Journal of Materials and Environmental Science
ISSN : 2028-2508
e-ISSN : 2737-890X
CODEN : JMESCN

J. Mater. Environ. Sci., 2023, Volume 14, Issue 01, Page 41-61

http://www.jmaterenvironsci.com

Assessment of metallic pollution of water and soil from illegal gold mining sites in Kong 2, Hiré and Degbézéré (Ivory Coast)

Kouadio L. M. [1*], Tillous K. E. N. [2], Coulibaly V. [1], Sei J. [1], Martinez H.[3,4,5], Pannier F [3].

[1] *Laboratory of Constitution and Reaction of Matter (LCRM), UFR SSMT, Félix Houphouët-Boigny University, Abidjan, Ivory Coast.*
[2] *Laboratory of Technology (LabTech), UFR SSMT, Félix Houphouët-Boigny University, Abidjan, Ivory Coast.*
[3] *University of Pau and Pays de l'Adour, E2S UPPA, CNRS, IPREM, 64053 Pau, France*
[4] *Ecole Centrale Casablanca ECC, Centre Systèmes Complexes et Interaction, Bouskoura, Morocco*
[5] *Electrochemical Energy Storage Network (RS2E), CNRS FR3459, 33 Rue Saint Leu, 80039 Amiens Cedex, France*
**Corresponding author, Email address: moseskouadio41@gmail.com*

Received *01 Dec 2022,*
Revised *03 Jan 2023,*
Accepted *05 Jan 2023*

Keywords:
- ✓ *Pollution;*
- ✓ *metals;*
- ✓ *illegal gold mining;*
- ✓ *Atomic absorption*

Citation*: Kouadio L. M., Tillous K. E. N., Coulibaly V., SEI J., Martinez H., Pannier F. (2023) Assessment of metallic pollution of water and soil from illegal gold mining sites in Kong 2, Hiré and Degbézéré (Ivory Coast), J. Mater. Environ. Sci., 14(1), 41-61.*

Abstract: Illegal gold mining is an environmentally irresponsible activity that has grown in Ivory Coast. The level of metal and metalloid pollution in three localities (Kong 2, Hiré and Degbézéré) hosting illegal gold mining sites in Ivory Coast were assessed. Water and soil samples collected at these and other sites were analyzed by atomic absorption spectroscopy (AAS) and their contents of Hg, Pb, Cd, Fe and As were determined. Carcinogenic (CR) and non-carcinogenic (HQ and HI) risk indices were calculated in the waters. Soil pollution and environmental risk were assessed using the enrichment factor (EF), contamination factor (CF), degree of contamination (DC) and potential ecological risk indices (E_r^iet RI). Measured concentrations of metals and metalloids differ according to the site and the metal considered. The concentrations of mercury in the water sampled are very often above the limit value set by the WHO (1 µg/L). The carcinogenic and non-carcinogenic risk assessment showed that health problems are higher in children and at the gold mining site. The pollution indices show that the localities are more contaminated with Hg and As. For all the studied chemical species, the locality of Degbézéré is considerably contaminated with a very high ecological risk, whereas those of Kong 2 and Hiré present moderate contaminations.

1. Introduction

The problems caused by chemical contaminants, particularly metals and metalloids, in the environment continue to attract the attention of the scientific community. Indeed, the protection of the environment requires knowledge of the level of contamination and the effects of these contaminants on the living beings that depend on them. Their presence in environmental matrices is often caused by anthropogenic activities. Among the anthropogenic sources of metals, we can point out : mining, metallurgy and steel industry, fertilizers and pesticides applied in the cultivation of soils, incinerators and ashes of waste incineration, medical waste, city waste dumps, emissions from factories and combustion engines, sewage effluents and sludge...(Aranguren, 2008). However, it seems that the main anthropogenic source of metals for the environment is that produced by mining and associated industries. The mining industry uses chemical products (mercury, cyanide, sulfuric and nitric acids,

ammonium nitrate, detergents...) with high toxicity which constitute important reservoirs of metals (Hg, Cd, Pb...) and metalloids (As...). The discharge of untreated effluents from this activity into surface waters or onto the ground causes considerable pollution. Thus, the evaluation of the level of contamination of the mining sites is of concern in several research works throughout the world (Makhoukh *et al.*, 2011, Djade *et al.*, 2020). Numerous researchers have assessed the level of metal pollution at mining sites in order to estimate thelevel of contamination. These studies have revealed high concentrations of metals and metalloids in water, soil, plants and sediments of mining sites in several countries of the world (5 ppm of Hg; 6576.699 ppm of Pb; 165 ppm of Cd and 411 ppm of As) (Ibrahim *et al.*, 2019), (Smouni *et al.*, 2010), (Adeyi and Babalola, 2017).

Ivory Coast is not exempt from the harmful effects caused by mining activity, particularly that practiced by artisanal miners, generally illiterate peasants operating illicitly and clandestinely in gold mining (Yobo and Nassa, 2018).

Clandestine gold mining has developed at a prodigious rate in recent years in Côte d'Ivoire and there are now more than one thousand (1000) sites (Affessi and Koffi, 2016). This phenomenon, which has developed rapidly and wildly over the past ten years, affects 24 regions out of 31 in the country and involves more than five hundred thousand (500,000) people (Goh, 2016).

This activity, although lucrative, is carried out under unregulated conditions and presents numerous risks for health, the environment and agriculture because of the destruction of soils, water pollution and contamination of living beings. Several rivers are polluted by this activity, including the Cavally river in the west, the Bandama and N'zi rivers in the center and the Bia river in the east of the country. Studies have found concentrations of arsenic, cadmium, mercury, nickel and lead well above the limit values set by the WHO in sediments, drinking water and irrigation water in the sub-prefecture of Hiré and in Aboisso (Kinimo *et al.*, 2018), (Yapi *et al.*, 2014). The populations living in these localities and in the surrounding area use mostly waters that are often polluted by these metals. These pollutants are very toxic and have a harmful effect on human and animal health, as well as on the formation of plants (Alaqarbeh et *al.*, 2022; Harmandon, 2004; Goix et *al.*, 2014; Koller and Pletscher, 2013; Carex, 2009).

The objective of this work is to assess the levels of mercury (Hg), lead (Pb), cadmium (Cd) and arsenic (As) contamination of soil and water at the illegal gold mining sites in Kong 2, Hiré and Degbézéré. To achieve this, the levels of these metals and metalloids were measured.

2. *Materials and Methods*

2.1 Studied samples

Soil and water samples were collected from three (03) localities located in Ivory Coast: Kong 2 (6°10' north latitude and 3°39' west longitude in Yakassé-Attobrou department in southern Ivory Coast); Hiré (6°11' north latitude and 5°17′ west longitude in Divo department, southern Ivory Coast) and Degbézéré (Bouaflé department in west-central Ivory Coast, at 6°58' north latitude and 5°39' west longitude). Samples were taken from the soils and rivers of the sites as well as from outside the sites for comparison. Glass bottles of one liter (1L) capacity were used to hold the water. The soil samples (approximately 1 kg) were taken using a trowel and placed in freezer bags. The samples taken were immediately stored in a cooler in the presence of ice and taken to the laboratory. Before the analysis, the water samples were kept at 4°C in a refrigerator to avoid any degradation. A total of 18 water samples and 18 soil samples were collected from all three locations. Index numbers 1 through 3 represent samples from illegal gold mining sites and index numbers 4 through 6 indicate samples from outside the mining location (**Table 1**).

Table 1. List of water and soil samples

Localities	No-mining areas		Mining areas	
	Waters	Soils	Waters	Soils
Hiré	H_{E1}; H_{E2} ;H_{E3}	H_{S1} ;H_{S2} ; H_{S3}	H_{E4} ;H_{E5} ;H_{E6}	H_{S4} ;H_{S5} ;H_{S6}
Kong 2	K_{E1} ;K_{E2} ;K_{E3}	K_{S1} ; K_{S2} ;K_{S3}	K_{E4} ;K_{E5} ; K_{E6}	K_{S4} ;K_{S5} ;K_{S6}
Degbézéré	D_{E1} ;D_{E2} ;D_{E3}	D_{S1} ;D_{S2} ; D_{S3}	D_{E4} ;D_{E5} ; D_{E6}	D_{S4} ;D_{S5} ;D_{S6}

2.2 Measurement of physico-chemical parameters

2.2.1 pH

The pH of the water and soil samples was measured using a HANNA HI 2211 pH meter. For the soil, the pH was determined by dissolving the soil in a soil/distilled water ratio of 1/2.5 (Sako and Semdé, 2018). Therefore, a mass of 20 g of soil is put in a beaker with 50 mL of distilled water. The mixture is stirred at 500 rpm using a magnetic stirrer. After 1 hour of stirring, the mixture is allowed to stand for 30 min, and then the electrode of the pH meter is dipped into the solution.

2.2.2 Organic Matter (OM)

The determination of organic matter was done by the method of loss on fire or combustion. This method involves the destruction of organic elements by high heat. A porcelain crucible is placed in the oven and heated to 550 °C for 20 min. The mass of the empty crucible is measured to the nearest milligram on an analytical balance (m_0). Then, 10g of soil sample is placed in the crucible and weighed (m_1). The crucible and sample are heated to 550 °C in the oven for 4 h. After cooling, the mass of the crucible and sample is measured (m_2) (Institut scientifique de service public, 2017).

The percentage organic matter content is determined according to **Eqn. 1** below :

$$\% \text{ OM} = \frac{(m_1 - m_0) - (m_2 - m_0)}{(m_1 - m_0)} \times 100 \qquad \textbf{Eqn 1.}$$

2.2.3 Determination of metal and metalloid concentration

The metal and metalloid contents of the samples were determined by means of an Australian-made Varian SpectrAA 110 atomic absorption spectrometer. Soil samples were dried, ground and sieved at 63 µm. They were mineralized as follow : 0.2 g of each soil sample, is introduced into Teflon tubes and digested in aqua regia (mL of HNO_3 (65%) and 3mL of HCl (37%)). The mixtures are left to rest under the hood after adding 6 ml of hydrofluoric acid (HF). 1 hour later, 2 mL of H_2O_2 (30-33%) are added to the contents of the vials. The flasks are closed and heated to 120°C for 3 hours using a heating plate. After heating, a volume of 10 ml of HBr (4%) is added to each content. The flasks are then closed and heated (120° C) for another 1 hour. After this heating time, the mixtures are left to cool to room temperature under the hood. The mineralizate is made up to 50 mL using distilled water.

For this work, the methods used are: the graphite furnace method for lead (Pb at 283.3 nm), cadmium (Cd at 228.8 nm) and arsenic (As at 193.7 nm), flame for iron (Fe at 248.3 nm) and cold vapor for mercury (Hg at 253.7 nm). Each sample was analyzed in duplicate.

2.2.4 Statistical analysis of results

The R version R 4.1.2 software was used for the statistical analysis of the levels of chemical species in water and soil. Multiple comparison analysis tests were applied using the agricolae package. These

tests made it possible to observe whether the difference between the levels of chemical species in the non-mining and gold panning zones of each locality is significant or not. The mean and the standard deviation were determined for each chemical element analyzed. All tests were performed at $p < 0.05$. Origin software was used to make the graphics.

2.2.5 Assessment of health risks related to water intake

The health risks related to the ingestion of metals and metalloids were evaluated by calculating indices such as : carcinogenic risk (CR), exposure quotient (HQ) and toxicity index (HI). The HQ and HI indices constitute the non-carcinogenic risks. These calculations were based on the average daily intake (ADI) of water ingested by residents of these localities. The expression of the ADI is given by the equation **Eqn. 2**.

$$ADI = \frac{C \times IR \times EF \times ED}{BW \times AT} \qquad \textbf{Eqn. 2}$$

where C is the average concentration (mg/L) of metal or metalloid, IR is the daily intake rate (L/day), EF is the frequency of exposure (days/year), ED is the duration of exposure (years), BW is the average body weight (Kg) and AT is the average time of exposure (days) (Bempah and Ewusi, 2016), (Bortey-Sam *et al.*, 2015). IR, EF, ED, BW and AT are called exposure parameters (**Table 2**).

Table 2. Reference values for exposure parameters

Parameters	Adults	Children	References
IR	2 L/day	1 L/day	(Taiwo and Awomeso, 2017)
EF	350 days/year	350 days/year	(USEPA, 2001)
ED	30 years	6 years	(Taiwo et Awomeso, 2017), (USEPA, 2001)
BW	60 Kg	10 Kg	(Taiwo and Awomeso, 2017)

Note: Life expectancy in Ivory Coast is 53 years (52 years for men and 54 years for women) (WHO 2015). For adults, for non-carcinogenic effects, AT = ED x 365 and for carcinogenic effects AT = 53 x 365. However, for children, AT = ED x 365 (Bempah and Ewusi, 2016), (Taiwo and Awomeso, 2017).

Of the chemical species studied, arsenic and cadmium have carcinogenic effects. The CR are determined by the following relationship (**Eqn. 3**) :

$$CR = CSF \times ADI \qquad \textbf{Eqn. 3}$$

The carcinogenicity factor (CSF) values are 1.5 and 0.380 $(mg/Kg/day)^{-1}$ for arsenic and cadmium respectively (Bortey-Sam *et al.*, 2015). The CR values over 10^{-4} mean that there is a possibility of developing cancer. A CR value lower than 10^{-6} is considered to be of no concern for cancer, while a CR value between 10^{-6} and 10^{-4} is generally considered acceptable, depending on the situation and circumstances of exposure (Bempah and Ewusi, 2016), (USEPA, 2001). HQ for a metal or metalloid is determined by **Eqn. 4** (Li *et al.*, 2014), (Adewoyin *et al.*, 2019) :

$$HQ = \frac{ADI}{RFD} \qquad \textbf{Eqn. 4}$$

The reference dose values (RFD) are: 3.10^{-4}; 5.10^{-4}; 3.10^{-4} and $3.5.10^{-4}$ mg/Kg/day respectively for arsenic, cadmium, mercury and lead (Bortey-Sam *et al.*, 2015).

The non-carcinogenic toxicity index (HI) was calculated as the sum of the exposure quotients (HQ) according to **Eqn. 5** below (Li *et al.*, 2014):

$$HI = \sum_{i=1}^{n} HQ_i \qquad \textbf{Eqn. 5}$$

If HI < 1, it is unlikely that the exposed population could experience obvious adverse health effects. However, if HI > 1, adverse health effects could occur (Nkansah *et al.*, 2017).

2.2.6 Assessment of soil contamination levels

To estimate the level of contamination, pollution indices have been used. The principle is based on the comparison of measured values with reference values. In the case of this study, the reference values used are those defined by Wedepohl and recognized worldwide as reference concentrations in unpolluted areas (UCC) (Ekengele and Mabrey, 2016; Wedepohl, 1995).

The enrichment factor (EF) is used to evaluate the intensity of a metallic pollution by differentiating the anthropogenic signal from the natural signal. Its calculation was defined by relating the content of a contaminant element in the sample to the concentration of an element considered relatively immobile in this sample (ech), compared with the same ratio found in the reference material (ref) (Aranguren, 2008). In this study, iron was chosen as the immobile reference element to perform this calculation.

The EF of an element is calculated according to the following formula (**Eqn.6**) :

$$EF = \frac{\frac{[M]_{éch}}{[Fe]_{éch}}}{\frac{[M]_{réf}}{[Fe]_{réf}}} \qquad \textbf{Eqn. 6}$$

$[M]_{ech}$: concentration of the studied metal in the sample, $[Fe]_{ech}$: concentration of iron in the sample. $[M]_{ref}$ and $[Fe]_{ref}$ are the reference concentrations of the studied metal and iron in the upper continental crust (UCC) defined by wedelpohl (Wedepohl, 1995).

Depending on the EF values, different levels of enrichment are observed (**Table 4**).

Table 4. Enrichment levels according to EF values (Ekengele and Mabrey, 2016)

EF values	Enrichment levels
EF < 1	No enrichment
1 < EF < 3	Low Enrichment
3 < EF < 5	Moderate Enrichment
5 < EF < 10	Moderate to high enrichment
10 < EF < 25	High enrichment
25 < EF < 50	Very high enrichment
EF > 50	Extreme Enrichment

The contamination factor (CF) is used to express the level of contamination by each metal. It is defined by the ratio of the content of a given metal element to the geochemical background of the same metal element taken as a normalizing factor. This contamination factor is expressed by the following formula (**Eqn.7**) (Sahli *et al.*, 2014):

$$CF = \frac{C_n}{B_n} \qquad \textbf{Eqn. 7}$$

Cn: concentration of metal n studied in the sample, Bn: geochemical background of the metal considered.

The different levels of contamination according to the CF values were established by Hakanson (Hakanson, 1980; Nadem *et al.*, 2015) and are shown in **Table 5**. The degree of contamination (DC) is the sum of the CF. It allows the estimation of the polymetallic contamination for each sampling point. It is calculated according to the following formula (**Eqn.8**) (Sahli *et al.*, 2014):

$DCi = \sum FC$; i designates the site under consideration. **Eqn. 8**

Table 5. Contamination levels as a function of CF values

CF values	Contamination level
CF < 1	Low contamination
1 ≤ CF < 3	Moderate contamination
3 ≤ CF < 6	Significant contamination
CF ≥ 6	Very high contamination

This index is associated with 4 quality classes according to Hakanson. These different classes are presented in **Table 6** below.

Table 6. Contamination levels as a function of DC values (Hakanson, 1980)

DC values	Level of contamination
DC < 8	Low contamination
8 ≤ DC < 16	Moderate contamination
16 ≤ DC < 32	Considerable contamination
DC ≥ 32	Very high contamination

Finally, the ecological risk factor for a given metal is symbolized by E_r^i and is calculated from **Eqn.9** (Ke *et al.*, 2017) :

$$E_r^i = T_r^i x \left(\frac{C_i}{C_0}\right) \quad \textbf{Eqn. 9}$$

Where C_i is the concentration of metal i in soils, C_0 is the crustal reference concentration (UCC), T_r^i is the biological toxicity factor. The values of T_r^i for the different elements are : Cu = Pb = Ni = 5, As = 10, Hg = 40 et Cd = 30.

RI is the polymetallic ecological risk for a given sampling station. It is calculated by summing the ecological risk factors for each metal using the expression (Hakanson, 1980), (Cui *et al.*, 2018), (Pobi *et al.*, 2019) (**Eqn.10**) :

$$RI = \sum_i^n T_r^i \text{ x } (\frac{C_i}{C_0}) = \sum_i^n E_r^i \quad \textbf{Eqn. 10}$$

The different levels of potential ecological risk are classified in the Table 7 According to the values of E_r^i and RI.

Table 7. Potential ecological risk according to the values of E_r^i and RI (Hakanson, 1980; Nsambu and Musibono, 2020)

Values of E_r^i	Values of RI	Level of potential ecological risk
$E_r^i < 40$	RI < 150	Low risk
$40 \leq E_r^i < 80$	150 ≤ RI < 300	Moderate risk
$80 \leq E_r^i < 160$	300 ≤ RI < 600	Considerable risk
$160 \leq E_r^i < 320$	RI ≥ 600	High risk
$E_r^i \geq 320$	-	Very high risk

E_r^i and RI not only assess the state of pollution, but also give the ecological and environmental effects allowing a better estimation of the potential risks of contamination by metals and metalloids with the index level.

3. Results and Discussion

3.1 Physico-chemical parameters

3.1.1 pH of water and soil

In Kong 2, the pH of the water samples collected vary from 7.03 to 7.20 (7.14 ± 0.08) in the non-mining area and from 6.95 to 7.11 (7.04 ± 0.07) in the illegal gold mining area. In Hiré, they vary from 7.08 to 7.12 (7.10 ± 0.02) in the no-mining zone and from 6.70 to 6.94 (6.83 ± 0.09) in the gold mining zone. In Degbézéré, these values vary from 6.82 to 7.50 (7.16 ± 0.28) and from 6.85 to 7.05 (6.94 ± 0.08) in the no-mining site and the illegal gold mining area, respectively.

For the sampled soils, pH values range from 6.54 to 6.82 (6.72 ± 0.13) and from 6.74 to 6.80 (6.73 ± 0.07) respectively in the no-mining and mining areas of Kong 2. At Hiré, soil pH values range from 6.89 to 7.06 (6.99 ± 0.07) and from 7.03 to 7.32 (7.22 ± 0.13) in the no-mining area and the gold mining site, respectively. At Degbézéré, these values vary from 6.80 to 7.13 (6.96 ± 0.08) in the no-mining area and from 6.74 to 7.21 (6.95 ± 0.11) at the gold mining site.

From these results, it can be seen that the pH values obtained tend towards neutrality. In several studies, the pH of the waters where gold mining is practiced was low (acidic) such as Bempah and Ewusi in Ghana (pH ∈ [3.12 -5.87]) (Bempah and Ewusi, 2016) and Lusilao-Makiese *et al.* in South Africa (pH ∈ [2.9 -5]) (Lusilao-Makiese *et al.*, 2013). Indeed, the process of acid mine drainage (AMD) contributes to the achievement of a low pH value by the infiltration of sulfuric acid from open pit tailings on the gold mining site (Bamba *et al.*, 2013). In contrast to this possibility, the relatively high pH values obtained in this study may be derived from the lack of sulfide minerals in the tailings dam. Thus, little sulfuric acid was generated from the oxidation of sulfide minerals, which did not substantially lower the pH of the gold mining waters (Bempah *et al.*, 2013). In addition, the pH of all the water samples studied complied with the international standard set by the WHO (pH ∈ [6.5; 9.5]) (Cheikh and Kacemi, 2011; Abdouni *et al.*, 2012)). Concerning the soils, the pH values are substantially similar to those of the waters in this study. In addition, the pH values of the soils studied are similar to those obtained in some works such as Bempah *et al.* (6.12 - 7.94) (Bempah *et al.*, 2013) and Petelka *et al.* (6.56 - 7.88) (Petelka *et al.*, 2019).

3.1.2 Organic matter (OM)

OM grades range from 4.54 to 15.01% at all sites surveyed. At Kong 2, OM vary from 4.54 to 4.63% and from 5.76 to 7.99% in the no-mining and mining areas, respectively. At Hiré, these values vary from 5.06 to 10.14% in the no-mining area and from 5.71 to 9.19% at the gold mining site. In Degbézéré, OM range from 7.74 to 8.73% in the no-mining area and from 12.88 to 15.01% in the gold mining area. The maximum OM value is obtained at station D_{S4} (15.01%) at the Degbézéré clandestine gold mining site while the minimum is determined at station K_{S1} (4.54%) in the Kong 2 no-mining area. The average OM value for all no-mining areas is (6.89 ± 1.62)% and for the illegal gold mining sites is (9.29 ± 3.49)%. These values are significantly higher than those obtained in several other studies such as those presented by Naji *et al.* (0.19 - 4.50%) in sediments from a river in Malaysia (Naji and Ismail, 2010) and Xu et Li (0.15 - 3.10%) of sediments from a Chinese river basin (Xu and Li, 2015). The relatively high values obtained in this work suggest an input of organic matter from anthropogenic activities such as mining, agriculture and others. The higher average content obtained in clandestine gold mining sites compared to no-mining areas would be due to an input of organic matter from clandestine gold mining. Thus, organic matter is a good reflection of illegal gold mining activity.

3.2 Concentration of metals (Hg, Pb and Cd) and metalloid (As)

3.2.1 Levels in water

3.2.1.1 Hg

Total mercury concentrations range from 0.40 to 4.07 µg/L at Kong 2, from < 0.006 to 3.96 µg/L at Hiré, and from 0.29 to 6.57 µg/L at Degbézéré. The average mercury concentrations of the no-mining areas of Kong 2, Hiré and Degbézéré are respectively (2.18 ± 0.45) µg/L, (1.51 ± 0.40) µg/L and (2.43 ± 2.93) µg/L. For areas where illegal gold mining is practiced, the average concentrations of Hg are (2.73 ± 1.65) µg/L, (2.47 ± 1.39) µg/L and (4.34 ± 1.39) µg/L respectively in Kong 2, Hiré and Degbézéré. For each locality, the average grade in the gold panning zone is higher than that of the no-mining site. However, this difference is not significant ($P < 0.05$). It appears from these values that the waters of the localities studied are polluted with mercury. Indeed, all the average mercury concentrations in both the mining and non-mining areas are above the limit value defined by the WHO (1 µg/L).

These relatively high mercury concentrations in these waters suggest an input of mercury from anthropogenic sources (gold mining). The average mercury concentrations vary according to the study locatities. This magnitude increases in the order of Hiré < Kong 2 < Degbézéré and correlates well with human activity. Indeed, no activity has been practiced at the Hiré gold mining site for over a year. The Kong 2 and Degbézéré sites are still active mines. In addition, the Degbézéré site is the oldest, having been in existence for over a decade. The high mercury content in the clandestine gold mining area compared to the no-mining site justifies the use of mercury in artisanal gold mining (Goh, 2016). In no-mining areas, high mercury values are caused by some gold miners, who after obtaining the gold concentrate, amalgamate it either at home or in the local river distant from the mining areas

3.2.1.2 Pb

Total lead concentrations are between < 0.05 to 25.78 µg/L for Kong 2, from 0.62 to 2.55 µg/L for Hiré, and from 0.99 to 1.64 µg/L for Degbézéré. The average concentrations at the no-mining sites are (0.72 ± 0.44) µg/L in Kong 2, (1.13 ± 0.26) µg/L at Hiré and (1.15 ± 0.11) µg/L in Degbézéré. At the illegal gold mining sites, the average concentrations at Kong 2, Hiré and Degbézéré are respectively (25.78 ± 0.00) µg/L, (1.81 ± 0.85) µg/L and (1.49 ± 0.15) µg/L. In Kong 2, the gold mining area is significantly contaminated in Pb compared to the no-mining area ($p < 0.05$). Whereas in Hiré and Degbézéré, there is no significant difference. The water samples collected generally have lead levels below the WHO limit value (10 µg/L) with the exception of sample K_{S6} (25.78 µg/L). In addition, average lead concentrations are generally low and vary very little from one site to another for both the mining and no-mining areas. The relatively high level obtained at the Kong 2 clandestine gold mining site is due to the use of motor pumps to wash the ore. Indeed, the used motor oils constitute lead reservoirs (Mohellebi *et al.*, 1999).

3.2.1.3 Cd

Total cadmium concentrations in water range from 0.11 to 0.31 µg/L at Kong 2 and from < 0.001 to 0.96 µg/L at Degbézéré. Cadmium is not detected in water samples from Hiré. For all no-mining sites, cadmium is only detected at Kong 2, with a mean value of (0.27 ± 0.04) µg/L. Concerning the illegal gold mining sites, the average concentrations are (0.15 ± 0.04) µg/L and (0.51 ± 0.45) µg/L respectively to Kong 2 and Degbézéré. Statistical analysis reveals that at Kong 2, the Cd content in the gold mining area is not significantly different from that of the no-mining site ($p < 0.05$). These results show that the

studied waters are weakly polluted with cadmium. Moreover, all the determined contents are lower than the world limit value (3 µg/L).

The average arsenic value was higher in the gold mining area than at the no-mining site at Degbézéré. Sample D_{E4} had the highest arsenic content (40.84 µg/L). The high arsenic content at the Degbézéré clandestine gold mining site could be explained by the influence of acid mine drainage (AMD) resulting from the oxidation of pyrite (FeS_2) (Lakrim *et al.*, 2016). Indeed, following the extraction of gold, large quantities of mine tailings containing sulphide minerals such as arsenopyrite (FeAsS) are generated. The dissolution of these minerals releases arsenic into rivers and water reservoirs (Assie, 2008). In addition, the use of fertilizers and pesticides in agriculture could explain the level above the global threshold (10 µg/L) detected in the no-mining area of Kong 2 (Duplay *et al.*, 2014). **Figure 1** shows the average concentrations of mercury, lead, cadmium and arsenic in the waters collected in the different localities studied.

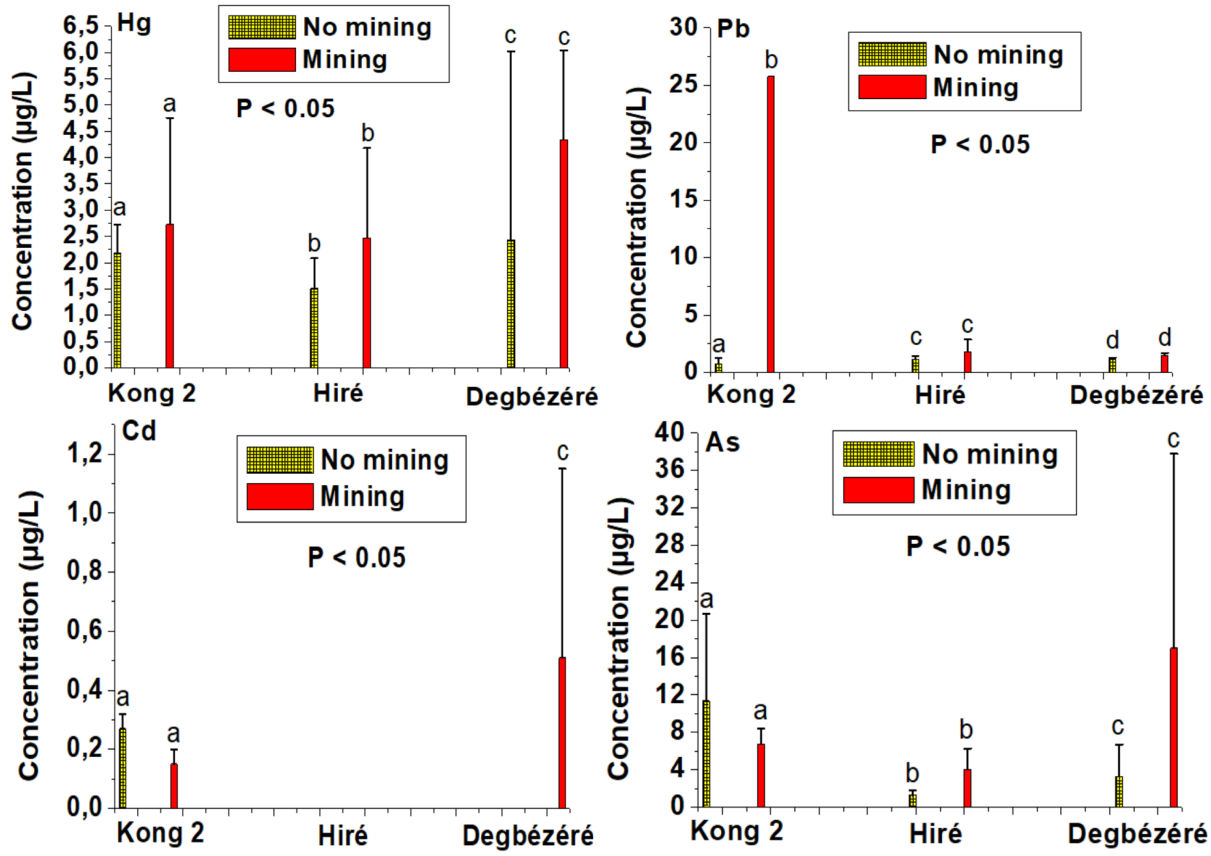

Figure 1. Average concentrations of Hg, Pb, Cd and As in water collected at Kong 2, Hiré and Degbézéré

3.2.1.4 As

Total arsenic concentrations in water range from 4.92 to 22.11 µg/L for Kong 2, from 0.71 to 5.34 µg/L for Hiré, and from 1.11 to 40.84 µg/L for Degbézéré. The average concentrations at the no-mining sites are (11.36 ± 7.61) µg/L at Kong 2, (1.28 ± 0.41) µg/L at Hiré and (3.27 ± 2.78) µg/L in Degbézéré. At the illegal gold mining sites, the average concentrations at Kong 2, Hiré and Degbézéré are respectively (6.74 ± 1.36) µg/L, (4.03 ± 1.82) µg/L and (17.01 ± 16.97) µg/L. These results show that there is no significant difference between the As contamination of the no-mining site and that of the gold mining area of each locality.

The average arsenic value was higher in the gold mining area than at the no-mining site at Degbézéré. Sample D_{E4} had the highest arsenic content (40.84 µg/L). The high arsenic content at the Degbézéré

clandestine gold mining site could be explained by the influence of acid mine drainage (AMD) resulting from the oxidation of pyrite (FeS_2) (Lakrim *et al.*, 2016). Indeed, following the extraction of gold, large quantities of mine tailings containing sulphide minerals such as arsenopyrite (FeAsS) are generated. The dissolution of these minerals releases arsenic into rivers and water reservoirs (Assie, 2008). In addition, the use of fertilizers and pesticides in agriculture could explain the level above the global threshold (10 µg/L) detected in the no-mining area of Kong 2 (Duplay *et al.*, 2014). **Figure 1** shows the average concentrations of mercury, lead, cadmium and arsenic in the waters collected in the different localities studied.

3.2.2 Health risks related to water ingestion

3.2.2.1 Carcinogenic risks (CR) of the elements As and Cd by the oral way

The risk of developing cancer from water consumption in adults and children was assessed using the carcinogenicity index (CR) for the elements As and Cd. The results are reported in **Table 8** below.

Table 8. Carcinogenic risk (CR) of arsenic and cadmium in water samples

Kong 2 no-mining			Kong 2 clandestine gold mining	
	Adult	Child	Adult	Child
As	$3.08\ 10^{-4}$	$1.63\ 10^{-3}$	$1.83\ 10^{-4}$	$9.70\ 10^{-4}$
Cd	$1.88\ 10^{-6}$	$9.96\ 10^{-6}$	$1.05\ 10^{-6}$	$5.59\ 10^{-6}$
Hiré no-mining			Hiré clandestine gold mining	
	Adult	Child	Adult	Child
As	$3.48\ 10^{-5}$	$1.85\ 10^{-4}$	$1.09\ 10^{-4}$	$5.79\ 10^{-4}$
Cd	ND	ND	ND	ND
Degbézéré no-mining			Degbézéré clandestine gold mining	
	Adult	Child	Adult	Child
As	$8.87\ 10^{-5}$	$4.70\ 10^{-4}$	$4.62\ 10^{-4}$	$2.45\ 10^{-3}$
Cd	ND	ND	$3.51\ 10^{-6}$	$1.86\ 10^{-5}$

At the various study sites, the CR values for arsenic are generally above the acceptable limit of carcinogenic risk (10^{-4}) for both adults and children. For cadmium, the CR values are in the acceptable range (10^{-4} to 10^{-6}). The values of the CR of no-mining sites are generally lower than those of clandestine gold mining areas with the exception of the locality of Kong 2. In addition, child CR values are significantly higher than adult CR values. These values suggest that the risks of developing arsenic-related cancer at the sites studied are high. In contrast, the cancer risk for both adults and children from cadmium at both the mine and no-mining sites is low. Overall, a high potential risk of developing cancer from drinking water contaminated by arsenic and cadmium from areas impacted by illegal gold mining is greater in children than in adults. In addition, this risk is generally higher at the mine site than in the no-mining area. The higher CR values for arsenic than for cadmium are due to both the concentration of the species and the carcinogenicity factor (CSF). Indeed, the measured arsenic concentrations are higher and its oral carcinogenicity factor is higher than that of cadmium (As = 1.5 > Cd = 0.380 (Bortey-Sam *et al.*, 2015)). They (Bortey-Sam *et al.*, 2015) also showed that children are at greater risk of cancer than adults, relative to the study in drinking water from communities near gold mines in Tarkwa, Ghana. However, the CR found are significantly lower than those in this study. This observation is due to the higher concentrations obtained in the present work.

3.2.2.2 Non-carcinogenic risks

The exposure coefficient (HQ) and toxicity index (HI) values are presented in **Table 9**. The HQ and HI of the child are significantly higher than those of the adult. At all sites, the HI for children is greater than 1 (the acceptable limit). In contrast, adult HI are greater than 1 only at the Kong 2 and Degbézéré mine sites. These observations indicate that the risk of developing all other diseases except cancer as a result of drinking contaminated water is greater in children than in adults. Indeed, this study was conducted under the assumption that the 60 kg adult is exposed to the effects of pollutants for an average of 30 years for non-carcinogenic elements and 53 years for carcinogenic elements. However, the 10 kg child is exposed to pollutants for an average of 6 years. HQ being inversely proportional to the average body weight (BW) and to the average exposure time (AT), justifies the fact that the child is more exposed to the harmful effects of pollutants than the adult. At the mining site, the higher HI values obtained suggest that health consequences are very likely at the gold mining site compared to the no-mining area. This observation is corroborated by Adewumi and Laniyan, in the study on ecological and health risks in artisanal gold mining waters in Anka, Nigeria. They show that HIs in mine waters are higher than those in off-mine waters. In addition, they report that children are more susceptible to health risks than adults (Adewumi and Laniyan, 2020).

Table 9. Non-carcinogenic risks (HQ and HI) of Hg, Pb, Cd and As

Kong 2 no mining			Kong 2 clandestine gold mining	
	Adult	Child	Adult	Child
HQ(Hg)	0.23	0.70	0.29	0.87
HQ (Pb)	0.07	0.20	2.35	7.06
HQ(Cd)	0.01	0.05	0.01	0.03
HQ (As)	0.69	3.63	0.41	2.16
HI	1	4.58	3.06	10.12
Hiré no mining			Hiré clandestine gold mining	
	Adult	Child	Adult	Child
HQ (Hg)	0.16	0.48	0.26	0.79
HQ (Pb)	0.10	0.31	0.17	0.50
HQ (Cd)	ND	ND	ND	ND
HQ (As)	0.08	0.41	0.24	1.29
HI	0.34	1.20	0.67	2.57
Degbézéré no mining			Degbézéré clandestine gold mining	
	Adulte	Child	Adult	Child
HQ (Hg)	0.26	0.78	0.46	1.39
HQ (Pb)	0.10	0.31	0.14	0.41
HQ (Cd)	ND	ND	0.02	0.10
HQ (As)	0.20	1.04	1.03	5.44
HI	0.56	2.14	1.65	7.34

3.2.3 Content in soils

3.2.2.1 Hg

Total mercury concentrations in the collected soils range from < 0.05 to 0.16 mg/kg at Kong 2, from < 0.05 to 0.50 mg/kg at Hiré, and from 0.09 to 1.05 mg/kg at Degbézéré. These levels are generally below the WHO threshold value for mercury in soil (1 mg/kg) with the exception of sample D_{S2} at Degbézéré (1.05 mg/kg). The average mercury levels in the no-mining areas of Kong 2, Hiré and Degbézéré are respectively (0.16 ± 0.00) ; (0.21 ± 0.22) and (0.69 ± 0.52) mg/Kg. On illegal gold mining sites, average

mercury levels are (0.05 ± 0.00) ; (0.28 ± 0.32) and (0.73 ± 0.19) mg/Kg in Kong 2, Hiré and Degbézéré respectively. These average mercury concentrations were 3 to 12 times higher than the UCC value for mercury (0.056 mg/kg) for all sites. Statistical analysis reveals that there is no significant difference between the average Hg content of the gold mining site and that of the no-mining area of each locality. This result suggests an enrichment of mercury in the different study areas both in the gold mining site and in the no-mining area. However, average mercury concentrations in soils from clandestine gold mining sites are generally higher than those from no-mining areas. The lack of appropriate methods for removing the mercury used to amalgamate the gold accounts for these relatively high soil mercury values. The mercury levels found in soils at no-mining sites correlate well with those found in water, and justify the fact that some gold miners amalgamate gold concentrate outside the mine.

3.2.2.2 Pb

Total soil lead concentrations range from 0.86 to 1.24 mg/kg for Kong 2, from 0.49 to 1.83 mg/kg for Hiré, and from 0.20 to 2.26 mg/kg for Degbézéré. These values emerge that there is no significant difference between contents in gold mining zone and those of no-mining sites ($p < 0.05$). From these values, it is clear that the lead concentrations in soils at all the sites studied are well below the UCC value for lead (17 mg/kg) and the WHO limit value (100 mg/kg). This low lead content in the studied soils suggests that the presence of lead would be only of natural origin.

3.2.2.3 Cd

Cadmium concentrations in soils vary from 0.15 to 0.22 mg/kg in Kong 2, from <0.002 to 0.17 mg/kg in Hiré, and from 0.07 to 0.23 mg/kg in Degbézéré. These concentrations vary very little from one locality to another ($p < 0.05$) with relatively low values. At Kong 2, the average cadmium concentration is (0.21 ± 0.01) mg/Kg at the no-mining site and (0.17 ± 0.02) mg/Kg in the gold mining area. At Hiré, the mean concentrations is (0.10 ± 0.06) and (0.15 ± 0.00) mg/Kg in the no-mining and mining areas respectively. For Degbézéré, the average concentrations in the no-mining and mining areas are (0.10 ± 0.03) and (0.15 ± 0.08) mg/Kg respectively. These mean values are slightly above or equal to the UCC value for cadmium (0.102 mg/kg) for all sites. However, compared to the WHO limit value (2 mg/kg), the cadmium concentrations in the soils of this study are significantly lower. Indeed, cadmium is generally associated with sulphide minerals such as sphalerite [(Fe, Zn)S] and degradation over time can release Cd^{2+} ions that will accumulate in the sediments of streams and rivers (Fashola and Ngole-Jeme, 2016). Therefore, these low concentrations obtained suggest that the geology of the sites studied is not dominated by cadmium-enriched rocks.

3.2.2.4 As

Arsenic concentrations in soils range from 0.27 to 42.10 mg/kg for Kong 2, from 0.09 to 1.32 mg/kg for Hiré, and from 6.96 to 39.12 mg/kg for Degbézéré. No significant difference is observed between the average contents in ace of no-mining areas and those of gold mining of each locality. At Kong 2 and Degbézéré, mean arsenic concentrations are 6 to 13 times the UCC value (2 mg/kg). However, compared to the WHO threshold value (40 mg/kg), these values are generally lower, with the exception of sample K_{S4} (42.10 mg/kg). The levels recorded at Hiré are significantly lower than the UCC value and the threshold value for arsenic. Indeed, the excavation of soil to reach the ore, the crushing and processing of rocks generate large quantities of tailings containing sulphide minerals and cause the leaching of large volumes of metals such as arsenic (Fashola and Ngole-Jeme, 2016), (Bretzler *et al.*, 2017). Therefore, the effect of acid mine drainage (AMD) could explain the relatively high concentrations of arsenic found in soils at the Kong 2 and Degbézéré gold mining sites. Agricultural

practices and the use of fertilizers may also be sources of arsenic contamination in soils (Kao and Mejahed, 2007). Therefore, the high arsenic levels at the no-mining sites of Kong 2 and Degbézéré may be due to agriculture. The low concentrations determined in the town of Hiré, justify the fact that no gold mining activity has been carried out at the clandestine gold mining site for a year. Thus, the mine tailings have been returned to the pits, thus avoiding leaching of metals and associated metalloids. **Figure 2** presents the average concentrations of mercury, lead, cadmium and arsenic in the soils collected at the different study sites.

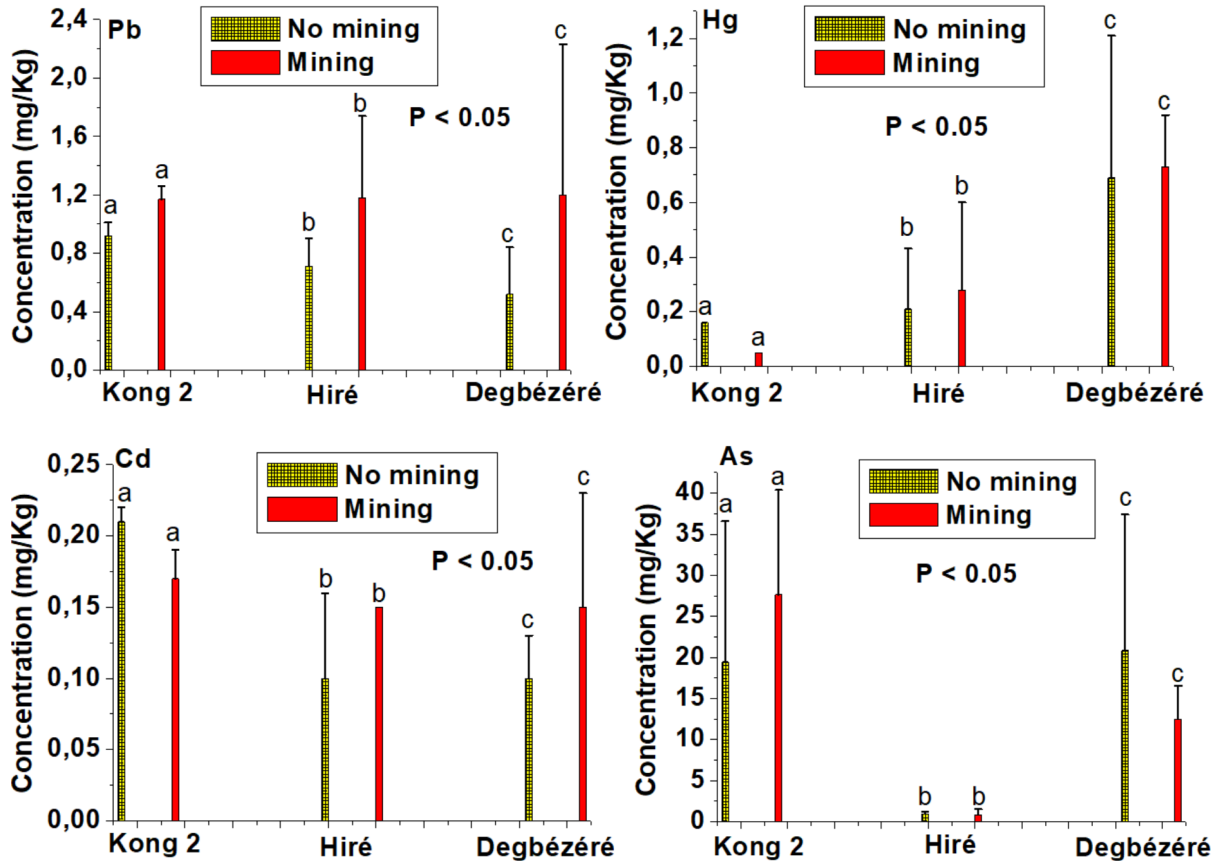

Figure 2. Average concentrations of Hg, Pb, Cd and As in soils collected at Kong 2, Hiré and Degbézéré

3.2.4 Soil contamination levels

The pollution indices are presented in the **Table 10 ; 11** et **12**.

3.2.4.1 Contamination factor (CF)

The values of mercury, lead, cadmium and arsenic contamination factors for soils collected in the clandestine and no-mining areas of Kong 2, Hiré and Degbézéré are reported in the **Table 10**. According to the Hakanson classification, these values indicate low mercury contamination at the Kong 2 mine site versus moderate contamination in the no-mining area. Mercury contamination is significant at Hiré in both the illegal gold mining area and the no-mining site. In Degbézéré, the soils in the areas studied are highly contaminated with mercury. For lead, the contamination factors are all less than 1. These values indicate low lead contamination at all sites studied. For all locations, cadmium contamination is moderate. Indeed, all the CF values are generally between 1 and 3. As for arsenic, at Kong 2 and Degbézéré, the average CF values are superior to 6 both in the clandestine gold mining zone and at the no-mining site. These results indicate low arsenic contamination at Hiré, but very high contamination at Kong 2 and Degbézéré.

Table 10. Contamination factors (CF) of mercury, cadmium, lead and arsenic in the collected soil samples

Site	Samples	Hg	Pb	Cd	As
Kong 2 no-mining	K_{S1}	ND	0.05	1.96	0.14
	K_{S2}	ND	0.05	2.16	12.38
	K_{S3}	2.86	0.06	1.96	16.64
	Average ± Standard deviation	2.86 ± 0.00	0.05 ± 0.01	2.03 ± 0.11	9.72 ± 8.57
Kong 2 Kong 2 clandestine gold mining	K_{S4}	0.89	0.07	1.76	21.05
	K_{S5}	ND	0.06	1.47	11.35
	K_{S6}	ND	0.07	1.76	9.06
	Average ± Standard deviation	0.89 ± 0.00	0.07 ± 0.01	1.67 ± 0.17	13.82 ± 6.37
Hiré no-mining	H_{S1}	8.21	0.05	0.88	0.37
	H_{S2}	1.43	0.03	0.49	0.47
	H_{S3}	1.43	0.05	1.67	0.59
	Average ± Standard deviation	3.69 ± 3.92	0.04 ± 0.01	1.01 ± 0.60	0.47 ± 0.11
Hiré Kong 2 clandestine gold mining	H_{S4}	8.93	0.11	ND	0.05
	H_{S5}	0.89	0.05	1.47	0.56
	H_{S6}	ND	0.05	ND	0.66
	Average ± Standard deviation	4.91 ± 5.68	0.07 ± 0.03	1.47 ± 0.00	0.42 ± 0.33
Degbézéré no-mining	D_{S1}	16.61	0.05	1.08	3.48
	D_{S2}	18.75	0.02	0.69	8.23
	D_{S3}	1.61	0.02	1.18	19.56
	Average ± Standard deviation	12.32 ± 9.34	0.03 ± 0.02	0.98 ± 0.26	10.42 ± 8.26
Degbézéré Kong 2 clandestine gold mining	D_{S4}	10.00	0.13	2.25	8.59
	D_{S5}	12.50	0.01	1.27	5.03
	D_{S6}	16.61	0.07	0.78	5.09
	Average ± Standard deviation	13.04 ± 3.34	0.07 ± 0.06	1.44 ± 0.75	6.24 ± 2.04

3.2.4.2 Degree of contamination (DC)

Table 11 presents soil contamination values for the studied sites. Both at the no-mining site and in the illegal gold mining area, the averages DC at Hiré are less than 8, while those at Kong 2 are between 8 and 16, and those at Degbézéré are between 16 and 32. Thus, for all the chemical species studied, these values indicate that Hiré is poorly contaminated, Kong 2 is moderately contaminated, and Degbézéré is significantly contaminated.

Table 11. Degree of contamination (DC) of the studied sites

	Kong 2 no-mining			Kong 2 clandestine gold mining		
	K_{S1}	K_{S2}	K_{S3}	K_{S4}	K_{S5}	K_{S6}
	2.15	14.59	21.52	23.78	12.88	10.89
Average ± Standard deviation	12.75 ± 9.81			15.85 ± 6.94		
	Hiré no-mining			Hiré clandestine gold mining		
	H_{S1}	H_{S2}	H_{S3}	H_{S4}	H_{S5}	H_{S6}
	9.51	2.42	3.74	9.09	2.97	0.71
Average ± Standard deviation	5.22 ± 3.78			4.26 ± 4.33		
	Degbézéré no-mining			Degbézéré clandestine gold mining		
	D_{S1}	D_{S2}	D_{S3}	D_{S4}	D_{S5}	D_{S6}
	21.22	27.69	22.37	20.97	18.81	22.55
Average ± Standard deviation	23.76 ± 3.45			20.78 ± 1.87		

3.2.4.3 Enrichment factor (FE)

Table 12 shows the enrichment factor results for soils at the study sites. The average values of enrichment factor indicate low mercury enrichment in the clandestine gold mining area at Kong 2 and moderate to high enrichment at the no-mining site. At Hiré, mercury enrichment in the soils studied is moderate in both the mining and no-mining areas. At Degbézéré, average EF indicates high mercury enrichment at both the no-mining site and the illegal gold mining area. For lead, all average EF are well less than 1. Thus, all the studied sites do not show lead enrichment. For cadmium, at the no-mining sites, mean EF values indicate moderate enrichment at Kong 2, low enrichment at Hiré, and no enrichment for Degbézéré. In contrast, in all of the clandestine gold mining areas, cadmium enrichment is low. As for arsenic, the average EF values for the Kong 2 sites show high enrichment both at the no-mining site and in the illegal gold mining area. Strong arsenic enrichment is also observed at the Degbézéré no-mining site. In contrast, in the Degbézéré illegal gold mining area, enrichment range from moderate to high. At Hiré, both in the clandestine and no-mining areas, the EF values indicate that there is no arsenic enrichment. In addition, these results indicate that arsenic and mercury are generally of anthropogenic origin at Kong 2 and Degbézéré (EF > 1.5) (Agyarko *et al.*, 2014). On the other hand, the lead would be of natural source whatever the locality studied, because in addition to the fact that its EF are less than 1.5, there is no significant difference between EF in no-mining areas and those in illegal gold mining.

3.2.4.4 Potential ecological risks to the environment

Monometallic potential ecological risk values (E_r^i) and polymetallic (RI) are recorded in **Table 13**. The average values of the different E_r^i show the following increasing orders: Pb < Cd < As < Hg at Degbézéré and Pb < As < Cd < Hg at Hiré, both in the non-mining area and at the clandestine gold mining site. In Kong 2, the average E_r^i show the following increasing orders: Pb < Hg < Cd < As in the clandestine gold mining area and Pb < Cd < As < Hg at the no-mining site. In all the sites studied, the average E_r^i increase in order : Pb < Cd < As < Hg. Mean E_r^i values for mercury in the collected soils range from 35.71 to 521.43, suggesting environmental ecological risks that vary from low to very high depending on the study area. In contrast, with E_r^i values well less than 40, lead presents low environmental ecological risks whatever the site.

Table 12. Enrichment factors (EF) of mercury, cadmium, lead and arsenic in collected soil samples

Site	Samples	Hg	Pb	Cd	As
Kong 2 no-mining	K_{S1}	ND	0.10	4.04	0.28
	K_{S2}	ND	0.14	5.64	32.34
	K_{S3}	5.58	0.12	3.83	32.50
	Average ± Standard Deviation	5.58 ± 0.00	0.12 ± 0.02	4.50 ± 0.99	21.71 ± 15.15
Kong 2 clandestine gold mining	K_{S4}	1.32	0.10	2.61	31.18
	K_{S5}	ND	0.12	2.80	21.63
	K_{S6}	ND	0.12	2.82	14.45
	Average ± Standard Deviation	1.32 ± 0.00	0.11 ± 0.01	2.74 ± 0.11	22.42 ± 8.40
Hiré no-mining	H_{S1}	6.84	0.04	0.73	0.30
	H_{S2}	2.05	0.04	0.70	0.67
	H_{S3}	1.68	0.05	1.96	0.69
	Average ± Standard Deviation	3.52 ± 2.88	0.04 ± 0.01	1.13 ± 0.71	0.55 ± 0.22
Hiré clandestine gold mining	H_{S4}	5.16	0.06	ND	0.03
	H_{S5}	1.25	0.07	2.05	0.77
	H_{S6}	ND	0.02	ND	0.29
	Average ± Standard Deviation	3.21 ± 2.77	0.05 ± 0.03	2.05 ± 0.00	0.36 ± 0.38
Degbézéré no-mining	D_{S1}	14.26	0.04	0.93	2.99
	D_{S2}	20.30	0.02	0.74	8.91
	D_{S3}	1.49	0.02	1.09	18.15
	Average ± Standard Deviation	12.02 ± 9.60	0.03 ± 0.01	0.92 ± 0.17	10.02 ± 7.64
Degbézéré clandestine gold mining	D_{S4}	8.97	0.12	2.02	7.70
	D_{S5}	9.52	0.01	0.97	3.83
	D_{S6}	12.87	0.05	0.61	3.95
	Average ± Standard Deviation	10.45 ± 2.11	0.06 ± 0.06	1.20 ± 0.73	5.16 ± 2.20

For all chemical species studied, the RI values in the clandestine and no-mining areas of Degbézéré are superior to 600, which suggests a very high ecological risk in this locality. Soils in the other study areas have moderate ecological risks, with RI values in the [150 ; 300] range.

Table 13. E_r^i values by metal and RI by sample point

Site	Samples	E_r^{Hg}	E_r^{Pb}	E_r^{Cd}	E_r^{As}	RI
Kong 2 no-mining	K_{S1}	ND	0.25	58.82	1.35	60.42
	K_{S2}	ND	0.26	64.71	123.75	188.72
	K_{S3}	114.29	0.30	58.82	166.35	339.76
	Average ± Standard Deviation	114.29 ± 0.00	0.27 ± 0.03	60.78 ± 3.40	97.15 ± 85.66	196.30 ± 139.82
Kong 2 clandestine gold mining	K_{S4}	35.71	0.35	52.94	210.50	299.5
	K_{S5}	ND	0.31	44.12	113.50	157.93
	K_{S6}	ND	0.36	52.94	90.55	143.85
	Average ± Standard Deviation	35.71 ± 0.00	0.34 ± 0.03	50.00 ± 5.09	138.18 ± 63.67	200.43 ± 86.09
Hiré no-mining	H_{S1}	328.57	0.25	26.47	3.65	358.94
	H_{S2}	57.14	0.14	14.71	4.65	76.64
	H_{S3}	57.14	0.23	50.00	5.85	113.22
	Average ± Standard Deviation	147.62 ± 156.71	0.21 ± 0.06	30.39 ± 17.97	4.72 ± 1.10	182.94 ± 153.52
Hiré clandestine gold mining	H_{S4}	357.14	0.54	ND	0.45	358.13
	H_{S5}	35.71	0.25	44.12	5.55	85.63
	H_{S6}	ND	0.25	ND	6.60	6.85
	Average ± Standard Deviation	196.43 ± 227.28	0.35 ± 0.17	44.12 ± 0.00	4.20 ± 3.29	150.20 ± 184.33
Degbézéré no-mining	D_{S1}	664.29	0.26	32.35	34.80	731.70
	D_{S2}	750.00	0.10	20.59	82.25	852.94
	D_{S3}	64.29	0.10	35.29	195.60	295.28
	Average ± Standard Deviation	492.86 ± 373.62	0.15 ± 0.09	29.41 ± 7.78	104.22 ± 82.62	626.64 ± 293.30
Degbézéré clandestine gold mining	D_{S4}	400.00	0.66	67.65	85.85	554.16
	D_{S5}	500.00	0.06	38.24	50.30	588.60
	D_{S6}	664.29	0.34	23.53	50.90	739.06
	Average ± Standard Deviation	521.43 ± 133.44	0.35 ± 0.30	43.14 ± 22.46	62.35 ± 20.35	627.27 ± 98.33

Conclusion

Hg, Pb, Cd, and As were measured in water and soil samples to assess the level of contamination at the Kong 2, Hiré, and Degbézéré illegal gold mining sites. For soils, pollution indices such as enrichment factor (EF), contamination factor (CF) and degree of contamination (DC) were calculated. Environmental risks were also estimated from the ecological risk indices (E_r^i and RI). Carcinogenic and non-carcinogenic risks related to water ingestion were determined.

Physicochemical characteristics such as pH of water and soils are essentially neutral. The organic matter measured in the soils is consistent with gold mining activity. The concentrations of chemical species studied confirm that gold miners use chemicals, particularly mercury, in gold extraction.

Mercury levels in water are very often above the WHO limit value. Overall, the water and soil of the localities studied are more polluted with mercury and arsenic. This pollution extends beyond the illegal gold mining areas. In relation to the consumption of polluted water, the risks of developing cancer or other adverse health effects are higher in the illegal gold mining zone. In addition, children are more likely to develop adverse health effects than adults. Pollution in the study sites decreases in the direction Degbézéré > Kong 2 > Hiré, both in the no-mining site and in the illegal gold mining area. Consequently, Degbézéré is the most contaminated of the three sites studied, with very high environmental risks. At the end of this investigation, it was found that the water in the localities studied should not be used for domestic purposes without treatment because of the harmful effects on the health of the user. Thus, a feasability study of the depollution of the contaminated waters with low cost treatments such as efficient adsorption processes is necessary to propose a simple, cheap and easy local implementation of water treatment units.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

References

Adewoyin O. O., Kayode O. T., Omeje O., Odetunmibi O. A., (2019) Risk assessment of heavy metal and trace elements contamination in groundwater in some parts of Ogun state, *Cogent Engineering.*, 6(1), 12p. doi:10.1080/23311916.2019.1632555.

Adewumi A. J., Laniyan T. A., (2020) Ecological and human health risks associated with metals in water from Anka artisanal gold mining area, Nigeria, *Human and Ecological Risk Assessment : An International Journal.*, 27(2), 307-326. doi:10.1080/10807039.2019.1710694.

Adeyi A. A., Babalola, B. A., (2017) Lead and cadmium levels in residential soils of Lagos and Ibadan, Nigeria, *Journal of Health and Pollution.*, 7, 42–55. doi: 10.5696/2156-9614-7-13.42.

Affessi A. S., Koffi G. J.-C. K., Sangaré, M., (2016) Impacts sociaux et environnementaux de l'orpaillage sur les populations de la région du Bounkani (Côte d'Ivoire), *European Scientific Journal.*, 12(26), 288-308.

Agyarko K., Dartey E., Kuffour R. A., Sarkodie, P. A., (2014) Assessment of trace elements levels in sediment and water in some artisanal and small-scale mining (ASM) localities in Ghana, *Current World Environment.*, 9(1), 07-16. doi:10.12944/CWE.9.1.02.

Alaqarbeh M., Al-hadidi L., Hammouti B., Bouachrine M., (2022). Water pollutions: sources and human health impact. A mini-review, *Mor. J. Chem.* 10, 891-900, https://doi.org/10.48317/IMIST.PRSM/morjchem-v10i4.34497

Aranguren M. M. S., (2008) Contamination en métaux lourds des eaux de surface et des sédiments du Valde Milluni (AndesBoliviennes) par des déchets miniers Approches géochimique, minéralogique et hydrochimique, Thèse de doctorat, *Université Paul Sabatier-Toulouse*, 381p.

Assie K. E., (2008) Lode gold mineralization in the Paleoproterozoic (Birimian) volcano-sedimentary sequence of Afema gold district, southeastern Côte d'Ivoire, Doctoral thesis, *Technical University of Clausthal*, 198p.

Bamba O., Pelede S., Sako A., Kagambega N., Miningou M. Y. W., (2013) Impact de l'artisanat minier sur les sols d'un environnement agricole aménagé au Burkina Faso, *Journal of Sciences.*, 13(1), 1-11.

Bempah C. K., Ewusi A., (2016) Heavy metals contamination and human health risk assessment around Obuasi gold mine in Ghana, *Environmental Monitoring and Assessment.*, 188(261), 13p. doi:10.1007/s10661-016-5241-3.

Bempah C. K., Ewusi A., Obiri-Yeboah S., Asabere S. B., Mensah F., Boateng J., Voigt H.-J., (2013) Distribution of arsenic and heavy metals from mine tailings dams at Obuasi municipality of Ghana, *American Journal of Engineering Research.*, 2(5), 61-70.

Bortey-Sam N., Nakayama S. M. M., Ikenaka Y., Akoto O., Baidoo E., Mizukawa H., Ishizuka M., (2015) Health risk assessment of heavy metals and metalloid in drinking water from communities near gold mines in Tarkwa, Ghana, *Environmental Monitoring and Assessment.*, 187(397). 12p. doi:10.1007/s10661-015-4630-3.

Bretzler A., *Lalanne* F. , *Nikiema* J. , *Podgorski* J., *Pfenninger* N., *Berg* M., *Schirmer* M., (2017) Groundwater arsenic contamination in Burkina Faso, West Africa : Predicting and verifying regions at risk, *Science of the Total Environment.*, 584-585, 958-970. doi: 10.1016/j.scitotenv.2017.01.147.

Carex., (2009) Le plomb et ses composés inorganiques. *School of Environmental Health*, 5p.

Cheikh M. E. K. O., Kacemi K. E., Idrissi L., (2011) Caractérisation physico-chimique des eaux d'alimentation de la ville de Tijikja (Mauritanie), *International Journal of Biology and Chemical Sciences.*, 5(5), 2133-2139. doi:10.4314/ijbcs.v5i5.33.

Cui Z., Yang W., Na Z., Rui Y., Guanghui X., Yong Y., (2018) Spatial distribution and risk assessment of heavy metals in paddy soils of yongshuyu irrigation area from Songhua river basin, north east China, *Chinese Geographical Science.*, 28(5), 797–809. https://doi.org/10.1007/s11769-018-0991-1.

Djadé P. J. O., Traoré A., Koffi K. J. T., Keumean K. N., Soro G., Soro N., (2020) Evaluation du niveau de contamination des eaux souterraines par les éléments traces dans le département de Zouan-Hounien (Ouest de la Côte d'Ivoire), *Journal of Applied Biosciences.*, 150, 15457-15468. https://doi.org/10.35759/JABs.150.6.

Duplay J., Semhi K., Errais E., Imfeld G., Babcsanyi I., Perrone T., (2014) Copper, zinc, lead and cadmium bioavailability and retention in vineyard soils (Rouffach, France) : The impact of cultural practices, *Geoderma.*, 230-231, 318-328. doi:10.1016/j.geoderma.2014.04.02.

Ekengele N. L., Mabrey S. S., Zo'o Z. P., (2016) Evaluation de la contamination métallique des sols exposés à l'incinération des pneus d'automobiles dans la ville de Ngaoundéré (Cameroun), *Journal of Materials and Environmental Science.*, 7(12), 4633-4645.

El Abdouni A., Bouhout S., Merimi I., Hammouti B., Haboubi K. (2012). Physicochemical characterization of wastewater from the Al-Hoceima slaughterhouse in Morocco, *Caspian Journal of Environmental Sciences* 19 (3), 423-429.

Fashola M. O., Ngole-Jeme V. M., Babalola O. O., (2016) Heavy metal pollution from gold mines: Environmental effects and bacterial strategies for resistance, *International Journal of Environmental Research and Public Health.*, 13(11), 1047. doi:10.3390/ijerph13111047.

Goh D., (2016) L'exploitation artisanale de l'or en Côte d'Ivoire : La Persistance d'une activité illégale, *European Scientific Journal.*, 12(3), 18-36. http://dx.doi.org/10.19044/esj.2016.v12n3p18.

Goix S., Lévêque T., Xiong T.-T., Schreck E., Baeza-Squiban A., Geret F., Uzu G., Austruy A., Dumat C., (2014) Environmental and health impacts of fine and ultrafine metallic particles: Assessment of threat scores, *Environmental Research.*, 133,185–194. doi:10.1016/j.envres.2014.05.015.

Hakanson L., (1980) An ecological risk index for aquatic pollution control. A sedimentological approach, *Water Research.*, 14, 975-1001.

Harmandon F., (2004) Effets toxiques de l'arsénite de sodium sur la santé humaine et exposition des utilisateurs, *Médecine du Travail-M.S.A. Tarn-Aveyron.,* Les Maladies du Bois en Midi-Pyrénées, 8-12.

Ibrahim O. Z., Dan-Badjo A. T., Guero Y., Idi F. M. M., Feidt C., Sterckeman T., Echevarria G., (2019) Distribution spatiale des éléments traces métalliques dans les sols de la zone aurifère de Komabangou au Niger, *International Journal of Biological and Chemical Sciences.*, 13(1), 557-573. https://doi.org/10.4314/ijbcs.v13.

Institut scientifique de service public., (2017) Détermination de la perte au feu des déchets, boues et des sédiments, *Compendium Wallon des méthodes d'Echantillonnage et d'Analyse (CWEA).*, 4p.
Kao T., Mejahed K. E., Bouzidi A., (2007) Evaluation de la pollution métallique dans les sols agricoles irrigués par les eaux usées de la ville de Settat (Maroc), *Bulletin de l'Institut Scientifique., Rabat, section Sciences de la Vie*, 29, 89-92.
Ke X., Gui S., Huang H., Zhang H., Wang C., Guo W., (2017) Ecological risk assessment and source identification for heavy metals in surface sediment from the Liaohe, River protected area, China*, Chemosphère.*, 175, 473-481. doi: 10.1016/j.chemosphere.2017.02.029.
Kinimo K. C., Yao K. M., Marcotte S., Kouassi N. L. B., Trokourey A., (2018) Distribution trends and ecological risks of arsenic and trace metals in wetland sediments around gold mining activities in central-southern and southeastern Côte d'Ivoire, *Journal of Geochemical Exploration.,* 190, 265–280. doi:10.1016/j.gexplo.2018.03.013.
Koller M., Pletscher C., M. Jost., (2013) Mercure, *Division médecine du travail.*, 13p.
Lakrim M., Mesrar L., O. Aroussi E., Jabrane R., (2016) Application géomatique pour la cartographie de la vulnérabilité environnementale engendrée par les déchets miniers de la mine ferrifère de Nador(nord-est du Maroc), *European Scientific Journal.*, 12(15), 287-307. doi: 10.19044/esj.2016.v12n15p287.
Li Z., Ma Z., Van der Kuijp T. J., Yuan Z., Huang L., (2014) A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment, *Science of The Total Environment.*, 468-469, 843–853. doi:10.1016/j.scitotenv.2013.08.0.
Lusilao-Makiese J. G., Cukrowska E. M., Tessier E., Amouroux D., Weiersbye I., (2013) The impact of post gold mining on mercury pollution in the West Rand region, Gauteng, South Africa, *Journal of Geochemical Exploration.*, 134, 111-119. doi:10.1016/j.gexplo.2013.08.010.
Makhoukh M., Sbaa M., Berrahou A., Vanclooster M., (2011) Contribution à l'étude de l'impact d'un site minier abandonné dans la haute Moulouya sur la qualité de l'Oued Moulouya, Maroc, *Afrique Science.*, 07(3), 33-48.
Mohellebi F., Bouchekhou A., Harbi N., Hadjoudj R., Chitour C. E., (1999) Étude de la purification d'huiles usagées de type « moteur » au moyen d'une argile montmorillonitique, *Oil & Gas Science and Technology.*, 54(3), 403-418.
Nadem S., M. Baghdadi E., Rais J., Barakat A., (2015) Evaluation de la contamination en métaux lourds des sédiments de l'estuaire de Bou Regreg (Côte atlantique, Maroc), *Journal of Materials and Environmental Science.*, 6(11), 3338-3345.
Naji A., Ismail A., Ismail A. R., (2010) Chemical speciation and contamination assessment of Zn and Cd by sequential extraction in surface sediment of Klang River, Malaysia, *Microchemical Journal.*, 95(2), 285–292. doi:10.1016/j.microc.2009.12.015.
Nkansah M. A., Darko G., Dodd M., Opoku F., Essuman T. B., Antwi-Boasiako J., (2017) Assessment of pollution levels, potential ecological risk and human health risk of heavy metals/metalloids in dust around fuel filling stations from the Kumasi Metropolis, Ghana, *Cogent Environmental Science.*, 3(1), 19p. doi:10.1080/23311843.2017.1412153.
Nsambu M., Musibono E., Mputu K., (2020) Contribution to the evaluation of the level of mercury pollution of the soils of gold mining sites in the territory of Fizi, Eastern of Democratic Republic of Congo, *Journal of Materials and Environmental Sciences.*, 11(1), 85-100. doi: 10.4236/gep.2020.82007.
Petelka J., Abraham J., Bockreis A., Deikumah J. P., Zerbe S., (2019) Soil heavy metal(loid) pollution and phytoremediation potential of native plants on a former gold mine in Ghana, *Water, Air, & Soil Pollution.*, 230(267), 16p. doi:10.1007/s11270-019-4317-4.
Pobi K. K., Satpati S., Dutta S., Nayek S., Saha R. N., Gupta S., (2019) Sources evaluation and ecological risk assessment of heavy metals accumulated within a natural stream of Durgapur industrial zone, India, by using multivariate analysis and pollution indices, *Applied Water Science.*, 9(58), 16p. https://doi.org/10.1007/s13201-019-0946-4.

Sahli L., Okki M. E. H. E., Afri-Mehennaoui F.-Z., Mehennaoui S., (2014) Utilisation d'indices pour l'évaluation de la qualité des sédiments : cas du bassin Boumerzoug (Algérie), *European Scientific Journal.*, 10(35), 336-346.

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, *Journal of African Earth Sciences*., 145, 297-316. doi:10.1016/j.jafrearsci.2018.05.

Smouni A., Ater M., Auguy F., Laplaze L., El Mzibri M., Berhada F., Filali-Maltouf A., Doumas P., (2010) Évaluation de la contamination par les éléments-traces métalliques dans une zone minière du Maroc oriental, Cahiers Agricultures, *EDP Sciences.*, 19(4), 273-279.

Taiwo A. M., Awomeso J. A., (2017) Assessment of trace metal concentration and health risk of artisanal gold mining activities in Ijeshaland, Osun State Nigeria- Part1, *Journal of Geochemical Exploration.*, 177, 1-10. doi: 10.1016/j.gexplo.2017.01.009.

USEPA., (2001) Risk assessment guidance for superfund : Process for conducting probabilistic risk assessment, *Office of Emergency and Remedial Response U.S. Environmental Protection Agency Washington.,* DC 20460, Volume 3 - Part A, 385p.

Wedepohl K. H., (1995) The Composition of the Continental Crust, *Geochimica et Cosmochimica Acta.*, 59, 1217-1232. https://doi.org/10.1016/0016-7037(95)00038-2.

WHO., (2015) Global health indicators, *World health statistics.,* Part II, 164p.

Xu L., Li J., (2015) Speciation and degrees of contamination of metals in sediments from upstream and downstream reaches along the catchment of the southern Bohai Sea, China, *International Journal of Environmental Research and Public Health.*, 12(7), 7959-7973. doi:10.3390/ijerph120707959.

Yapi Y. H. A., Dongui B. K., Trokourey A., Barima Y. S. S., Essis Y., Atheba P., (2014) Evaluation de la pollution métallique des eaux souterraines et de surface dans un environnement minier aurifère à Hiré (Côte d'Ivoire), *International Journal of Biological and Chemical Sciences*., 8(3), 1281-1289. doi :10.4314/ijbcs.v8i3.41.

Yobo J., Nassa D. D. A., (2018) L'exploitation minière, facteur de récession de l'activité agricole à Hiré Watta en Côte d'Ivoire, *Revue de Géographie Tropicale et d'Environnement.,* 1, 91-101.