

Ecological and human health risks assessment of Arsenic in sediments around gold mining areas in northern Côte d'Ivoire

Abstract

Arsenic contamination of sediments is a worldwide concern, both for the environment and for human health. However, few data are available on the state of arsenic pollution in sediments near artisanal and industrial gold mining areas in Côte d'Ivoire. The aim of this study is to assess the spatial distribution of arsenic and its ecological and human health risks in sediments around gold mining areas in northern Côte d'Ivoire. Sampling was carried out in artisanal and industrial mining areas in Korhogo and Tengrela, northern Côte d'Ivoire. Spatial differences were determined using analysis of variance. Pollution indices were studied using the contamination factor and the enrichment factor. Non-carcinogenic and carcinogenic risk indices were used to investigate human health risks. The study revealed total arsenic concentrations ranging from 1.64 ± 0.04 to 159.72 ± 51.91 $\mu\text{g/g}$. It found Arsenic concentrations in sediments varied considerably from station to station. The results of the contamination factor indicated that the sediments were weakly to very strongly contaminated with arsenic. Non-carcinogenic risk index values ranged from $1.83\text{E-}04$ to $1.78\text{E-}02$, indicating low adverse effects on the surrounding habitats. In addition, the results of the potential risk (CRt) for human health revealed the existence of significant carcinogenic risks from arsenic for residents in the vicinity of the Tongon mining area.

Keywords: Arsenic, Gold mining, Sediment, Pollution Indices, Potential risk, Carcinogenic risk index

1. Introduction

Mining activities are widespread in many developing countries, such as Côte d'Ivoire [1, 2]. These various mining activities provide incomes around three to five times higher than other small-scale rural activities in agriculture, forestry, and fishing [3, 4]. "However, gold mining is one of the main anthropogenic activities responsible for the release of arsenic (As) into the environment. This activity poses a potential threat to environmental resources and health problems for humans and animals" [5, 6]. "Once arsenic is present in the environment, it transforms into various inorganic and organic chemical forms: arsenite (As(III)), arsenate (As(V)), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), trimethyl arsine oxide (TMAO), and arsenobetaine (AsB). The toxicity, mobility, and solubility differ among species, in such a way that inorganic As(III) is more toxic than As(V), and in turn, organic As is less toxic" [7,8]. "For example, chronic exposure to arsenic has been found to provoke humungous diseases such as kidney and lung cancers, these include peripheral neuropathy, diabetes, ischemic heart disease, melanosis, keratosis and impaired liver and lung function, as well as dysfunction of the reproductive organs, neurological, cardiovascular and dermatological effects, and reproductive organ dysfunction" [9,10]. "For this reason, environmental studies of mining areas are important to protect the health of residents and the levels of arsenic contamination" [11, 12]. "High concentrations of arsenic in air, sediments, soils, fishery products, and water due to mining activities have been reported in many countries including China, Côte d'Ivoire, and Morocco. Excessive amounts of arsenic in aquatic systems are mainly linked to mining and other activities such as agriculture" [13, 14]. "In addition, in aquatic systems, sediments represent a sink for chemical pollutants" [15]. "They are therefore considered as a suitable indicator of aquatic arsenic

pollution. Nevertheless, adsorbed pollutants in sediments can be released into the water column under varying physicochemical conditions” [10]. “In Côte d'Ivoire, there has been significant development of agricultural and mining activities in the north of the country, especially in the Poro District. These activities have proved to be potential sources of arsenic in the environment” [10]. Numerous research studies have documented arsenic contamination in sediments around mining areas in West Africa, with studies focusing on Nigeria [16, 17], Senegal [18], and Ghana [19, 20]. Recently, Kinimo et al. [21] showed that “sediments from the gold mining area in southeastern Côte d'Ivoire were contaminated with arsenic”. “Furthermore, in our study area, the use of chemical fertilizers in vegetable and fruit production in market garden crops around the Bandama and Bagoué rivers in northern Côte d'Ivoire, can contain large amounts of arsenic” [22]. Consequently, soil leaching by rainwater can lead to the presence of large quantities of arsenic in surface waters. Thus, arsenic must be taken into account when assessing the level of environmental pollution in this area. The objectives of the present study were (i) to determine total arsenic concentrations in surface sediments, (ii) to assess the level of contamination using pollution indices (CF and EF), (iii) to evaluate the potential ecological risk index (MRI), (iv) health risk assessment (v) to explore arsenic mobility using the sequential extraction procedure.

2. Material and methods

2.1. Study area

The study area covers the Bandama and Bagoué rivers in the Savannah District of northern Côte d'Ivoire (Figure 1). The Bandama River is in the Korhogo region, while the Bagoué River is in the Tengrela region. The Bandama River is the largest river in Côte d'Ivoire, with its source in northern Côte d'Ivoire, between Korhogo and Boundiali [23-25]. The Bagoué river is a small river in northern Côte d'Ivoire. It rises in the Kokoum region, near the border between Côte d'Ivoire and Mali, passing through Tengrela (Côte d'Ivoire). In northern Côte d'Ivoire, the geology is predominately made up of feral soils. 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 [26]. The Savannah District is well known through activities such as livestock, cotton, cashew and food activities [26], in addition to a number of industrial (Ran Gold (Korhogo) and Perseus Mining (Tengrela)), and artisanal and small-scale gold mining extractions [26]. In this study, two towns were selected in the Savannah District (Korhogo and Tengrela) to get an idea of the state of arsenic contamination in their environments. The selected sites in Korhogo are: Tongon (Stations M1 to M5), where samples were taken in the vicinity of the Tongon mine (an open-pit mine). Other samples were taken in the artisanal mining areas of Badénou (stations R1 to R5), Taoura (K1 to K5), and Bevogo (K6 to K10). For the selected sites in Tengrela, the various stations in Sissingué (stations T1 to T5) and Kanakono (stations T6 to T10) are considered to be artisanal gold mining areas, as industrial gold mining had not yet begun at the time of sampling. Sediments were collected using a Van Veen stainless steel grab sampler.

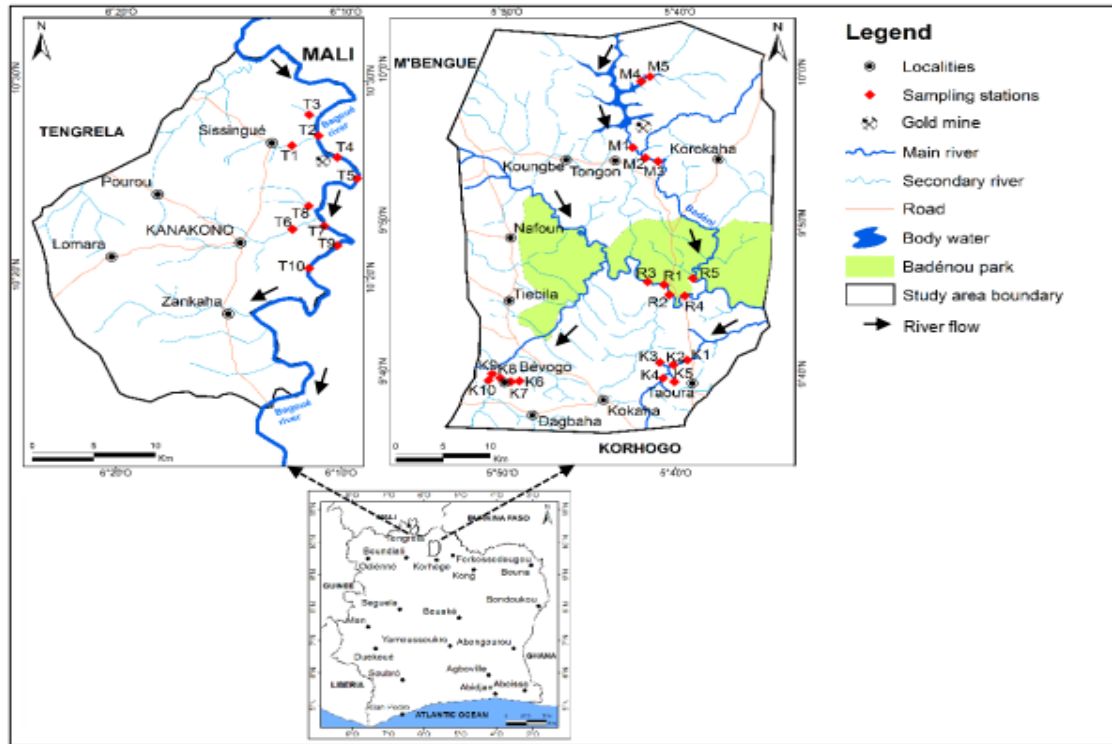


Figure 1. Location of the Savannah District and sediments sampling sites

**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)**

2.2. Sediment characterization and heavy metal analysis

Surface sediment sampling campaigns took place in 2016 during the dry season. Sediments were collected in accordance with USEPA (2001) using a Van Veen stainless steel grab sampler. Samples were sealed in plastic bags. Then, they were kept at 4°C and transported to the laboratory. Afterwards, they were oven-dried at 60°C, homogenized, and stored at 4°C until analysis [10]. After collection of the sediment samples, digestion and measurement of arsenic concentrations were described by N'goran et al. [26].

2.3. Sequential extraction of heavy metals

A modified BCR sequential extraction procedure [27] was performed on 1g of dried samples. 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, it was heated at 80°C for 1h. After cooling down, 20 mL of 1.0 M ammonium acetate (pH = 2) was added to the obtained sample at room temperature for 16h in order to extract oxidizable fraction (F3) (step 3). The

residue from step 3 was digested using a mixture of HNO₃-HCl (1:3) at 180°C for 2h 30 min (residual fraction) [26]. Previous study upon river sediment showed recoveries (Recovery = $\frac{F1+F2+F3+R}{Pseudo-total} \times 100$) of this method in the range of 96–103% for As.

2.4. Environmental assessment

2.4.1. Contamination factor (CF)

The contamination factor (CF) was calculated to assess the level of arsenic contamination. The contamination factor was calculated as follows [28]:

$$CF = \frac{C_{\text{arsenic (sediment)}}}{C_{\text{arsenic (background)}}} \quad (1)$$

Where $C_{\text{arsenic (sediment)}}$ is the concentration of arsenic in the sediment sample and $C_{\text{arsenic (background)}}$ is arsenic background value given by Wedepohl [26]. Four classes of CF have been distinguished by Hakanson [28]: class 1 (low contaminated) $CF < 1$; class 2 (moderately contaminated) $1 < CF < 3$; class 3 (considerably contaminated) $3 < CF < 6$; and, class 4 (very high contaminated) $CF > 6$.

2.4.2. Enrichment factor (EF)

Enrichment factor (EF) is a useful tool for determining the degree of anthropogenic heavy metal pollution. The EF is computed using the relationship below:

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

$(C_{\text{Metal}}/C_{\text{Fe}})_{\text{sample}}$ is the ratio of each metal and iron concentration in the sample; $(C_{\text{Metal}}/C_{\text{Fe}})_{\text{background}}$ 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 [26]. 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. [29], where: $EF < 1$ indicates no enrichment; $1 < EF < 3$ is minor enrichment; $3 < EF < 5$ is moderate enrichment; $5 < EF < 10$ shows moderately severe enrichment; $10 < EF < 25$ is severe enrichment; $25 < EF < 50$ is very severe enrichment; and $EF > 50$ determines 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 entered 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. 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% one [30].

2.4.4. Modified potential ecological risk index (MRI)

Although RAC evaluates the mobility of individual metals, the risk of heavy metal pollution depends not only on the total content of heavy metals but also on their chemical speciation [31, 32]. To assess the ecological risk of heavy metals in sediments considering these two aspects, the potential ecological risk index (MRI) proposed by Zhu et al. [32] was used in this study. MRI considers the toxicity of the metals and assumes that the metals are mostly in the mobile fraction (exchangeable):

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

Wherever E_i^r is the potential risk of arsenic; T_i^r is the toxic-response factor of arsenic (As =10) [33, 33]; C_D^i is the present concentration of arsenic in sediments; Ω is the modified index of arsenic concentration calculating (is percentage of the F1 fraction, is the toxic index of the F1 fraction); C_R^i is the pre-industrial record of metal concentrations in sediments. 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) [32]. In this study, metal concentrations of the upper crust proposed by Hu and Gao [35], which is the revision of Gusiati et al. [36], were used as the background level (Table 1). The classification of MRI is presented in Table 1 [32].

Table 1: Classification of contamination and ecological risk.

Class	Degree	Ecological risk
		MRI
I	Low	<150
II	Moderate	150-300
III	Considerable	300-600
IV	High	>600

2.4.5. Human exposure and health risk assessment

A human health risk assessment method applied to sediments has been presented in many studies [37; 38]. Generally, the three main pathways of trace metal transformation in ecological systems that are usually involved in human health risk assessment are ingestion, dermal contact, and respiration. This study examined the ingestion (CDI_{ing}) and dermal contact (CDI_{derm}) pathways of trace metal transport in sediment to evaluate human health risk. The following equations are used to calculate the different exposure values [38].

$$CDI_{ing} = \frac{C_{sed} \times IngR \times CF \times EF \times ED}{BW \times AT} \quad (4)$$

Where, CDI_{ing} is defined as the exposure risk by ingestion of sediment metals (mg/kg/day); C_{sed} is the determined content in the current sediment; $IngR$ is defined as the daily ingestion amount; CF is the unit of measurement conversion factor; EF is defined as the frequency of exposure on the sediment; ED is the duration of exposure; BW is defined as the adult weight; AT is the number of days in 24 years [39].

$$CDI_{derm} = \frac{C_{sed} \times CF \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \quad (5)$$

Where, CDI_{derm} is defined as the dermal absorption risk; SA is considered as the exposed skin surface area on the sediment; AF is defined as the trace metal adhesion index on the unit skin surface; and ABS is considered as the dermal adsorption rate (Table 3) of the sediment [37]. Other exposure factors and values used in the risk assessment are presented in Table 2.

Hazardous quotients (HQ) were applied to determine the health risks of trace metal exposure from surface sediments in accordance with health risk assessment guidelines [38]. The potential adverse health effects associated with such exposure with the quantification of carcinogenic or non-carcinogenic risk.

Table 2: Description of the parameters and the values used in the study

Factor	Definition	Unit	Value	Reference
$C_{sediment}$	Heavy metal concentration in sediment	mg/kg	Adults	This Study
IngR	Ingestion rate	mg/day	100	[40,10]
ED	Exposure duration	years	24	[39,40]
EF	Exposure frequency	days/year	350	[40,10]
BW	Average body weight	kg	70	[40,10]
SA	Exposure skin area	cm ²	5700	[38,10]
AF	Skin adherence factor	mg/cm ² h	0.07	[38,10]
AT	Average time	days	8760	[40,10]
CF	Unit conversion factor	kg mg ⁻¹	10 ⁻⁶	[40,7]

AT = ED x 365. For carcinogenic effects: LT x 365 [40]. In Côte d'Ivoire, LT (lifetime) is 58 [41]. For carcinogenic effects: AT = 21.17

2.4.6. Non-carcinogenic risk assessment

CDI for each element and route of exposure was then divided by the corresponding reference dose (RfD) to obtain a hazardous quotient (HQ, or non-carcinogenic risk; equations 4 and 5) for systemic toxicity. The HQ equations for the ingestion and dermal contact routes are as follows:

$$HQ_{ing} = \frac{CDI_{ing}}{RfD_{ing}} \quad (6)$$

$$HQ_{derm} = \frac{CDI_{derm}}{RfD_{derm}} \quad (7)$$

Where HQ is the hazardous quotient by an ingestion or dermal contact exposure route under the respective exposure concentration; RfD is the reference value for adverse health effect resulting from metal contaminations. The reference values by skin contact (RfD_{derm}) and by the ingestion route (RfD_{ing}) are represented in Table 3.

Assuming that all metal risks were additive, we calculated the cumulative HQ expressed as a risk index (HI) using equations (8). If HQ and HI are less than 1, no adverse health effects will be found while if HQ and HI are greater than 1, indicate adverse human health effects [43].

$$HI = HQ_{ing} + HQ_{derm} \quad (8)$$

Table 3: The used relative toxicity values and dermal absorption factor (ABS) obtained from relevant studies

Metal	RfD _{ing}	RfD _{derm}	ABS _{derm}	ABSGI	SF _{ing}	SF _{derm}
As	3.00E-04 ^{ab}	1.23E-04 ^{ab}	0.03 ^{ae}	1 ^f	1.5E+00 ^{ad}	1.5E+00

a [40], b[43] ,c[37] ,d [45], e [46], f[47]

2.4.7. Carcinogenic risk assessment

For the carcinogenic risk, the various CDI for As were multiplied by the corresponding cancer slope factor (SF) to produce an excess lifetime cancer risk level induced by contaminated ingestion and skin contact. The oral cancer slope factor (SF_{ing}) values as well as the gastrointestinal ABS values are reported in Table 3. By account cancer slope factor (SF_{derm}) values for dermal exposure are not available, extrapolation can be found by dividing the oral cancer slope (SF_{ing}) by the gastrointestinal absorption factor [48]. Commonly, the total CR is the sum of the CR_{ing} and CR_{derm} of the two exposure routes:

$$SF_{derm} = \frac{SF_{ing}}{ABS_{GI}} \quad (9)$$

$$CR_{ing} = CDI_{ing} \times SF_{ing} \quad (10)$$

$$CR_{derm} = CDI_{derm} \times SF_{derm} \quad (11)$$

$$CR_{tot} = CR_{ing} + CR_{derm} \quad (12)$$

In this study, the CR due to the ingestion and dermal routes were calculated for all studied samples. The carcinogenic health risk can be ignored if $CR < 10^{-6}$, while for $CR > 10^{-4}$ the human cancer risk probably increases and values between 10^{-4} and 10^{-6} will lead to an acceptable human health risk [49].

2.5. Statistical analysis

Multivariate statistical analysis including principal component and cluster analysis were performed to estimate geochemical factors controlling trace metals distribution in the sediments. The One Way Analysis of variance (ANOVA) was employed to examine differences among the sites and the activity types. The pairwise multiple comparison procedures were performed using the Tukey Test when the tests of normality and equal variance were positive. The Kruskal-Wallis One Way Analysis of Variance on Ranks was used when the equal variance test failed. The difference was considered statistically significant at $p < 0.05$. Statistical analysis were carried out with SigmaPlot 12.5, except cluster analysis that was performed with Statistica 7.1 Software. Spatial analysis was performed by the geostatistical analyst tool in ArcGIS V (10.2).

3. Results and discussion

3.1. Arsenic content in the studied sediments

The total concentrations of arsenic measured in the sediment samples are shown in **Figure2**. These different arsenic concentrations will be compared with other concentrations in sediments from mining areas in several countries. Arsenic concentrations in Korhogo areas varied from 1.64 ± 0.04 in Badenou to 159.72 ± 51.91 $\mu\text{g/g}$ in Tongon to 1.36 ± 0.28 $\mu\text{g/g}$ in Taoura to 8.72 ± 6.9 $\mu\text{g/g}$ at Bevogo. **In Tengrele areas, arsenic concentrations ranged from 20.44 ± 4.83 $\mu\text{g/g}$ in kanakono to 26.40 ± 23.93 $\mu\text{g/g}$ in Sissingue.** The average of arsenic concentrations in sediments were significantly higher ($p < 0.05$) in industrial mining areas of Tongon than in artisanal mining (Badenou, Taoura, and Bevogo). In contrast, data from artisanal sites showed that sediments collected from Tengrele sites were heavily contaminated with As compared to those in Korhogo. Nevertheless, industrial gold mining areas were significantly contaminated than artisanal areas when considering all the sites. **The high concentration of arsenic in the Tongon industrial gold mining area is generally associated with large-scale mechanized operations. During mining, it is often necessary to finely grind the ore to release metals and ore into the environment [50]. In addition, the mining industry produces huge quantities of fine rock particles. Most of the ore extracted is eventually transformed into tailings. This dissolution of arsenical minerals associated with gold mines and their tailings leads to increased concentrations of arsenical species in the sediment. In contrast, artisanal mining, most of which is not mechanized, produces fewer tailings in the environment [50].** On the other hand, artisanal mining, most of which is not mechanized, produces fewer tailings in the environment. Taking all into account regardless the activity, the average of arsenic concentration in sediments was the highest in Tongon and the lowest in Taoura. **Overall, mean arsenic concentrations at all the studied sites were lower than those obtained in Afema Côte d'Ivoire [21], China [49], Indonesia [51], Burkina Faso [52], Ghana [53]. However, arsenic values in the study were higher than those obtained in Australia [54], Burkina Faso [55], Côte d'Ivoire [56], Ghana [57] and Malaysia [37].**

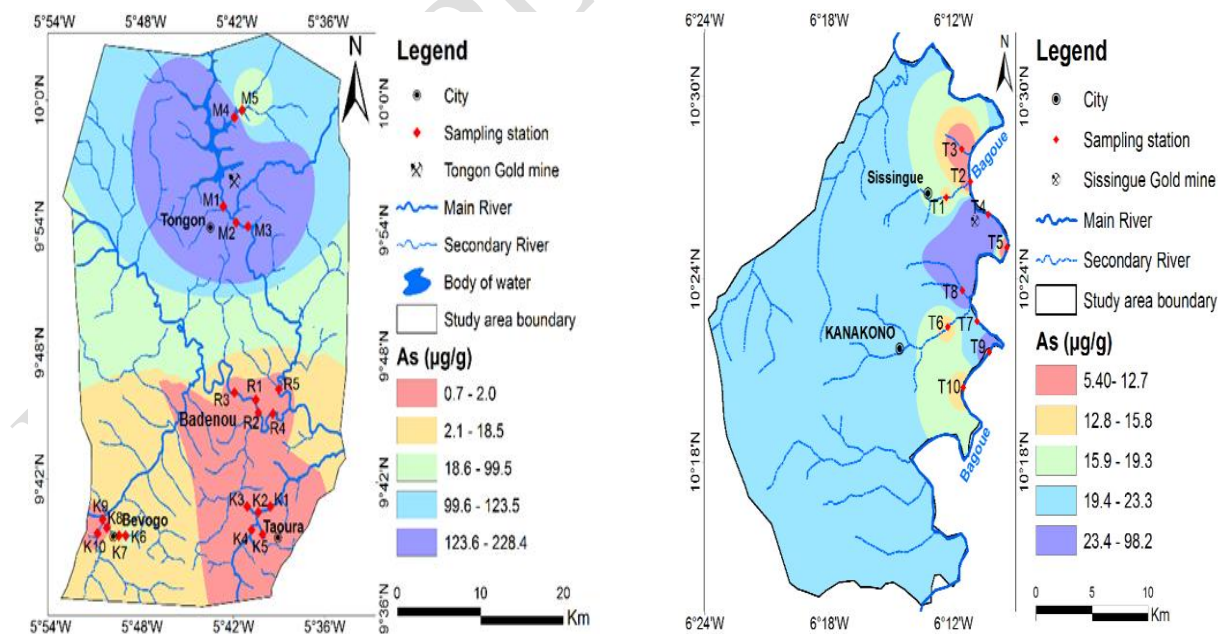


Figure2:The distribution patterns of concentrations of examinedarsenic in gold mining areas

3.2. The values of pollution indices

The mean values of the contamination factor (CF) and enrichment factor (EF) calculated to assess the level of arsenic contamination are shown in Table 4.

Table 4: Contamination factor (CF) and Enrichment Factors (EF) of arsenic in surface sediments collected from Korhogo and Tengrela gold mining areas

City	Stations		EF(As)	CF(As)
Korhogo	Badenou	mean	0.54	0.82
		SD	0.04	0.02
	Tongon	mean	45.1	79.86
		SD	61.5	5.95
	Taoura	mean	0.43	0.68
		SD	0.23	0.20
	Bevogo	mean	3.79	4.36
		SD	10.4	0.39
Tengrela	Sissingue	mean	13.2	13.75
		SD	34	1.94
	Kanakono	mean	10.7	10.22
		SD	9.01	2.41

3.2.1. Contamination factor (CF)

Table 4 shows the mean contamination factor (CF) values in sediments from Korhogo and Tengrela. Mean CF values were 0.82 ± 0.02 and 0.68 ± 0.2 at the Badenou and Taoura stations, respectively. These values showed that the sediments in Badenou and Taoura were low in arsenic contamination. However, the mean value of the contamination factor for Bevogo sediments (4.36 ± 0.39) presented considerable contamination. On the other hand, there was a very high level of contamination in the Tongon sediments, with a mean value of 79.86 ± 5.95 . Average arsenic contamination factor values in Tengrela sediments ranged from 10.22 ± 2.41 in Kanakono to 13.75 ± 1.94 in Sissingue. These values indicated that the sediments were highly contaminated with arsenic. Overall, the mean values of the arsenic contamination factor were lower than the contamination factors for the studied sites at Afema in Côte d'Ivoire [21], Burkina Faso [52], and Ghana [53]. However, the mean values of the arsenic contamination factor in the study were higher than those obtained in Burkina Faso [55], Côte d'Ivoire [56], and Ghana [57].

3.2.2. Enrichment Factor (EF)

The Enrichment Factor (EF) is used to evaluate the possible impact of anthropogenic activities on the arsenic concentrations in the sediment. In order to identify the expected effect of anthropogenesis on heavy metal accumulation, the content of Fe was used, which is characterized by a low variability in its occurrence in sediment [58, 59]. The EF values are shown in Table 4. On the Hakanson [28] scale, EF values calculated using mean arsenic concentrations in Korhogo (Badenou, Taoura, and Bevogo) showed sediments from naught to highly arsenic, except for the sediments of the Tongon mining area which were very severe contaminated. The high total arsenic concentration obtained may point to various anthropogenic activities such as agricultural

practices and mining. On the other hand, all the sediments of Tengrela (Sissingue and Kanakona) were strongly contaminated in arsenic. This comparison showed that the mean values of the arsenic enrichment factor were lower than the enrichment factors of the studied sites at Afema in Côte d'Ivoire [21], Burkina Faso [52], and Ghana [53]. In addition, the mean arsenic enrichment factor values in the study were higher than those obtained in Burkina Faso [55], Côte d'Ivoire [56] and Ghana [57].

3.3. Chemical fractionation of arsenic

The percentages of the arsenic fractions in the sediments (F1-R), as previously described, are shown in Figure 3. The predominant residual fraction (R) was very high for arsenic, ranging from 53.04% (Tongon) to 67.42% (Badenou). The concentration ranged from $80.83 \pm 39.42 \mu\text{g/g}$ to $1.10 \pm 0.08 \mu\text{g/g}$ out of a total of $161.42 \mu\text{g/g}$ to $1.64 \mu\text{g/g}$. These results suggested that an important part of arsenic was related to the crystalline structure of the sediment [10]. The proportion obtained in the sediments from the Tongon industrial extraction zone resulted in significantly higher concentrations without any remarkable difference according to ANOVA analysis ($p < 0.05$). This observation corresponded to a concentration of $80.83 \pm 39.42 \mu\text{g/g}$ out of a total of $161.42 \mu\text{g/g}$. These concentration values show that the R fraction was incorporated into the silicate crystal structures of the sediments. And the arsenic fraction was very stable and was unlikely to be released into the sediment water [60, 61]. Therefore, these results denote that the area presents a low environmental risk for arsenic. The results of this study were similar to those of Rodrigues et al. [62] who reported that arsenic was predominantly associated with the residual fraction of sediments collected around the Caveira mine in Portugal. The percentage fraction (F3) of arsenic bound to organic matter and sulphides varied between 21.04 (Badenou) and 30.92% (Tongon). The ANOVA analysis ($p < 0.05$) showed that there was no noticeable difference between the stations. Indeed, the fraction (F3) represented the second most important reactive fraction for these different sediments. That fraction marked distribution for the organic phase reflected the affinity of arsenic with organic matter. The proportions of the arsenic fraction (F2) bound to iron and manganese oxides varied between 10.37 (Badenou) and 18.35% (Taoura). There was no significant difference (ANOVA, $p < 0.05$) between the stations. The percentages of the F1 fraction corresponding to the fraction of exchangeable and carbonate-bound arsenic ranged from 1.23% (Badenou) to 2.12% (Tongon). That fraction represented the most important reactive fraction for the different sediments. Sediments from the industrial extraction area of Tongon recorded the highest percentage without any considerable difference ($p < 0.05$). That percentage in the Tongon industrial extraction zone gave $3.55 \mu\text{g/g}$ out of a total of $161.42 \mu\text{g/g}$. The distribution of arsenic in the different phases of the sediments of the study areas is ordered as follows: Badenou, Tongon, Taoura, Bevogo, Kanakono, and Sissingue (i.e., $R > F_3 > F_2 > F_1$).

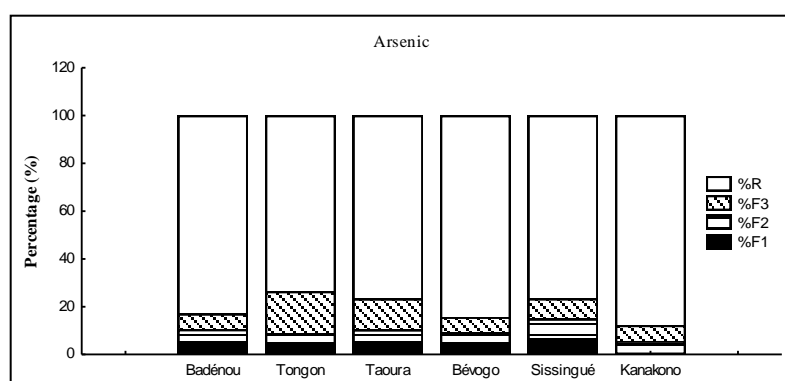


Figure 3. Mean percentages of arsenic distributed in the acid soluble, reducible, oxidizable, and residual fractions in sediment from the study area

3.4. Risk assessment code (RAC) and modified potential ecological risk index (MRI)

Risk assessment code percentages of arsenic in studied sediments are shown in table 5. It can be observed that arsenic can cause a low risk in all the studied stations ($0.87 \leq \text{RAC} (\%) \leq 2.91$). The MRI values of arsenic ranged from 6.80 to 798.60 (Table 5) all over the studied sites. Overall, the MRI values of As ($\text{MRI} < 150$) showed a low environmental risk over the studied mining areas, except the industrial mining area of Tongon ($\text{MRI} > 600$), which depicted a very high environmental risk.

Table 5: Environmental risk assessment of sediment (RAC) and modified potential risk index (MRI)

City	stations	RAC (%)	MRI
Korhogo	Badenou	1.23	8.20
	Tongon	2.12	798.60
	Taoura	1.36	6.80
Tengrela	Bevogo	1.65	43.60
	Sissingue	1.60	132.00
	Kanakono	1.49	102.20

3.5. Human health risk assessment

The HQ, HI, and CR values for each element for adults were calculated using the mean values of bioavailable arsenic concentrations from Table 6.

Table 6: The results of health risk assessment (non-carcinogenic and carcinogenic risks) of arsenic in sediments

Metal	Stations	Non-carcinogenic Risks			Carcinogenic Risks		
		HQ _{ing}	HQ _{derm}	HI	CR _{ing}	CR _{derm}	CR _{tot}
As	Badenou	1.82E-04	5.58E-07	1.83E-04	1.63E-06	1.63E-06	3.26E-06
	Tongon	1.77E-02	5.43E-05	1.78E-02	1.59E-04	1.59E-04	3.17E-04
	Taoura	1.51E-04	4.62E-07	1.51E-04	1.35E-06	1.35E-06	2.70E-06
	Bevogo	9.68E-04	2.96E-06	9.71E-04	8.66E-06	8.66E-06	1.73E-05
	Sissingue	2.93E-03	8.98E-06	2.94E-03	2.62E-05	2.62E-05	5.24E-05
	Kanakono	2.27E-03	6.95E-06	2.27E-03	2.03E-05	2.03E-05	4.06E-05

3.5.1. Non-carcinogenic health risk assessment

HQ and HI values greater than 1 suggest adverse health effects of arsenic in sediment. In the present study, HQ and HI values for arsenic in sediments from all studied sites were below 1 (Table 6), a reference threshold suggested by USEPA [63]. These values suggested that a non-carcinogenic health risk was present, and the risks from both ingestion and dermal contact routes of arsenic were low. However, the sequence of distinctive exposure ran for non-carcinogenic doses was $HQ_{ing} > HQ_{derm}$ of adults for arsenic in all studied stations. Therefore, we can conclude that arsenic may have potential adverse effects through ingestion due to an HQ_{ing} value higher than the HQ_{derm} value. The highest value of $HQ_{ing} = 1.77E-2$ was determined in the sediments of Tongon, which is located in an industrial gold mining area. In this region, arsenic concentrations were found to be the highest ones.

Thus, the industrial gold mining area was the representative arsenic pollutant.

3.5.2. Carcinogenic health risk assessment

The values for CR_{ing} , CR_{derm} , and total risk (CRT) are shown in Table 6. The carcinogenic risk assessment (CRT) showed that the potential risk values for arsenic at all the studied stations ranged from 10^{-6} to 10^{-4} with the exception of the CRT value in the Tongon sediments, which was greater than 10^{-4} . Based on these results, the arsenic levels in the sediments of Badenou, Taoura, Bevogo, Sissingue, and Kanakono indicated an acceptable carcinogenic risk to human health. However, the CRT value for arsenic related to carcinogenic risk in Tongon sediments was very high and caused a serious threat to human health. Thus, Tongon populations could be prone to a risk of developing skin, lung, prostate, liver, kidney, and bladder cancer [64]. In this study, CR_{ing} averages were virtually identical to CR_{derm} averages. Therefore, ingestion and skin contact may be the routes of exposure to arsenic from sediments.

4. Conclusion

The CF, EF, MRI, and RAC methods applied to the analysis of ecological arsenic pollution risks in the sediments of the studied mining areas and the obtained results provided the following information. The high arsenic content in some of the studied stations revealed that the highest level of pollution was distributed in the research area where mining activities were concentrated. Furthermore, this study suggested that most of the arsenic was caused by anthropogenic factors such as mining activities. The chemical speciation of arsenic was

determined using a BCR sequential extraction procedure to assess mobility potential. The result showed that arsenic was mainly bound to the residual fraction. This implied that the R fraction was embedded into the silicate crystalline structures of the sediments and that this arsenic fraction was highly stable. According to the RAC, arsenic presented a low risk to the ecosystem due to their percentages in marketable fractions. Overall, arsenic was weakly to very highly contaminated in the studied sediments. However, MRI values showed a low environmental risk in the studied mining areas, with the exception of the Tongon industrial mining zone, which presented a very high environmental risk. The potential human health risk results indicated that there was no significant non-carcinogenic risk from arsenic for residents at any of the study sites. On the other hand, the results of the potential risk (CRt) to human health revealed that there were significant carcinogenic risks for residents living in the vicinity of the Tongon mining areas for arsenic.

References

- [1] Githiria JM, Onifade M. The impact of mining on sustainable practices and the traditional culture of developing countries. *Journal of Environmental Studies and Sciences*. 2020;10(4): 394-410.
- [2] Hilson G. Small-scale mining and its socio-economic impact in developing countries. In *Natural resources forum*, Oxford, UK and Boston, USA: Blackwell Publishing Ltd. 2002;26(1): 3-13.
- [3] Ingram V, Tieguhong JC, Schure J, Nkamgnia E, Tadjuidje MH. Where artisanal mines and forest meet: Socio-economic and environmental impacts in the Congo Basin. In *Natural Resources Forum*, Oxford, UK: Blackwell Publishing Ltd. 2011; 35(4): 304-320.
- [4] Ofosu G, Dittmann A, Sarpong D, Botchie D. Socio-economic and environmental implications of Artisanal and Small-scale Mining (ASM) on agriculture and livelihoods. *Environmental Science & Policy*. 2020; 106: 210-220.
- [5] DeSisto SL, Jamieson HE, Parsons MB. Arsenic mobility in weathered gold mine tailings under a low-organic soil cover. *Environmental Earth Sciences*. 2017; 76: 1-16.
- [6] Ali H, Khan E, Ilahi I. Environmental chemistry and ecotoxicology of hazardous heavy metals: environmental persistence, toxicity, and bioaccumulation. *Journal of chemistry*. 2019; 2019:14-29.
- [7] Patel KS, Pandey PK, Martín-Ramos, P, Corns W T, Varol S, Bhattacharya, P Zhu Y. A review on arsenic in the environment: contamination, mobility, sources, and exposure. *RSC advances*. 2023; 13(13):8803-8821.
- [8] Kanel SR, Das TK, Varma RS, Kurwadkar S, Chakraborty S, Joshi TP, Nadagouda MN. Arsenic Contamination in Groundwater: Geochemical Basis of Treatment Technologies. *ACS Environmental Au*. 2023; 3(3):135-152.
- [9] Hull EA, Stiling RR, Barajas M, Neumann RB, Olden JD, Gawel JE. Littoral sediment arsenic concentrations predict arsenic trophic transfer and human health risk in contaminated lakes. *Plos one*. 2023; 18(10):1-16.
- [10] Mamadou C, N'guessan, LBK, N'goran KPDA, Diabate D, Trokourey A. Distribution, Ecological and Health Risks of Arsenic in Sediment from the Mixing Zone of the Comoé River and the Ebrié Lagoon, Côte d'Ivoire, West Africa. *American Journal of Applied Chemistry*. 2022;10(4):89-96.

- [11] Marrugo-Madrid S, Pinedo-Hernández J, Paternina-Urbe R, Marrugo-Negrete J, Díez S. Health risk assessment for human exposure to mercury species and arsenic via consumption of local food in a gold mining area in Colombia. *Environmental research*.2022; 215(3): 113950-113968.
- [12] Basu N, Clarke E, Green A, Calys-Tagoe B, Chan L, Dzodzomenyo M, Wilson ML. Integrated assessment of artisanal and small-scale gold mining in Ghana—Part 1: Human health review. *International journal of environmental research and public health*.2015; 12(5): 5143-5176.
- [13] Sardar K, Ali S, Hameed S, Afzal S, Fatima S, Shakoor MB, Tauqeer HM. Heavy metals contamination and what are the impacts on living organisms. *Greener Journal of Environmental management and public safety*.2013; 2(4):172-179.
- [14] Loukola-Ruskeeniemi K, Müller I, Reichel S, Jones C, Battaglia-Brunet F, Elert M, Valkama H. Risk management for arsenic in agricultural soil–water systems: lessons learned from case studies in Europe. *Journal of Hazardous Materials*. 2022;424:127677-127695.
- [15] Nakata H, Kannan K, Nasu T, Cho HS, Sinclair E, Takemura A. Perfluorinated contaminants in sediments and aquatic organisms collected from shallow water and tidal flat areas of the Ariake Sea, Japan: environmental fate of perfluorooctane sulfonate in aquatic ecosystems. *Environmental science & technology*. 2006; 40(16): 4916-4921.
- [16] Makinde WO, Ayodele OE, Ayodele TI, Oluremi OI, Temitope OK, Temitope FO. Heavy metal contamination in river water and sediments in gold-mining areas of southwestern Nigeria. *Afr J Environ Sci Technol*. 2017; 10(5):150-161.
- [17] Taiwo AM, Awomeso JA. Assessment of trace metal concentration and health risks associated with artisanal gold mining activities in Ijeshaland, Osun State, Nigeria - Part 1. *J Geochem Explor*. 2017; 177:1–10.
- [18] Niane B, Naresh D, John P, Robert M. Quantification and characterization of mercury-resistant bacteria in sediments contaminated by small-scale artisanal gold mining activities, Kédougou region, Senegal. *J Geochem Explor*. 2019; 205: 106353-106359.
- [19] Klubi E, Abril JM, Nyarko E, Delgado A. Impact of gold-mining activity on trace elements enrichment in the West African estuaries: the case of Pra and Ankobra rivers with the Volta estuary (Ghana) as the reference. *J Geochem Explor*. 2018; 190:229–244.
- [20] Sunkari ED, Appiah-Twum M, Lermi A. Spatial distribution and trace element geochemistry of laterites in Kunche area: implication for gold exploration targets in NW. Ghana. *J Afr Earth Sci*.2019; 158:103519-103538.
- [21] Kinimo KC, Yao KM, Marcotte S, Kouassi NLB, Trokourey A. Distribution trends and ecological risks of arsenic and trace metals in wetland sediments around gold mining activities in central southern and south eastern Côte d'Ivoire. *Journal of Geochemical Exploration*. 2018; S0375-6742(17):30304-7.
- [22] Hejna M, Moscatelli A, Onelli E, Baldi A, Piluc S, Rossi L. Evaluation of heavy metal concentration in the breeding system. *Ital J Anim Sci*. 2019; 18(1):1372-1384.

- [23] Sako A, Semdé S, Wenmenga U. Geochemical evaluation of soil, surface water and groundwater around the Tongon gold mining area, northern Côte d'Ivoire, West Africa. *J Afr Earth Sci.* 2018; 145: 297-316.
- [24] Traore IW, Houhamdi M. Bioassessment of Artisanal Mining's Impact on Bagoé River Water Quality in Sikasso Region. *World J Environ Biosci.* 2017; 6(4): 7-14.
- [25] Girard G, Sircoulon J, Touchebeuf P. Aperçu sur les régimes hydrologiques de Côte d'Ivoire. ORSTOM Editions, Côte d'Ivoire. 1971;50 :109-155.
- [26] N'goran KP DA, Diabate D, Kouassi NGLB, Yao KM, Kinimo KC, Ouattara, AA, Trokourey A. Geochemical speciation and distribution of trace metals in sediments around industrial and artisanal gold mining areas in northern Côte d'Ivoire. *Environmental Earth Sciences.* 2022; 81(12):333-351.
- [27] Rodgers KJ, Hursthouse A, Cuthbert S. The potential of sequential extraction in the characterisation and management of wastes from steel processing: a prospective review. *Int J Environ Res Public Health.* 2015; 12(9): 11724-11755.
- [28] Hakanson L. Ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research.* 1980; 14: 975- 1001.
- [29] Maanan M, Saddik M, Maanan M, Chaibi M, Assobhei O, Zourarah B. Environmental and ecological risk assessment of heavy metals in sediments of Nador lagoon, Morocco. *Ecol Indic.* 2015; 48: 616–626.
- [30] Marrugo-Negrete J, Pinedo-Hernández J, Díez S. Assessment of heavy metal pollution, spatial distribution and origin in agricultural soils along the Sinú River Basin, Colombia. *Environmental research.* 2017; 154, 380-388.
- [31] Jung JM, Choi KY, Chung CS, Kim CJ, Kim SH. Fractionation and risk assessment of metals in sediments of an ocean dumping site. *Marine pollution bulletin.* 2019; 141:227-235.
- [32] Zhu HN, Yuan XZ, Zeng GM, Jiang M, Liang J, Zhang C, Jiang HW. Ecological risk assessment of heavy metals in sediments of Xiawan Port based on modified potential ecological risk index. *Transactions of Nonferrous Metals Society of Chin.* 2012; 22(6):1470-1477.
- [33] Hakanson L. Ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research.* 1980; 14 (5): 975-1001.
- [34] Gong Y, Yang S, Chen S, Zhao S, Ai Y, Huang D, Cheng H. Soil microbial responses to simultaneous contamination of antimony and arsenic in the surrounding area of an abandoned antimony smelter in Southwest China. *Environment International.* 2023;174:107897-107908.
- [35] Hu Z, Gao S. Upper crustal abundances of trace elements: A revision and update. *Chemical Geology.* 2008; 253(3-4): 205-221.
- [36] Gusiati ZM, Kulikowska D. The usability of the IR, RAC and MRI indices of heavy metal distribution to assess the environmental quality of sewage sludge composts. *Waste management.* 2014; 34(7): 1227-1236.

- [37] Kusina FM, Azania NNM, Hasana SNMHS, Sulong NA. Distribution of heavy metals and metalloid in surface sediments of heavily mined area for bauxite ore in Pengerang, Malaysia and associated risk assessment. *Catena*. 2018; 165:454-464.
- [38] Song J, Liu Q, Sheng Y. Distribution and risk assessment of trace metals in riverine surface sediments in gold mining area. *Environmental monitoring and assessment*. 2019; 191(3): 1-13.
- [39] Iqbal J, Tirmizi SA, Shah MH. Statistical distribution and risk assessment of selected metals in sediments of Rawal Lake, Pakistan. *Environmental monitoring and assessment*. 2013; 185 (1): 729-743.
- [41] Pecina V, Brtnický M, Baltazár T, Juříčka D, Kynický J, Galiová MV. Human health and ecological risk assessment of trace elements in urban soils of 101 cities in China: A meta-analysis. *Chemosphere*. 2020; 129215-129257.
- [42] World Bank. The World Bank Group: Average Life Expectancy in Côte d'Ivoire: 2009- 2019.
- [43] Soltani-Gerdefaramarzi S, Ghasemi M, Gheysouri M. Pollution, human health risk assessment and spatial distribution of toxic metals in urban soil of Yazd City, Iran. *Environmental Geochemistry and Health*. 2021; 1-16.
- [44] Lu X, Zhang X, Li LY, Chen H. Assessment of metals pollution and health risk in dust from nursery schools in Xi'an, China. *Environmental research*. 2014; 128: 27-34.
- [45] Ferreira-Baptista L, De Miguel E. Geochemistry and risk assessment of street dust in Luanda, Angola: a tropical urban environment. *Atmos. Environ*. 2005; 38: 4501-4512.
- [46] US Environmental Protection Agency (USEPA). Human Health and Ecological Risk Assessment Chesterfield Power Station Ash Ponds November 9, 2018; 1-144.
- [47] Kaur M, Kumar A, Mehra R, Kaur I. Quantitative assessment of exposure of heavy metals in groundwater and soil on human health in Reasi district, Jammu and Kashmir. *Environmental geochemistry and health*. 2020; 42(1): 77-94.
- [48] Xiao Q, Zong Y, Malik Z, Lu S. Source identification and risk assessment of heavy metals in road dust of steel industrial city (Anshan), Liaoning, Northeast China. *Human and Ecological Risk Assessment: An International Journal*. 2020; 26(5): 1359-1378.
- [49] Zhang H, Yu J, Zhou S. Spatial Distribution of As, Cr, Pb, Cd, Cu, and Zn in the Water and Sediment of a River Impacted by Gold Mining. *Mine Water Environ*. 2013; 33: 206-216.
- [50] Manga VE, Neba GN, Suh, CE. Environmental geochemistry of mine tailings soils in the artisanal gold mining district of Bétaré-Oya, Cameroon. *Environ Pollut*. 2017; 6(1): 52-61.
- [51] Gafur AN, Sakakibara M, Sano S, Sera K. A Case Study of Heavy Metal Pollution in Water of Bone River by Artisanal Small-Scale Gold Mine Activities in Eastern Part of Gorontalo, Indonesia. *Water*. 2018; 10(11): 1507-1517.

- [52] Kagambega N, Ouedraogo M, Sam U. Assessment of Water and Stream Sediment Pollution Related to Artisanal Mining in Alga, Burkina Faso, West Africa. *International Journal of Environment and Climate Change*. 2023; 13(11): 461-473.
- [53] Hogarh JN, Adu-Gyamfi E, Nukpezah D, Akoto O, Adu-Kumi S. Contamination from mercury and other heavy metals in a mining district in Ghana: discerning recent trends from sediment core analysis. *Environmental Systems Research*. 2016; 5: 1-9.
- [54] Wadige CPM, Taylor AM, Krikowa F, Maher WA. Sediment metal concentration survey along the mine-affected Molonglo River, NSW, Australia. *Archives of environmental contamination and toxicology*. 2016; 70(3):572-582.
- [55] Sako A, Nimi M, Sawadogo S, Hema A A K. Occurrence, behaviour and environmental risk assessment of trace metals in stream sediments from southwestern Burkina Faso, West Africa. *Environmental Monitoring and Assessment*. 2021; 193(3): 133-155.
- [56] Ahoussi KE, Yapo AP, Kouassi AM, Koffi YB. Surface Water Sediments Characterization Using Metallic Trace Elements (MTEs): Case of the Artisanal Gold Mining Sites of Kokumbo (Côte d'Ivoire). *Journal of Environmental Protection*. 2020; 11: 649-663.
- [57] Donkor AK, Bonzongo JCJ, Nartey VK, Adotey DK. Heavy metals in sediments of the gold mining impacted Pra River basin, Ghana, West Africa. *Soil & sediment contamination*. 2005; 14(6), 479-503.
- [58] Elias P, Gbadegesin A. Spatial relationships of urban land use, soils and heavy metal concentrations in Lagos Mainland area. *J. Appl. Sci. Environ. Manage*. 2011; 15 (2):391 – 399.
- [59] Kowalska J, Mazurek R, Gąsiorek M, Setlak M, Zaleski T, Waroszewski J. Soil pollution indices conditioned by medieval metallurgical activity—A case study from Krakow (Poland). *Environmental Pollution*. 2016; 218: 1023-1036.
- [60] Nemati K, Bakar NKA, Abas MR, Sobhanzadeh E. Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. *Journal of hazardous materials*. 2011; 192(1): 402-410.
- [61] Palleiro L, Patinha C, Rodríguez-Blanco ML, Taboada-Castro MM, Taboada-Castro MT. Metal fractionation in topsoils and bed sediments in the Mero River rural basin: bioavailability and relationship with soil and sediment properties. *Catena*. 2016; 144: 34-44.
- [62] Rodrigues SM, Henriques B, Coimbra J, Ferreira da Silva E, Pereira ME, Duarte AC. Water-soluble fraction of mercury, arsenic and other potentially toxic elements in highly contaminated sediments and soils. *Chemosphere*. 2010; (78): 1301-1312.
- [63] US Environmental Protection Agency (USEPA). Supplemental guidance for developing soil screening levels for superfund sites, OSWER 9355. Office of Emergency and Remedial Response, Washington, 2002.
- [64] Abdul KSM, Jayasinghe SS, Chandana EP, Jayasumana C, De Silva PMC. Arsenic and human health effects: A review. *Environmental toxicology and pharmacology*. 2015; 40(3), 828-846.