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Pollution and Ecological Risk Assessment of Traces Metals in the Sediments of Gold Mining in Savanna District (Korhogo and Tengrela), Côte d'Ivoire

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Abstract: Metallic contamination of the environment by mining activities constitute a major problem, regarding the exposure risks of the populations and wildlife. Unfortunately, few data are available on metallic contamination of water resources in West Africa. The present study aims to understand the distribution, mobility and potential toxicity of some trace metals (Co, Cr and Zn) in mining sediments and their impact on human health. Sediment samples were analysed for total metal concentration by acid digestion and then by chemical fractionation of trace metals using the modified BCR sequential extraction method. The pollution index results for Cr, Co, and Zn, in the study area sediments, indicated the spread of heavy metal pollution. The sequential extraction demonstrated that most of the trace metals such as Cr (71.02-84.32%), Co (62.00-72.83%) and Zn (66.61-72.01%) were present in a residual form. Overall, Co, Cr and Zn exhibited low individual contamination in the studied sediments. Indeed, their IFC values were less than 1. The GCF results (GCF <6) showed an overall low risk potential related to the complex influence of metals on the environment. Generally, the MRI values for trace metals (Co, Cr and Zn) are below 150, indicating a low environmental risk in all the studied mining areas.

Keywords: Trace Metal, Fractionation, BCR-Sequential Extraction, Potential Ecological Risk

1. Introduction

Metallic contamination of the environment from mining activities remains a major problem due to the non-biodegradability and toxicity of metals [1, 2]. During these mining activities, waste and wastewater are generated and dust is emitted too. This obviously results in severe contamination of the mining areas and its surroundings [3]. The emission of trace metals can act as contaminant of groundwater, surface water, and agricultural soils, leading to human contamination through the food chain [4]. Therefore, contamination of soils, sediments, atmosphere, surface waters, and biota with trace metal elements is a fundamental concern in mining areas [5]. Sediments in aquatic environments act as reservoirs or sinks for metals and play a key role in metal remobilization [6]. Therefore, the study of trace metal contamination in sediments is an important asset. Thus, metal contamination levels in air, soil, sediment and water have been reported to be significantly higher in areas affected by mining activities in many countries such as China [7, 8], Tunisia [9], South Africa [10] and Morocco [11].

However, several of these trace metals like chromium (Cr), cobalt (Co) and zinc (Zn) can cause deleterious effects on the environment and obviously on human health beyond their tolerance values [12]. Metals such as Co, Cr, and Zn are essential minerals that play a precious role in the metabolic and physiological activities of the body. Yet, their concentrations should not exceed the permissible limit or else damage the target tissues. When Co, Cr, and Zn exceed the body's amount, they can cause damage to DNA, lipids, proteins, and carbohydrates in tissues that eventually lead to oxidative stress [13]. However, in West Africa, Côte d'Ivoire is not spared from this mining contamination. More and more, gold mining activities are developing throughout the country. More specifically in the northern part of the country in the savannah district (Korhogo and Tengrela), where these mining activities are materialized by artisanal gold panning and industrial exploitation sites. They are distinguished by the coexistence of large-scale mining by big companies, which is an important source of income for the country, and small-scale mining by individuals [14]. Thus, some artisanal gold mining sites are also important sources of trace metal contamination, with mercury being used to extract gold from ores [15]. In these mining areas, villagers use slow-moving rivers for drinking water without treatment. These surface waters are also used for crop irrigation and as washing facilities for artisanal gold mining [16]. In these mining areas, local people live off many traditional food crops of sorghum, maize, lowland rice, peanuts, and yams. Despite the negative effects of trace metals on human health in mining areas of South America, Asia, and Africa, no studies were conducted on the distribution and mobility of trace metals in the savannah district where several mining sites are located. Therefore, a study of the degree of metal contamination in this district is necessary to establish baseline data to protect the populations living in the mining environment. Indeed, several studies have been conducted in different mining sites in Côte d'Ivoire showing trace metal contamination of sediments [17, 18]. However, these studies were limited to the determination of total trace metal concentrations in the studied sediments. Yet, several studies have shown that the determination of total concentration of trace metals in sediments does not provide any information regarding its mobility, bioavailability or toxicity [19, 20]. Indeed, depending on the physicochemical conditions of the environment (pH, salinity, redox potential, ionic strength, etc.), trace metals are likely to be released into the water column [21]. Mobilization of these trace metals in the water column can lead to their accumulation in aquatic species consumed by humans. Thus, much attention must be paid to studying the chemical speciation of trace metals in sediments. In fact, sequential extraction technique can detect the geochemical presence of trace metals providing information on their sources, existence forms, bioavailability and mobility in natural spaces [22]. The objective of this work is to understand the distribution, mobility and potential toxicity of trace metals (Co, Cr and Zn) in sediments near mining areas in northern Côte d'Ivoire (Korhogo and Tengrela), through the study of the chemical speciation of trace metals (Co, Cr and Zn). To achieve this objective, we will first determine trace metal pollution indices (the geoaccumulation index (Igeo) and enrichment factor (EF)) and sediment mobility. Next, we will assess the ecological risks of trace metals (Cr, Co and Zn) with speciation indices (ICF, GCF, MRI and RAC).

2. Material and Methods

2.1. Description of Study Area

The savanna district (90 25 '00 "North and 50 35' 00" West) is located in northern Côte d'Ivoire, close to Mali and Burkina Faso. It has an area of 40323 km² and an estimated population of 1.607 million inhabitants in 2014 [23]. The climate is Sudanese hot and dry with two distinct seasons: a rainy season from mid-June to October and a dry season from November to mid-June. The dry season is characterized by the presence of harmattan (December to February) with an average temperature of 30°C. In northern Côte d'Ivoire, the geology is predominately made up of feral sols. These soils are derived from felsic or intermediate parent rocks (granite, gneiss, phyllite and schist) of the underlying Precambrian rocks. The rocks are mainly composed of green schist of low metamorphic grade, bounded on either side by tectonized granitoid gneiss Terrans. The dominant lithological unit in the area consists of mafic rocks and dislocated clastic sediments, intercalated with volcano-sedimentary formations and intruded by a large body of granodiorite [24]. Korhogo lies in the Bandama River basin, while Tengrela is drained by the Bagoé River. The Bandama River is the longest and the largest river in Côte d'Ivoire. It takes its source in the northern Côte d'Ivoire, between Korhogo and Boundiali at an altitude of 480 m and flows into the lagoon of Grand-Lahou and the Gulf of Guinea in the south. With a length of 1050 km, its catchment area covers 97,500 km^2 with an annual average discharge about 263 m^3/s [25]. The Bagoe River is a small river located in the north of Côte d'Ivoire. It originates from the Kokoum region near Côte d'Ivoire–Mali borderland with an altitude of 425 m and passes through Tengrela (Côte d'Ivoire). The length of the Bagoé River is approximately 230 km, the drainage basin is 4740 km^2, and the annual average discharge is 170 m^3/s [26].

The savannah district is well known through activities such as livestock, cotton, cashew and food activities [23], in addition to a number of industrial and artisanal and small-scale gold mining extractions [24]. In this study, two cities have been selected in the savannah district (Korhogo and Tengrela) to get an idea of the state of contamination in metallic trace elements on their environments. The selected sites are the gold of Korhogo zone (R_1 to R_5 station, M_1 to M_5 and K_1 to K_{10}) and the Tengrela's gold zone (T_1 to T_{10} station). This was favored by the establishment of two gold mining industries, Ran gold (Korhogo) and Perseus Mining (Tengrela) in these cities, as well as the existence of several artisanal and small-scale gold extractions.

The Tongon mine is located in the sub-prefecture of M'bengue more than 65 km from the city of Korhogo and 2.5 km from the village of Tongon. This open-pit mine covers an area of 1000 km^2 and is 55 km south of the Malian border. To carry out our study several samples were collected in the gold mining zones of Korhogo. Stations R_1 to R_5 are very far from the Rand gold industrial extraction in the classified forest Badenou and not far from an abandoned artisanal mining area. On the other hand, the M_1 to M_5 stations are located in the vicinity of the Rand gold industry, an active open pit gold mining mine. The other stations are located in two artisanal gold mining villages Taoura (K_1 to K_5) and Bevogo (K_6 to K_{10}).

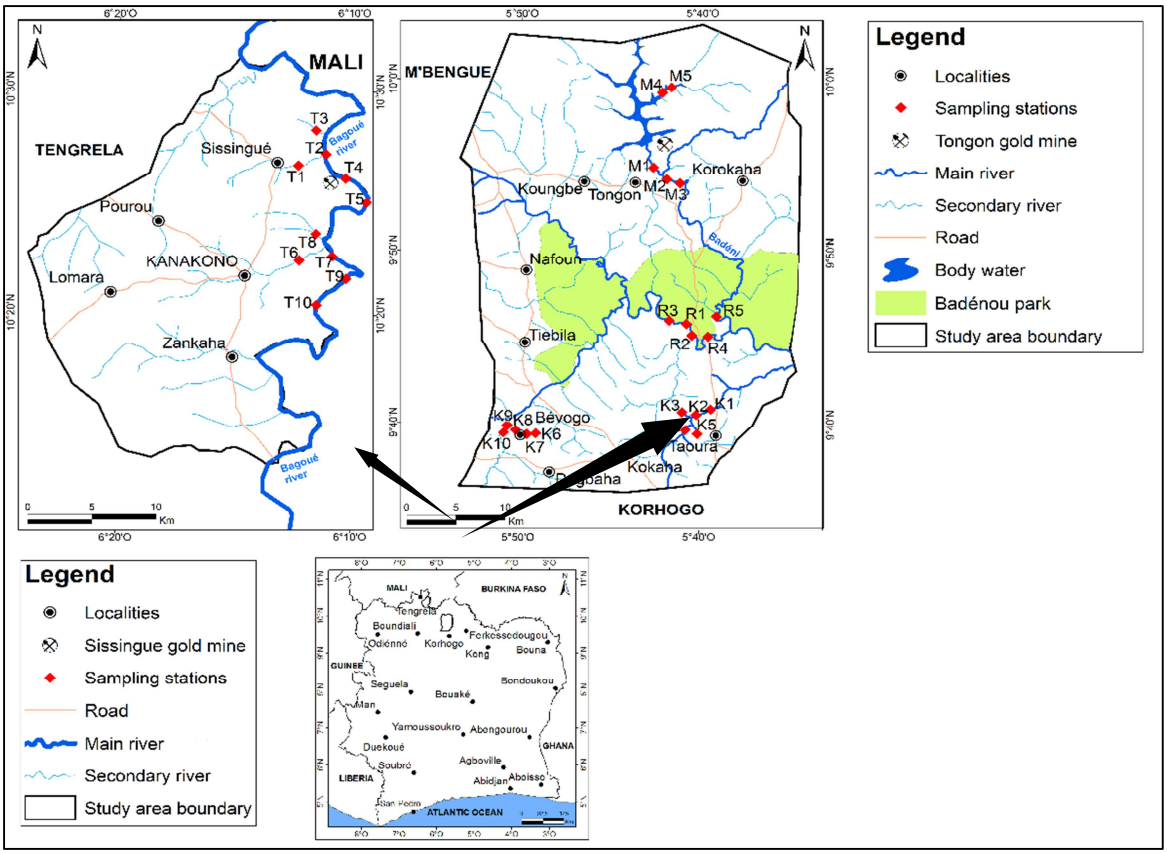

Figure 1. *Location of the study area and the sediments sampling sites.*

2.2. Sediments Characterization and Heavy Metal Analysis

Sampling campaigns took place in 2016 during the dry season. The collection of the sediment samples, digestion, and total metal concentration measurements have been described by Kinimo et al. [17]. A total of 5 samples surfaces of sediment (0-5 cm) were collected from each site (Figure 1). In order to take the local variability into account, each sample (300 g) was made of five subsamples collected using a Van Veen stainless steel grab (with an area of 0.02 m^2) [27]. Without emptying the grab, a sample was taken from the centre with a polyethylene spoon (acid washed) to avoid contamination by the metallic parts of the dredge. Samples were then put into ice bags and transported to the laboratory, stored in a deep-freeze unit before the drying procedure. Sediment samples were air-dried at room temperature [28], ground with an agate mortar to pass through a 63 µm sieve, and stored in polyethylene zip-type bags and shipped to Laboratoire de Chimie Organique Bioorganique Réactivité et Analyse (COBRA), Université de Rouen, France for further analysis. All sampling devices were cleaned by rinsing with pure water and kept in 0.1 M HNO_3 (68%, Fischer Scientific) for several days before sampling. Sediment samples were digested using a microwave-assisted digestion system (Milestone Ethos 1 microwave, Shelton, US), following Method 3051 A [29]. About 0.5 g of homogenized sediments were first left to react with a mixture of 3 mL 68% HNO_3 and 9 mL 37% HCl (trace metal grade, Fisher Scientific) in loosely capped Teflon reactors for 30 min at room temperature, in a fume hood, to avoid an overpressure during the heating step [29, 30]. Then, the digestion was performed under high power at programmed temperatures and time intervals: 0 to 10 min, 25 to 150°C; 10 to 15 min, 150°C; 15 to 20 min, 150 to 165°C; 20 to 25 min, 165°C; 25 to 30 min, 180°C [17]. After cooling, the solutions were diluted to 50 mL with ultrapure 2% HNO_3 in Teflon tubes and centrifuged at 4000 rpm for 5 min prior analysis of the supernatant. Duplicate blanks were prepared and analysed with each batch of digested samples. Trace metals (Fe, Al, Cr, Co and Zn) were measured using an inductively coupled plasma-optical emission spectrometer (ICP OES Icap 6200, Thermo Fisher, Cambridge, UK). Three

replicates of each sample analysed presented an error that was within 6%. Accuracy of the analytical procedures were evaluated through the analysis of the certified reference material CRM CNS 301-04-050 (Sigma-Aldrich; Missouri, U.S.A) for freshwater sediment. The measured concentrations fell within the range of certified values (Table 1).

Table 1. *Analytical results of the certified reference material CRM CNS 301-04-050 (Sigma-Aldrich; Missouri, S. A) used in this study [17].*

Trace metals	Concentration measured	Reference Value	Recovery (%)
Co (µg/g)	26.0 ± 0.50	26.3±1.84	99
Cr (µg/g)	33.5 ± 0.50	30.7±4.04	109
Zn (µg/g)	91.2±4.00	89.0±8.56	102

Sissingue (T1, T2, T3, T4, T5); Kanakono (T6, T7, T8, T9, T10); Tongon (M1, M2, M3, M4, M5); Badenou (R1, R2, R3, R4, R5); Taoura (K1, K2, K3, K4, K5); Bevogo (K6, K7, K8, K9, K10).

2.3. Chemical Speciation of Traces Metals

We applied BCR sequential extraction method in our study on 1g of dried samples [31]. This method allows the separation of heavy metals bound to different parts of sediment into for fractions: Acid-soluble fraction (F1) was extracted by 40 mL of 0.11 M acetic acid at room temperature for 16h (step 1). The residue from step 1 was leached with 40 mL of 0.5 M hydroxylamine hydrochloride, pH = 1.5 at room temperature for 16h (step 2) to receive reducible fraction (F2). The residue from the second extraction step was treated twice with 5 mL of 8.8 M hydrogen peroxide, pH = 2 at room temperature for 1h and then 80°C for 1h. After cooling down, 20 mL of 1.0 M ammonium acetate (pH = 2) was added at room temperature for 16h to extract oxidizable fraction (F3) (step 3). The residue from step 3 was digested using a mixture of HNO_3-HCl (1:3) at 180°C for 2h 30 min (residual fraction) [32, 33]. Previous study upon river sediment showed recoveries (Recovery $=\frac{F1+F2+F3+F4}{Pseudo-total} \times 100$) of this method in the range of 96–106% for Cr, Co and Zn.

2.4. Environmental Assessment

2.4.1. Geo-accumulation Index (Igeo)

The geo-accumulation index (Igeo) is a tool used to assess the level of heavy metal contamination in sediment. The Igeo was introduced by Müller [34] and is expressed by the following relationship.

$$I_{geo}=log_2 \frac{C_n}{1.5\ B_n} \quad (1)$$

Where C_n represents the measured concentration of metal (n) in samples (mg/kg), B_n represents the geochemical background value of metal (n) (mg/kg). Factor 1.5 is used to account the possible variation in the background values. B_n values used in the study are the UCC values. The Igeo values define seven level of contamination sediment: Class 0 ($Igeo \leq 0$), uncontaminated; Class 1 ($0 < Igeo < 1$), uncontaminated to moderately contaminated; Class 2 ($1 < Igeo < 2$), moderately contaminated; Class 3 ($2 < Igeo < 3$), moderately to heavily contaminated; Class 4 ($3 < Igeo < 4$), heavily contaminated; Class 5 ($4 < Igeo < 5$), heavily to extremely contaminated; Class 6 ($Igeo \geq 5$), extremely contaminated [35].

2.4.2. Enrichment Factor (EF) of Trace Metals

The enrichment factor has been proposed to discriminate anthropogenic inputs from natural sources. It is calculated using the following relationship:

$$EF=\frac{(C_{Metal}/C_{Fe})\ Sample}{(C_{Metal}/C_{Fe})Backgroung} \quad (2)$$

(C_{Metal}/C_{Fe}) sample is the ratio of each metal and iron concentration in the sample; (C_{Metal}/C_{Fe}) background is the ratio of each metal and iron concentration in the background.

In this study, iron (Fe) was used as a reference element for geochemical normalization because sequential extraction showed that Fe was relatively present in the residual fraction (89%) relative to Al (85%). Therefore, Fe has been chosen as the most appropriate reference element. Local geochemical backgrounds calculated from the value at down-core were used as background data. EF values were interpreted as suggested by Maanan et al. [36], where: $EF < 1$ indicates no enrichment; $1 < EF < 3$ is minor enrichment; $3 < EF < 5$ is moderate enrichment; $5 < EF < 10$ is moderately severe enrichment; $10 < EF < 25$ is severe enrichment; $25 < EF < 50$ is very severe enrichment; and $EF > 50$ is extremely severe enrichment.

2.4.3. Risk Assessment Code (RAC)

The Risk Assessment Code (RAC) considers the ability of metals to be released and subsequently enter into the food chain and is based on the strength of the bond between metals and other components in sediments. Therefore, the RAC assesses the availability of metals by applying a scale to the percentage of metal in the carbonate and exchangeable fractions (F_1). When the percentage F_1 is less than 1% there is no risk (NR). For a range of 1–10%, there is low risk (LR), medium risk (MR) for a range of 11–30%, high risk (HR) for 31–50%, and very high risk (VHR) for 51–100% [37].

2.5. Assessment of Environmental Pollution in Sediments

2.5.1. Individual Contamination Factor (ICF) and Global Contamination Factor (GCF)

The individual contamination factor (ICF) is used to evaluate the contamination of single elements and is an important index used to assess the potential ecological risk of traces metals to the environment [22, 38]. The high ICF of traces metals indicates low retention time and high risk to the environment. The ICF for different sediments was defined as the sum of the non-residual fraction (F1+F2+F3) divided by the residual fraction (F4) of each sample and the global contamination factor (GCF) for each site was calculated by summing the ICF of all metals at a site [22, 38]. The GCF reflects the overall potential risk posed by the complex influence of metals to the environment. The classification of

ICF and GCF was suggested by Zhao et al. [39] and described in Table 2 [22, 39].

2.5.2. Modified Potential Ecological Risk Index (MRI)

Finally to evaluate the potential ecological risk index of trace metals in sediments, we used the method proposed by Zhu et al [40]. MRI considers the toxicity of the metals and assumes that the metals are mostly in the mobile fraction (exchangeable):

$$MRI = \sum_{i=1}^{m} E_i^r = \sum_{i=1}^{m} T_i^r . C_f^i = \sum_{i=1}^{m} T_i^r . \frac{\Omega . C_D^i}{C_R^i} \quad (3)$$

Wherever E_i^r is the potential risk of a metal; T_i^r is the toxic-response factor of a metal (Zn = 1; Cr = 2; Co=5) [41]; C_f^i is the contamination coefficient; C_D^i is the present concentration of metals in sediments; C_R^i is the pre-industrial record of metal concentrations in sediments; Ω is the modified index of heavy metal concentration calculating (is percentage of the F_1 fraction, is the toxic index of the F_1 fraction). The values vary depending on the RAC value: 1.0 (RAC ≤ 10), 1.2 (10 < RAC ≤ 30), 1.4 (30 < RAC ≤ 50), and 1.6 (RAC > 50) [40]. In this study, metal concentrations of the upper crust proposed by Hu and Gao [42], which is the revision of Rudnick and Gao [43], were used as the background level (Table 2). The classification of MRI, ICF and GCF are presented in Table 2 [22, 39].

Table 2. *Classification of contamination and ecological risk.*

Class	Degree	Contamination		Ecological risk
		ICF	GCF	MRI
I	Low	<1	<6	<150
II	Moderate	1-3	6-12	150-300
III	Considerable	3-6	12-24	300-600
IV	High	>6	>24	>600

2.6. Statistical Analyses and Spatial Distribution Method

In the study, the statistical data were analysed by using Sigmaplot 12.5, except cluster analysis that was performed with Statistica 7.1 Software. To estimate the geochemical factors controlling heavy metals distribution in the sediments, multivariate statistical analyses including cluster analyses and principal component were been performed. The geostatistical analyst tool in ArcGIS V (10.2) was used of spatial analysis.

3. Results and Discussion

3.1. Spatial Distribution of Trace Metals (Co, Cr and Zn)

Spatial distributions of a trace metals (Co, Cr and Zn) in sediments collected from Korhogo and Tengrela sites are mapped on Figure 2. These different concentrations of trace metals will be compared with other concentrations in the sediments of mining areas in a few countries (Table 3).

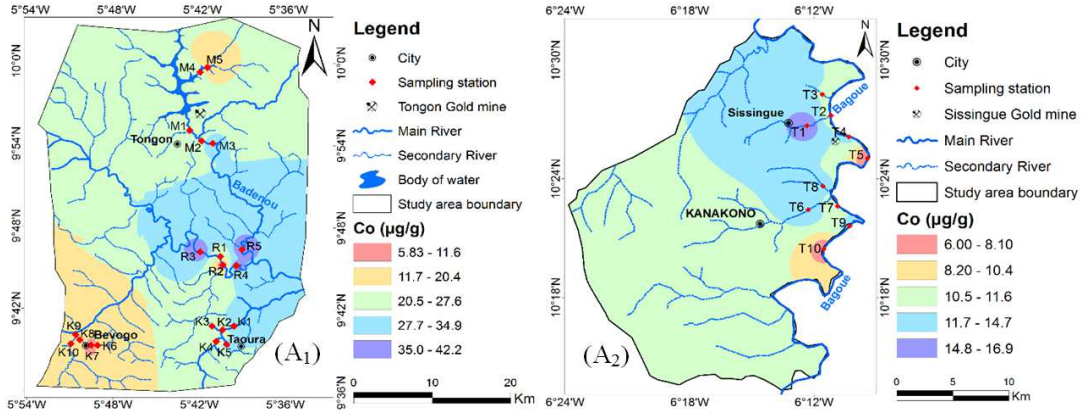

Figure 2. *Examined the distribution patterns of concentrations of cobalt in gold mining areas.*

Table 3. *Comparison of average total concentrations of trace metals with data from similar areas.*

City	Cr (µg/g)	Co (µg/g)	Zn (µg/g)	References
Korhogo	43.24-174.98	14.6-30.4	30.7-58.94	This study
Tengrela	59.42-60.58	11.8-11.98	24.76-56.8	This study
Ghana	-	-	-	[44]
Indonesia	-	-	-	[45]
Tunisia	39-90	-	350-2500	[46]
Ghana	9.84-281	-	-	[47]
Malaysia	0.5-17.9	0.1-2.7	8.2-45	[48]
Australia	-	-	697-6818	[49]
China	24.1-726	-	53.5-5484	[50]
Côte d'Ivoire	86.71-144.27	12.14-45.08	23.62-75.94	[17]

3.1.1. Spatial Distributions of Cobalt

Figure 2 reported the spatial distributions of Co in surface sediments from Korhogo and Tengrela, respectively. Co concentrations ranged from 5.7µg/g to 42.2 µg/g. The pattern of mapping of Co distributions in the artisanal mining areas in Korhogo was different, indicated by the colors blue,

orange and purple. Nevertheless, sediment Co concentrations did not vary significantly ($p < 0.05$) between all artisanal stations. At Tongon site, an opposite spatial distribution mapping of Co was observed. There was a significant difference ($p < 0.05$) between the artisanal site (Bevego) and the industrial station (Tongon) in Korhogo. The highest concentration (42.2 µg/g) was found at Badenou. The mapping of the spatial distribution of Co in Tengrela sediments was almost similar at all stations except T_1 and T_{10}. However, no spatial variability ($p < 0.05$) of Co was observed at Tengrela. One-way ANOVA analysis ($p < 0.05$) showed no significant difference between artisanal sites in Korhogo and artisanal sites in Tengrela. Generally, mean Co concentrations at all sites studied are in the same range as the concentration values obtained in Côte d'Ivoire [17] and higher than those obtained in Malaysia [48] (Table 3).

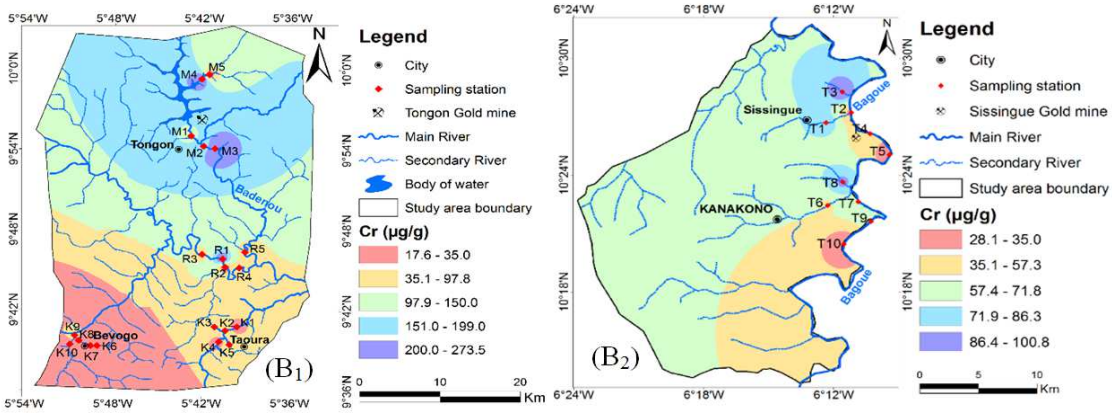

Figure 3. *Examined the distribution patterns of concentrations of chromium in gold mining areas.*

3.1.2. Spatial Distributions of Chromium

As shown in Figure 3, Cr concentrations ranged from 17.4 to 273.5 µg/g. Cr concentrations in sediments from artisanal mining areas did not show significant spatial variability ($p < 0.05$) in Korhogo. On the contrary, the Cr distribution mapping varied by station. Cr concentrations in artisanal and industrial sediments in Korhogo did not differ significantly ($p < 0.05$). However, the mapping of the spatial distribution of Cr in the sediments at all stations was different. The ANOVA analysis showed no significant ($p < 0.05$) spatial variability in Cr concentrations in sediments at Tengrela. Conversely, the spatial map distributions of Cr were different at all stations at Kanakono and Sissingue. Overall, the mean Cr concentrations throughout the sites studied are the same range as the concentration values obtained in Côte d'Ivoire [17] and higher than those obtained in Malaysia [48], Tunisia [46]. However, the concentrations are low compared to those in China [50] and Ghana [47] (Table 3).

3.1.3. Spatial Distributions of Zinc

As shown in Figure 4, Zn concentrations ranged from 5.7 to 148.2 µg/g. Zn concentrations in sediments from artisanal mining areas did not show significant spatial variability ($p < 0.05$) in Korhogo. On the contrary, Zn distribution mapping varied by station. Zn concentrations in artisanal and industrial sediments in Korhogo did not differ significantly ($p < 0.05$). However, the mapping of the spatial distribution of Zn in sediments at Tongon was different from the artisanal mining areas. The ANOVA analysis showed no significant ($p < 0.05$) spatial variability in sediment Zn concentrations at Tengrela. Conversely, the spatial mapping distributions of Zn were different at all stations in Kanakono and Sissingue. Overall, the average of Zn concentrations at all sites studied are lower than the concentration values obtained in China [50], Tunisia [46] and Côte d'Ivoire [17], except in Malaysia [48] where our Zn values are higher (Table 3).

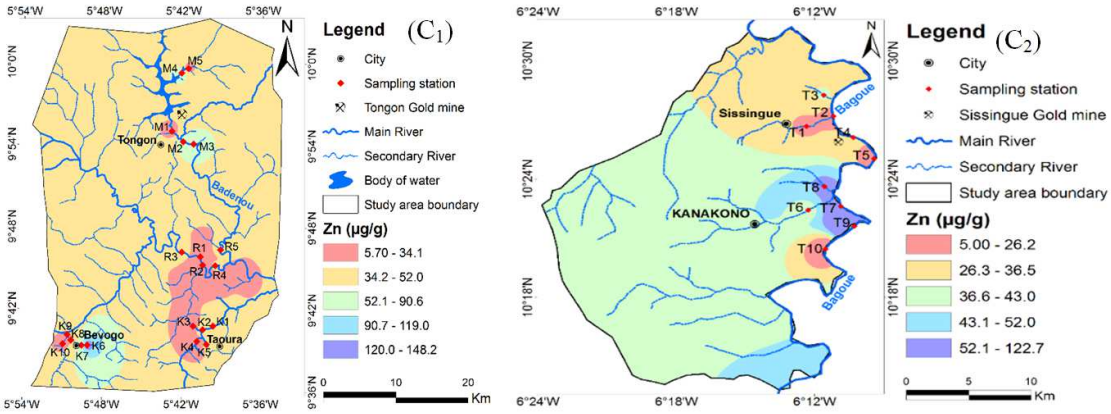

Figure 4. *Examined the distribution patterns of concentrations of zinc in gold mining areas.*

3.2. Pollution Indices

3.2.1. Geo-accumulation Index (Igeo)

The results of the Geoaccumulation index proposed by Muller [51, 52] are shown in Table 4. The mining areas studied in sediments have practically no contamination of Co, Cr and Zn as all of them fall under class 0. Moreover, the sediments of Bevogo and Taoura are moderately contaminated in Cr respectively in Bevogo and Taoura.

Table 4. *Geo-accumulation index (Igeo) of ETM (Cr, Co and Zn) in surface sediments.*

locality	Stations		Co	Cr	Zn
Korhogo	Badenou	mean	0.80	1.04	-1.35
		SD	1.11	1.13	1.09
	Tongon	mean	0.44	1.74	-0.53
		SD	0.51	1.11	0.88
	Taoura	mean	0.60	0.35	-1.19
		SD	0.34	0.32	0.54
Tengrela	Bevogo	mean	-0.25	-0.28	-0.40
		SD	0.41	0.88	1.02
	Sissingue	mean	-0.54	0.18	-1.66
		SD	0.50	0.63	0.50
	Kanakono	mean	-0.56	0.21	-0.46
		SD	0.41	0.56	1.58

3.2.2. Enrichment Factor (EF)

To qualitatively assess the impact of anthropogenic activities on trace metal concentrations in sediments. We calculated the enrichment factor (EF) for each metal to identify the expected effect of anthropogenesis on the accumulation of these trace metals. Fe was used as a reference element, which is characterized by low variability in its occurrence in sediments [53, 54]. The EF values are shown in Table 5. On the Hakanson [41] scale, EF values calculated using mean Zn concentrations in Korhogo and Tengrela sediments from indicates no enrichment, except for the sediments of the Kanakono mining area which is minor enrichment. On the other hand, all the sediments of Tengrela and Korhogo have is minor enrichment in Cr and Co.

Table 5. *Enrichment Factors (EF) of ETM (Cr, Co and Zn) in surface sediments collected from Korhogo and Tengrela gold mining areas.*

Ville	Stations		EF(Co)	EF(Cr)	EF(Zn)
Korhogo	Badenou	mean	1.73	2.03	0.39
		SD	1.92	3.80	0.39
	Tongon	mean	1.15	2.82	0.59
		SD	0.87	3.89	0.79
	Taoura	mean	1.44	1.21	0.41
		SD	0.88	0.68	0.38
Tengrela	Bevogo	mean	1.09	1.07	0.99
		SD	0.68	1.66	2.01
	Sissingue	mean	1.03	1.70	0.48
		SD	5.61	14.1	2.95
	Kanakono	mean	1.06	1.81	1.14
		SD	0.70	1.65	2.13

3.3. Speciation Distribution of Sediment Heavy Metals

3.3.1. Chemical Fractionation of Chromium

The percentages of Cr in the different sediment fractions are shown in Figure 5. Chromium is mostly related to the residual faction (F4) with a percentage varying between 71.02 (Sissingue) and 84.32% (Kanakono). Whether at a concentration varying between 41.87 µg/g and 51.04 µg/g on a total oscillating between 58.83µg/g and 60.55 µg/g. These results suggest that an important part of Cr is related to the crystalline structure of the sediment. No significant difference at $p < 0.05$ was observed between stations. Our results are in agreement with those of Sebei et al [46], which showed that Chromium is mostly bound to the residual fraction (55%) in the sediments of the Tessa River in the vicinity of a mine in Tunisia. The percentage of the fraction (F3) of Cr bound to organic matter and sulphides varies between 4.98 (Tongon) and 13.16% (Sissingue). ANOVA analysis ($p<0.05$) showed that there was no significant difference between stations. The proportions of the copper faction (F2) bound to iron and manganese oxides vary between 3.51% (Badenou) and 11.02% (Taoura). There is no significant difference (ANOVA, $p<0.05$) between stations. The percentages of the F1 fraction corresponding to the fraction of exchangeable and carbonate-bound copper range from 1.48 (Bevogo) to 12.86% (Badenou). This fraction represents the most important reactive fraction for the different sediments. Sediments from the Badenou area recorded the highest percentage without any significant difference ($p<0.05$). This percentage in the Badenou zone represents 14.00 µg/g out of a total of 105.84 µg/g. The retention of Cr by the different phases of the sediments allows to make four types of classification. The first in the Badenou area: F4> F1> F3> F2. The second in the zone of Tongon: F4> F2> F1> F3. The third one in the zone of Taoura and Kanakono: F4> F2> F3> F1. And the fourth in the zones of Sissingue and Bevogo: F4> F3> F2> F1.

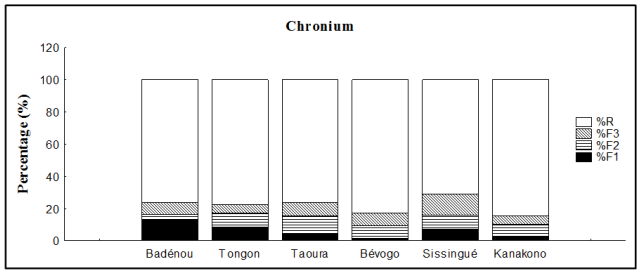

Figure 5. *Mean percentages of Cr distributed in the acid soluble, reducible, oxidizable, and residual fractions in sediment from the study area.*

3.3.2. Chemical Fractionation of Cobalt

The percentages of Co in the different sediment fractions are shown in Figure 6. It is clear that Co is mainly related to the residual fraction (F4), with a proportion varying between 62.00 (Kanakono) and 72.83% (Taoura). This corresponds to the range of 7.37 - 19.33 µg/g out of a total concentration of 11.62 - 26.42 µg/g. These different results suggest that a significant proportion of Co is strongly related to the crystal structure of the sediment. No significant differences were observed between the stations. The F3 fraction of Co corresponds to the fraction related to organic matter and

sulphides, with a proportion varying between 7.14 (Tongon) and 12.96% (Sissingue). The percentages of the reducible fraction (F2) of Co vary between 6.70 (Taoura) and 13.85% (Kanakono). This fraction represents the most important reactive fraction in the sediments of the different zones studied. This shows a weak dissolution of Co and manganese oxides in these zones. The acid-soluble fraction (F1) of Co is low in all the stations. The proportions vary between 7.22 (Bevogo) and 15.15% (Badenou). These proportions are equivalent to concentrations ranging from 1.01 µg/g (Bevogo) - 4.64 µg/g (Badenou) out of a total of14.34 µg/g (Bevogo)-30.36 µg/g (Badenou). Statistical analysis (ANOVA, $p<0.05$) shows that there is no significant difference between stations. The retention of Co by the different phases of the sediments allows three types of classification. The first in the Badenou and Tongon zones: F4> F1> F2> F3. The second in the Taoura and Sissingue zones: F4> F1> F3> F2. Finally, the third in the area of Bevogo and Kanakono: F4> F2> F3> F1.

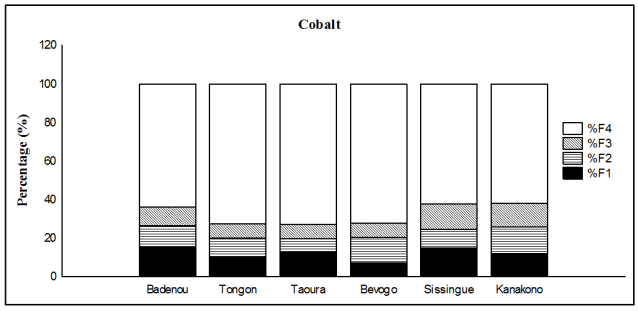

Figure 6. *Mean percentages of Co distributed in the acid soluble, reducible, oxidizable, and residual fractions in sediment from the study area.*

3.3.3. Chemical Fractionation of Zinc

The percentages of Zn in the different sediment fractions are shown in Figure 7. The residual fraction (F4) controls the distribution of Zn in the different sediments with percentages ranging from 66.61% (Taoura) to 72.01% (Badenou). This is equivalent to the range of 22.21 - 23.48 µg/g with respect to the total concentration 30.49 - 33.58 µg/g. The stations are not significantly different (ANOVA, $p<0.05$). Our results are in agreement with those of Sebei et al [46], which showed that zinc is mostly bound to the residual fraction (53%) in the sediments of the Tessa River in the vicinity of a mine in Tunisia. The F3 fraction related to organic matter and sulphides varies between 7.00 (Badenou) and 10.52% (Kanakono). The proportion obtained in Kanakono sediments is significantly higher without any significant difference ($p<0.05$). This corresponds to a concentration of 4.99 µg/g out of a total of 55.92 µg/g. The fraction (F2) of zinc is between 6.70 (Taoura) and 13.85% (Kanakono). Statistical analysis revealed no significant differences between stations. Nevertheless, Kanakono sediments recorded the highest proportion. Moreover, this fraction represents the largest reactive fraction in this area with a concentration of 3.59 µg/g out of a total of 55.92 µg/g. The proportions of the fraction (F1), corresponding to the fraction of exchangeable zinc and the fraction of zinc bound to carbonates, range from 7.57 (Tongon) to 14.83% (Sissingue). No significant difference (Anova, $p<0.05$) was observed between stations. The highest percentage obtained in Kanakono sediments corresponds to 3.27 µg/g out of a total of 24.39 µg/g. This availability of concentration is lower than the average value for the earth's crust (52 µg/g). This suggests that the presence of Zn in the Kanakono area would be without threat to organisms. The distribution of Zn in the different sediment fractions is not identical. The order of distribution in the sediments studied is as follows:

Badenou: $F_4> F_1> F_3> F_2$

Tongon: $F_4> F_2> F_3> F_1$

Taoura, Bevogo, Sissingue: $F_4> F_1> F_2> F_3$

Kanakono: $F_4> F_1> F_3> F_2$.

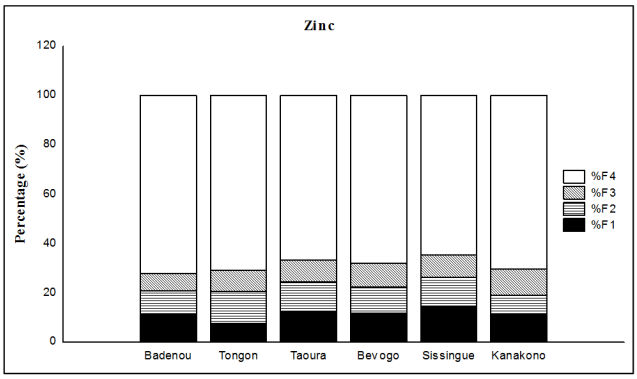

Figure 7. *Mean percentages of Zn distributed in the acid soluble, reducible, oxidizable, and residual fractions in sediment from the study area.*

3.4. Risk Assessment of Environmental Pollution

3.4.1. Risk Assessment Code (RAC)

The risk of toxicity percentages of traces metals in sediments are shown in Table 6. The RAC values show that Cr can cause a low risk in all the sediments studied. ($1.48 \leq$ RAC (%) ≤ 8.34), with the exception of the Badenou sediments which have a medium risk (RAC (%) =12.86). The proportions of Zn in all studied sediments related to F1 were 11.32% to 14.38%, which corresponds to the medium risk category. In contrast, there is a low risk in the Tongon sediments. Overall, Co is at moderate risk at all of the sites surveyed, with the exception of Badenou, which has low toxicity.

Table 6. *Environmental risk assessment of sediment (RAC).*

stations	Cr	Zn	Co
Badenou	12.86	11.56	14.97
Tongon	8.34	7.57	10.30
Taoura	4.56	12.30	13.04
Bevogo	1.48	11.80	7.22
Sissingue	7.00	14.38	14.83
Kanakono	2.91	11.32	11.99

3.4.2. Individual Contamination Factor (ICF) and Global Contamination Factor (GCF)

The ICF and the GCF results of the trace metals in the sediments of Korhogo and Tengrela are shown in Figure 8

and Figure 9 respectively. Generally, Cr, Co and Zn have low individual contamination in the studied sediments as ICF<1. This means a low risk for the environment because these metals are stable in sediments and their mobility is low is low because of the high residual fraction (F4) [33]. The average ICF values of Cr, Co and Zn in the sediments of the different sites, with the following order:

Badenou: Co> Zn> Cr>; Tongon: Zn>Co> Cr>; Taoura: Zn>Co> Cr>; Bevogo: Zn>Co> Cr>; Kanakono: Co > Zn > Cr>; Sissingue: Co > Zn > Cr>.

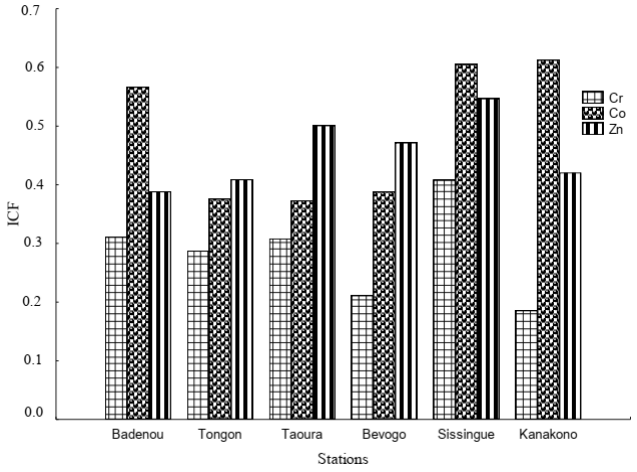

Figure 8. *The individual contamination factor (ICF) in the studied sediments.*

The result of the GCF (GCF<6) shows a low overall potential risk posed by the complex influence of metals on the environment. But the GCF of the industrial mining zone of Tongon is higher than the other GCF of the artisanal mining areas. Thus, it can be concluded that the trace metals in the industrial mining zone of Tongon show a higher global potential risk on the environment than the trace metals of the artisanal mining zones.

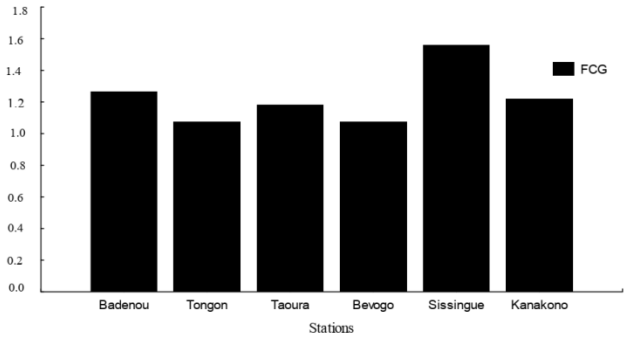

Figure 9. *Global contamination factor (GCF) in the studied sediments.*

3.4.3. Modified Potential Ecological Risk Index (MRI)

The MRI results of the trace metals in the Korhogo and Tengrela sediments are shown in Table 7. The MRI values of Cr, Co and Zn ranged from 1.04 to 52.82 all over the sites studied. The very low MRI values show a low environmental risk for Cr, Co and Zn.

Table 7. *Modified potential risk index (MRI) at different stations of the north of areas influenced by mining activities, Côte d'Ivoire.*

station	MRI		
	Cr	Co	Zn
Badenou	6.16	52.82	1.95
Tongon	10.00	31.07	1.04
Taoura	3.83	41.11	2.27
Bevogo	2.47	6.29	3.81
Sissingue	3.40	20.44	1.85
Kanakono	3.46	17.28	3.57

4. Conclusion

The RAC, GCF, ICF and MRI methods applied to the analysis of the ecological risk of heavy metals in sediments in the mining areas studied bore fruit and the results obtained gave the following information: The content of Cr, Co and Zn in the study area revealed that the low level of pollution was distributed in the research area where mining activities were concentrated. In addition, this study suggested that most of traces metals (Cr, Zn and Co) were due to anthropogenic and naturel factors. Chemical speciation of heavy metals (Co, Zn and Cr) was determined using a BCR sequential extraction procedure to evaluate the mobility potential. Metals such as Co, Zn and Cr are all bound to the residual fraction. This means that the most stable trace metals are mainly in the silicate crystal structures of the sediments. According to RAC, Co and Zn presented a medium risk to the ecosystem because of their percentages in fractions. Whereas the other sites presented relatively a low risk. In contrast, Cr has low toxicity at all study sites, with the exception of Badenou, which is at moderate risk. In general, Cr, Zn and Co have low individual contamination in the sediments studied. The GCF results (GCF <6) showed that the trace metals studied have a low overall potential risk to the environment. The very low MRI values show a low environmental risk for Cr, Co and Zn. Generaly, the MRI values of traces metals etudes (MRI <150) indicate a low environmental risk in all the mining areas studied. In view of our results, it is important to sensitize the population on the risks of living near mining areas and of consuming river water, fishing products and agricultural products grown near these areas.

Compliance with Ethical Standards

All authors have read the manuscript, agree with the journal's data deposition requirements and to our submission in Science Journal of Chemistry, and have no conflicts of interest.

Declaration

Consent to Participate

Informed consent was obtained from all individual participants included in the study.

Conflict to Interest

The authors declare that they have no conflict to interest.

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