neurodegenerative diseases [10].

In Côte d'Ivoire, mineral pollution in the ecosystem has attracted the attention of many researchers [11]-[13]. The environmental impacts associated with Ivorian mining activities are developing in a worrying manner. This leads to environmental degradation, the most obvious of which are: deforestation, loss of biodiversity, pollution and the impact on community and domestic sanitation. This concern affects the sub-prefecture of Zouan-Hounien, a town in the west of the Ivory Coast, where significant mining activity has been carried out since colonial times. This mining activity is materialized by several artisanal gold mining sites scattered throughout the Zouan-Hounien sub-prefecture and a gold mine, the Ity mine, fifteen (15) kilometers from the city. Therefore, it is important to study the results of contaminants in various abiotic and biological compartments and to determine the mechanisms that limit their transfer, capacity for bioaccumulation and toxic effects on different levels of biological integration. In this context, we assessed the level of contamination of sediments and agricultural soils in the Ity-Floleu area by nutrient salts, pesticides, major elements and metallic traces resulting from human activities.

2. Material and method

2.1. Study Area

Ity is a village located 15 km south-east of Zouan-Hounien

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(Ivory Coast), its county seat. 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 [14]. Located in the west of the Ivory Coast, the Cavally watershed is between $6 \circ 47$ and $6 \circ 52$ north latitude, and between $8 \circ 5$ and $8 \circ 6$ west longitude. The basic products are mainly coffee, cocoa, palm oil, cassava, etc.

The Zouan-Hounien region belongs to a mountain climate with alternation of two rainy seasons: large dry season from November to February, small rainy season from March to July, small dry season from late July to late August, large 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.

The local geology is difficult to define, as there is no outcrop in the area. 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 [15]. 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 [16]. Erosion, violent, is a feature of rejuvenation of these soils [17].

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2.2. Collection of samples

The sediment samples were taken from the waterbeds of the Cavally River, the river and the paddy fields (Figure 1). Agricultural soils have also been sampled where mining activities (around SMI and gold washing) are practiced. Measurements were performed twice during the dry season and twice during the rainy season over a period of an annual cycle for two consecutive years at the study site. Sampling points were located using a Garmin etrex 20 type Global Positioning System (GPS) receiver.

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

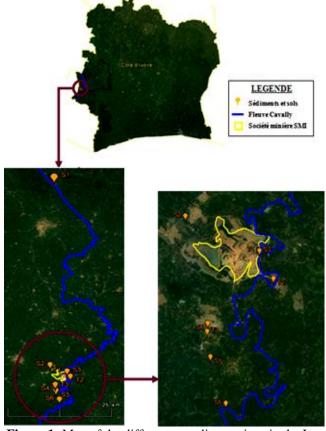


Figure 1: Map of the different sampling stations in the Ity-Floleu study area

2.3 Sample analysis

The measurements of nitrates (NO₃⁻), nitrites (NO₂⁻), ammonium ion (NH₄⁺), phosphates (PO₄³⁻) and sulfates (SO₄²⁻) were analyzed by colorimetric assay. The major elements (Ca, Fe, K, Mg, Mn and Na) and the mineral trace elements (As, B, Cd, Cr, Cu, Hg, Ni, Pb and Zn) were analyzed by the spectrophotometric method (precision \pm 1nm) using the Spectra 110 brand ICP-AAS method. The GC/MS was used for the analysis of all the molecules of the pesticide studied. The analyses were carried out at the Center for Research in Oceanology (CRO) in Abidjan (Côte d'Ivoire).

2.4. Data and Methods

The results are expressed as means with standard deviations calculated with Excel 2007 software. The comparison of means, correlations, Principal Component Analyses (PCA) and Ascending Hierarchical Classification (AHC) were made using the XLSTAT statistical software version 2016.02.27444.

3. Results

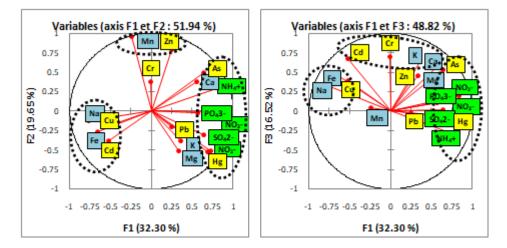
The seasonal values of nutrient salts $(NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, SO_4^{2-})$, major elements (Ca, Fe, K, Mg, Mn and Na) and trace elements (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) measured in sediments and agricultural soils of the Ity mining environment from January 2017 to October 20, 2018 are shown in the following tables.

Table 1: Seasonal variation in nutrient salt values (in mg/L) of sediments and agricultural soils

Stations	Seasons	NO ₂ ⁻	NO ₃	NH4 ⁺	PO4 ³⁻	SO4 ²⁻
S_1	SS	0.123	6.525	0.900	0.767	26.490
-	SP	0.342	25.300	2.156	2.290	107.090
S_2	SS	0.125	1.267	0.647	0.430	14.779
_	SP	0.215	4.400	1.324	0.300	78.850
S ₃	SS	0.086	0.865	0.089	0.019	58.985
	SP	0.139	1.700	0.807	1.730	57.720
S_4	SS	0.130	3.721	0.090	0.292	9.498
	SP	0.234	3.800	2.406	1.080	148.260
S_5	SS	0.006	0.756	0.199	0.065	16.410
	SP	0.079	3.800	2.257	1.950	89.260
S ₆	SS	0.084	0.986	0.544	0.102	25.367
	SP	0.102	11.900	2.332	1.520	88.640
T ₁	SS	0.098	0.048	0.052	0.547	7.300
	SP	0.019	0.800	0.581	0.140	29.760
T ₂	SS	0.011	0.857	0.246	0.038	6.802
	SP	0.135	2.300	2.151	2.600	69.660
T ₃	SS	0.003	0.199	0.654	0.031	14.333
	SP	0.056	1.800	0.900	0.390	53.490

Table 2: Seasonal variation of major elements (mg/kg) of sediments and agricultural soils

Stations	Seasons	Ca	Fe	K	Mg	Mn	Na
S_1	S ₁ SS		13504.65	82.23	26.00	5.63	8.52
	SP	691.68	4.41	391768.94	1135.93	0.02	94669.37
S_2	SS	11.28	7523.82	31.54	19.83	13.78	< 0.010
	SP	579.62	4175.00	377043.94	1121.90	0.01	90595.89
S ₃	SS	4.53	20996.60	6.23	12.09	12.23	< 0.010
	SP	589.87	9500.00	383894.84	1203.03	0.01	96689.96
S_4	SS	40.13	8404.31	39.89	32.96	< 0.005	< 0.010
	SP	664.12	3.31	381408.25	1317.99	< 0.005	21153.23
S_5	SS	30.84	7623.99	211.16	91.52	10.25	2.36
	SP	567.35	635.00	357991.83	1130.77	< 0.005	89068.64
S ₆	SS	376.62	8327.97	98.55	33.83	23.68	11.90
	SP	676.02	705.56	378298.08	1076.71	< 0.005	83616.13
T ₁	SS	48.71	16021.44	71.91	47.26	15.96	< 0.010
	SP	751.28	5160.10	464061.19	1429.53	0.33	96711.18
T ₂	SS	62.59	14988.07	234.42	102.54	27.12	7.21
	SP	456.08	8116.00	286825.69	803.81	0.12	90340.46
T ₃	SS	104.67	11581.13	118.26	43.27	17.26	< 0.010
	SP	366.65	4130.00	222685.25	566.83	< 0.005	95120.91



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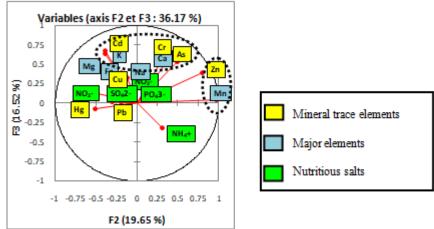


Figure 2: Representation of the concentrations of ETM, major elements, nutrient salts and in situ parameters for agricultural sediments and soils in three dimensions according to factors F1, F2 and F3 in a PCA

Table 5: Seasonal variation of trace initial elements (mg/kg) in sediments and agricultural sons									
Stations	Seasons	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
S_1	SS	614.27	0.00	6.74	7.05	5.93	< 0.005	118.89	58.41
	SP	< 0.005	< 0.0005	1.12	24.70	1.59	< 0.005	0.00	< 0.010
S_2	SS	0.49	< 0.0005	3.93	1.32	0.15	< 0.005	19.67	61.10
	SP	< 0.005	< 0.0005	0.98	90.74	0.59	< 0.005	213.50	< 0.010
S ₃	SS	12.58	19.54	6.79	76.61	0.13	< 0.005	< 0.005	59.16
	SP	58.50	< 0.0005	0.87	90.00	< 0.0001	18.64	1.44	< 0.010
S_4	SS	1.36	0.02	0.29	1.75	< 0.0001	< 0.005	0.44	25.84
	SP	< 0.005	< 0.0005	0.62	44.25	3.33	< 0.005	0.01	< 0.010
S ₅	SS	40.37	0.01	5.30	2.88	0.18	< 0.005	3.24	33.06
	SP	< 0.005	< 0.0005	0.61	41.20	< 0.0001	< 0.005	2.26	< 0.010
S ₆	SS	779.90	< 0.0005	6.63	12.49	0.13	< 0.005	21.50	476.00
	SP	< 0.005	< 0.0005	1.06	50.17	< 0.0001	< 0.005	2.36	< 0.010
T ₁	SS	463.73	6.39	5.21	16.62	2.30	< 0.005	15.76	49.63
	SP	0.16	5.84	0.74	0.17	0.22	< 0.005	5.25	< 0.010
T ₂	SS	2.14	0.05	4.78	39.14	< 0.0001	7.21	1.71	49.11
	SP	< 0.005	2.53	1.13	7.86	0.18	< 0.005	38.57	< 0.010
T ₃	SS	3.11	< 0.0005	3.91	5.09	< 0.0001	< 0.005	< 0.005	91.71
	SP	< 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

Table 3: Seasonal variation of trace mineral elements (mg/kg) in sediments and agricultural soils

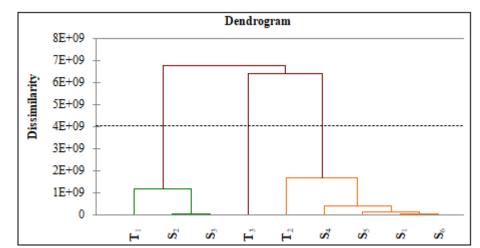


Figure 3: Dendrogram of the classification of sediments and agricultural soils in the region

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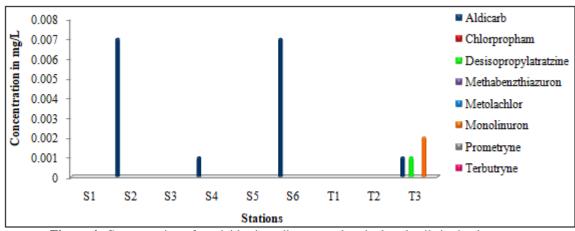


Figure 4: Concentration of pesticides in sediments and agricultural soils in the dry season

4. Discussion of Results

The results of the analyses (Table 1) showed that the degradation of the quality of sediments and agricultural soils in the study area is mainly due to alterations by sulphates (from 6.802 to 148.260 mg/L) and to a lesser degree alterations of nitrates (between 0.048 and 25.300 mg/L). The origin of sulphates always seems to be the formation and accumulation of iron sulphide, which in sediments appears in the presence of sulfur when the level of available (reactive) iron increases [18].

From the observation of Table 2, we retain that the sediments and agricultural soils contain many major elements, the most dominant of which are potassium (K) and sodium (Na) especially in the rainy season with respective averages 360 442.00 mg/kg and 84218.42 mg/kg and iron (Fe) in the dry season averaging 12108.00 mg/kg.

Table 3 shows that the concentrations of As, Cu, Pb and Zn in sediments and agricultural soils are relatively high in certain stations studied. The levels of As in some stations of sediment and agricultural soils exceed the standards set by WHO during both seasons, those of Cd in a few stations of sediment and agricultural soils in the dry season and those of Hg in certain agricultural soils in the dry season.

Figures 2 and 3 show that although there are different sources of sediment pollution, some stations have identical sources of pollution. The association of Fe and Na with F1 translates that this component expresses the action of clay minerals and iron oxides in the control of ETMs such as Cu and Cd. Indeed, Mn and Fe are generally associated with clayey and fine silty granulometric fractions, as well as iron oxides and hydroxides. Other work [19], [20] has shown an increase in trace elements during the enlargement of micas and chlorites.

ETMs are related to the main components of sediments (clays, carbonates, oxides, organic matter and residual mineral fractions) [21]. After a dry season, the intense floods favor the suspension, the remobilization and the transport of ETMs adsorbed in the sediments [22]. The geomorphology of surface water can contribute to sedimentation and therefore to the storage of ETM (as in the case of meanders) [23]. The Cavally River and the rivers in the study area are

constantly threatened by a series of natural and anthropogenic influences [5] during periods of flooding.

Figure 4 reveals that some of these phytosanitary products, in particular metabenzthiazuron and monolinuron, aldicarb are banned in the European Union for their toxicity and their ecotoxicity are used fraudulently in the study area. Authors [24] have also confirmed the fraudulent use of organochlorines (endosulfan, lindane, heptachlor) in coffee and cocoa production areas, in particular Buyo, Grand-Lahou and Yamoussoukro. Thus the agricultural products from these soils could constitute the risks of bioaccumulation and toxicity and generate negative impacts on the health of the population.

5. Conclusion

The levels of As, Cd and Hg in some agricultural sediment and soil stations exceed the standards set by WHO during both seasons. The presence of pesticides in certain soils highlights the fraudulent use of certain substances. The statistical tests (PCA and AHC) showed several sources of pollution. 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 pollution could constitute risks of bioaccumulation and toxicity and generate negative impacts on the health of the population.

6. Conflicts of interest

The authors declare no conflicts of interest in the publication of this article.

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