Speciation and spatial distribution of trace metals in sediments around gold mining areas in northern Côte d'Ivoire

Koffi Pierre Dit Adama N'GORAN1*, Donourou Diabate1, N'Guessan Louis Berenger Kouassi1, Koffi Marcellin Yao2, Kakou Charles Kinimo1, Ahbeauriet Ahmed Ouattara1, Albert Trokourey1

1 Université Félix Houphouët Boigny, Laboratoire de Chimie Physique, 22 BP 582 Abidjan 22 (Côte d’Ivoire)
2 Centre de Recherches Océanologiques (CRO), Département Environnement, 29 rue des Pêcheurs, BP V 18 Abidjan
3 Université Peleforo Gon Coulibaly, UFR Sciences Biologiques, Département de Mathématiques Physique Chimie BP 1328 Korhogo, Côte d’Ivoire

*Corresponding author: Email: ngorankoffipierre@gmail.com Telephone: (+225)0747721231

Abstract

The purpose of this study was to investigate the spatial distribution, possible sources, and potential ecological risks associated with traces metals Cu, Mn and Ni in sediments around gold mine areas in northern Côte d’Ivoire. The sampling was conducted in industrial and artisanal and small-scale gold mining sites in Korhogo and Tengrela. Analysis of variance was performed to ascertain spatial differences. The possible sources of pollution were identified using the enrichment factor, principal component, and hierarchical cluster analysis. Trace metals Cu, Ni and Mn concentrations in sediments did not vary across the stations. The same spatial mapping distribution trend was observed for Ni, while those of Cu and Mn differed among the stations. The geoaccumulation index indicated low to moderate contamination of Cu, Mn and Ni at Korhogo and Tengrela. The results of principal component and hierarchical cluster analysis indicated that Cu, Ni, and Mn were generated both by anthropogenic and natural inputs, which were confirmed by the enrichment factor. The potential ecological risks indicated that Cu, Mn and Ni could pose low risk to organisms at Korhogo and Tengrela. This study provides first trace metals data in sediments across Korhogo and Tengrela gold mine areas. The sequential extraction procedure proposed by the Community Bureau of Reference (BCR) showed that a major portion (between 59.68 to 79.22 %) of Cu, Ni and Mn is highly associated with the residual fraction, showing their low mobility.

Key words: traces metals, sediment, gold mining, pollution, Sequential extraction
Introduction

Traces metals are among the most serious pollutants in the aquatic environment and have attracted global attention due to their toxicity, persistence and bioaccumulation (Cai et al. 2015; Li et al. 2014). With the recent development of gold mining activities, an important quantity of trace metals is continuing to be introduced into the environment via mining waste, wastewater and dust. Consequently, severe contamination levels of environmental resources may be observed. Humans are also exposed to the negative effects throughout the food chain (Biggeri et al. 2006; Varrica et al. 2014). Therefore, environmental studies of mining areas are important in order to protect the health of the residents.

Traces metals, such as Cu, Ni and Mn are essential for the growth of plants, aquatic species, and humans, but when they exceed the desired concentrations, they can become toxins (Garrido et al. 2002; Donkor et al. 2005). The increasing amounts of Cu in the body can lead to lesions and dysfunction of human organs. In addition, it inhibits the processes of photosynthesis and reproduction (Abdul-Wahab et al. 2012). Exposure to Ni compounds has adverse effects on human health and causes serious illness related to the carcinogenic activity of certain insoluble nickel compounds (Kang et al. 2003; Gupta et al. 2019). Ni is also classified as possible carcinogen by the International Agency for Research on Cancer (Romanowicz-Makowska et al. 2011). Long-term exposure to Mn can lead to nervous system toxicity and Parkinson's-like symptoms, especially in children, the elderly and pregnant women (Gwiazda et al. 2007). It is therefore necessary to assess the contamination level of these pollutants in the environment.

High concentrations of traces metals (Cu, Ni and Mn) in air, sediments, soils, fishery products and water due to mining activities were reported in many countries such as China (Zheng et al. 2013; Xiaomin et al. 2016), Tunisia (Boussen et al. 2013), Spain (Monterroso et al. 2014), South Africa (Lusilao-Makiese et al. 2016) and Morocco (Yassir et al. 2015). In addition, the negative impacts of trace metals (Cu, Ni and Mn) on human health in the mining regions of South America, Europe, and Asia have been reported in the literature. For example, children cognitive functions have been affected by Mn exposure in a mining area in Mexico (Riojas-Rodríguez et al. 2010). High levels of Mn were observed in urine of children living near mining area in Andalusia (Spain) (Molina-Villalba et al. 2015). Countries in West Africa, are not left out of this mining contamination. More and more, there is a development of gold mining activities throughout the continent. Many investigations have documented the contamination of sediments around mining areas in West Africa, with studies focused in Nigeria (Makinde et al. 2017; Taiwo et al. 2017), Senegal (Niane et al. 2014; Niane et al. 2019) and Ghana (Sunkari et al. 2019; Klubi et al. 2018), but in Côte d’Ivoire, studies are in their infancy. Recently, Kinimo et al. (2018) showed that sediments from gold mining area in south-eastern Côte d’Ivoire were contaminated by Cd. In northern Côte d’Ivoire, industrial and artisanal small-scale gold mining activities are also practiced, but no data is available on metals Cu, Ni and Mn concentrations in sediments. Therefore, it is essential to establish first data on the contamination level of sediments in trace metals Cu, Ni, and Mn around gold mining areas in northern Côte d’Ivoire. However, estimating the total concentrations of trace metals in the sediments does not allow us to determine their mobility, distribution and speciation in these areas. (Saleem et al. 2015). In addition, speciation depends on the properties and composition of the sediment (e.g., pH, organic matter content, cation exchange capacity (CEC), redox potential, grain size), as well as the loading of trace metals (Saleem et al. 2015). Therefore, it would be important to perform sequential extraction (BCR) of trace elements in sediments in order to obtain
indications of mobility, biological availability and potential risks related to metal content in aquatic ecosystems.

This study aimed to (1) study the spatial distribution of trace metals (Cu, Ni and Mn) in surface sediments; (2) identify the possible sources of pollution using the enrichment factor (EF) and the principal component and hierarchical cluster analyses, (3) assess pollution levels and potential ecological risks associated with these heavy metals using the geoaccumulation index (Igeo), the potential ecological risk factor (Er), the potential ecological risk (IR) index (RAC).

1. Material and methods

1.1. Study Area

The savanna district (90 25 '00 "North and 50 35' 00" West) is located in northern Côte d'Ivoire, close to Mali and Burkina Faso. It has an area of 40323 km² and an estimated population of 1.607 million inhabitants in 2014 (Yapo et al.2016). The climate is Sudanese hot and dry with two distinct seasons: a rainy season from mid-June to October and a dry season from November to mid-June. The dry season is characterized by the presence of harmattan (December to February) with an average temperature of 30°C. In northern Côte d’Ivoire, the geology is predominately made up of feral sols. These soils are derived from felsic or intermediate parent rocks (granite, gneiss, phyllite and schist) of the underlying Precambrian rocks. The rocks are mainly composed of green schist of low metamorphic grade, bounded on either side by tectonized granitoid gneiss terranes. 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 (Sako et al.2018). Korhogo lies in the Bandama River basin, while Tengrela is drained by the Bagoé River. The Bandama River is the longest and the largest river in Côte d'Ivoire. It takes its source in the northern Côte d’Ivoire, between Korhogo and Boundiali at an altitude of 480 m and flows into Grand-Lahou Lagoon and the Gulf of Guinea in the south. With a length of 1050 km, its catchment area covers 97,500 km² with an annual average discharge about 263 m³/s (Girard et al.1970). The Bagoé River is a small river located in the north of Côte d’Ivoire. It originates from the Kokoum region near Côte d’Ivoire–Mali borderland at an altitude 425 m and traverses Tengrela (Côte d’Ivoire). The length of the Bagoé River is approximately 230 km, the drainage basin is 4740 km², and the annual average discharge is 170 m³/s (Traore et al.2017).

The savannah district is well known through activities such as livestock, cotton, cashew and food activities (Yapo et al.2016), in addition to a number of industrial and artisanal and small-scale gold mining extractions (Sako et al.2018). In this study, two cities have been selected in the savannah district (Korhogo and Tengrela) to get an idea of the state of contamination in metallic trace elements of their environments. The selected sites are the Korhogo gold zone (R₁ to R₅ station, M₁ to M₅ and K₁ to K₁₀) and the Tengrela gold zone (T₁ to T₁₀ station). This was favored by the establishment of two gold mining industries, Ran gold (Korhogo) and Perseus Mining (Tengrela) in these cities, as well as the existence of several artisanal and small-scale gold extractions.

The Tongon mine is located in the sub-prefecture of M'bengue more than 65 km from the city of Korhogo and 2.5 km from the village of Tongon. This open-pit mine covers an area of 1000 km² and is 55 km south of the Malian border. To carry out our study several samples were collected in the gold mining zones of Korhogo. Stations R₁ to R₅ are very far from the Rand gold industrial extraction in the classified forest Badenou and not far from an abandoned artisanal mining area. On the other hand, the M₁ to M₅ stations are located in the vicinity of the Rand...
gold industry, an active open pit gold mining mine. The other stations are located in two artisanal gold mining villages Taoura (K1 to K3) and Bevogo (K4 to K10).

1.2. Sediments characterization and heavy metal analysis

Sampling campaigns took place in 2016 during the dry season. The collection of the sediment samples, digestion, and total metal concentration measurements have been described by Kinimo et al. (2018). A total of 5 surface sediment samples (0-5 cm) were collected from each site (Fig.1). In order to take the local variability into account, each sample (300 g) was made of five subsamples collected using a Van Veen stainless steel grab (with an area of 0.02 m²) (Saleem et al.2015). Without emptying the grab, a sample was taken from the center with a polyethylene spoon (acid washed) to avoid contamination by the metallic parts of the dredge. Samples were then put into ice bags and transported to the laboratory, stored in a deep-freeze unit before the drying procedure.

Sediment samples were air-dried at room temperature (Zahra et al.2014), ground with an agate mortar to pass through a 63 μm sieve, and stored in polyethylene zip-type bags and shipped to Laboratoire de Chimie Bioorganique Réactivité et Analyse (COBRA), Université de Rouen, France for further analysis. All sampling devices were cleaned by rinsing with pure water and kept in 0.1 M HNO3 (68%, Fischer Scientific) for several days before sampling. Sediment samples were digested using a microwave-assisted digestion system (Milestone Ethos 1 microwave, Shelton, US), following Method 3051 A (USEPA 2007). About 0.5 g of homogenized sediments were first left to react with a mixture of 3 mL 68% HNO3 and 9 mL 37% HCl (trace metal grade, Fisher Scientific) in loosely capped Teflon reactors for 30 min at room temperature, in a fume hood, to avoid an overpressure during the heating step (USEPA 2007; Bettinelli et al.2000). Then, the digestion was performed under high power at programmed temperatures and time intervals: 0 to 10 min, 25 to 150°C; 10 to 15 min, 150°C; 15 to 20 min, 150 to 165°C; 20 to 25 min, 165°C; 25 to 30 min, 180°C (Kinimo et al.2018). After cooling, the solutions were diluted to 50 mL with ultrapure 2% HNO3 in Teflon tubes and centrifuged at 4000 rpm for 5 min prior to analysis of the supernatant. Duplicate blanks were prepared and analysed with each batch of digested samples.

Trace metals (Fe, Al, Cu, Mn, and Ni) were measured using an inductively coupled plasma-optical emission spectrometer (ICP OES Icap 6200, Thermo Fisher, Cambridge, UK). Three replicates of each sample analysed presented an error that was within 6%. Accuracy of the analytical procedures were evaluated through the analysis of the certified reference material CRM CNS 301-04-050 (Sigma-Aldrich; Missouri, U.S.A) for freshwater sediment. The measured concentrations fell within the range of certified values (Table 1) (Kinimo et al.2018).

The pH of the sediments was measured with a pH meter (HANNA HI.9828). For determination of pH, 10 g of the air-dried sample was mixed with 25 mL distilled water (sediment: water at a ratio of 1:2.5) and was stirred for 1 hour (Islam et al.2000; Halim et al.2013). The mixture was allowed to stand for 30 min for allowing it to settle. The slurry was decanted and pH was measured with a calibrated pH meter.

Total organic carbon (TOC) was determined by loss on ignition (in percentage) of 1.0 g of dried sediments in an oven at 550°C for 4 h (Kinimo et al.2018; Carbonell-Barrachina et al.2000; Touch et al.2017). The precision of three triplicate analyses of each sample fell within error ranges of 5-10%.

The sediments, previously gently crushed in an agate mortar, were carefully weighed and transferred to the highest part of a series of sieves. A 63 μm sieve was placed at the bottom of the sieve stack and care was taken using a pan under the finest sieve to capture the last fine material likely to pass (Atibu et al 2016).
1.3. Environmental assessment

1.3.1. Geo-accumulation index (Igeo) evaluation of trace metals

The degree of metal contamination in sediment was assessed by the geo-accumulation index (Igeo) which was originally introduced by Müller et al. (1969). The Igeo value was defined by the following equation:

\[ I_{\text{geo}} = \log_2 \left( \frac{C_n}{1.5 B_n} \right) \]  

(1)

Where \( C_n \) represents the measured concentration of metal (n) in samples (mg/kg), \( B_n \) represents the geochemical background value of metal (n) (mg/kg). Factor 1.5 is used to account for the possible variation in the background values. No trace metals background values are available for the study area. Therefore, the geochemical background concentrations in the Upper Continental Crust (UCC) from Wedepohl (1996), were used. The Igeo consists of seven classes, where: Class 0 (Igeo ≤ 0), uncontaminated; Class 1 (0 < Igeo < 1), uncontaminated to moderately contaminated; Class 2 (1 < Igeo < 2), moderately contaminated; Class 3 (2 < Igeo < 3), moderately to heavily contaminated; Class 4 (3 < Igeo < 4), heavily contaminated; Class 5 (4 < Igeo < 5), heavily to extremely contaminated; Class 6 (Igeo ≥ 5), extremely contaminated (Nilin et al. 2013).

1.3.2 Enrichment factor (EF)

Enrichment factor (EF) is a useful tool for determining the degree of anthropogenic heavy metal pollution (Elias et al. 2011; Kowalska et al. 2016). The EF is computed using the relationship below:

\[ EF = \frac{\left( \frac{C_{\text{Metal}}}{C_{\text{Fe}}} \right)_{\text{Sample}}}{\left( \frac{C_{\text{Metal}}}{C_{\text{Fe}}} \right)_{\text{Background}}} \]  

(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.

Fe and Al have been widely used as potential normalizing elements by several studies (Chakraborty et al. 2015; Saleem et al. 2018). However, the appropriate normalizing element varies depending on the location. Therefore, the sequential extraction procedure was performed on Fe and Al to select the most appropriate reference in the study area. At this level, the element more bound to the residual phase in percentage is considered the more conservative; thus, the best to be used as the normalizing element. In addition, the normalizing element correlates in general with traces elements in a given location. The residual phase in sediment represents the crystalline structure and trace metals strongly bound to this phase are therefore unavailable to the aquatic system (Saleem et al. 2018). The results of sequential extraction reported in the present study area (Fig. A1, supplementary material) showed that Fe (92 %) was relatively present in the residual fraction relative to Al (87 %). Moreover, in this study area, moderate to significant correlations were obtained between Fe and trace metals (Cu, r = 0.34; Mn, r = 0.38; Ni, r = 0.58) (Table A2, supplementary material). Therefore, Fe has been chosen as the most appropriate reference element. The background concentration of metals in the Upper Continental Crust (UCC) were used (Wedepohl 1996), EF values were interpreted as suggested by Hakanson (1980) and Maanan et al. (2015), where: EF < 1 indicates no enrichment; 1 < EF < 3 is minor enrichment; 3 < EF < 5 is moderate enrichment; 5 < EF < 10 is moderately severe enrichment; 10 < EF < 25 is severe enrichment; 25 < FE < 50 is very severe enrichment; and EF > 50 is extremely severe enrichment.
1.3.3 Risk assessment

The potential risk of individual metal (Er) and potential ecological risk index (IR) were proposed by Hakanson (1980) (Table 2), which express the toxicity of heavy metals and comprehensive effect of multiple contaminants (Cheng and Yap 2015; Liu et al. 2016).

Following equations were used to calculate Er and IR (Hakanson 1980):

\[ Er^i = T_{r}^i \times \left( \frac{C_i}{C_0} \right) \]  
[3]

\[ IR = \sum_{i=1}^{n} (T_{r}^i \times \left( \frac{C_i}{C_0} \right)) \]  
[4]

Where \( C_i \) is the average content for metal \( i \) in the sediment, \( C_0 \) is the background concentration of metal in the Upper Continental Crust (UCC), Er is the potential risk of individual metal, \( T_{r}^i \) is toxic response factor and IR is the potential ecological risk index. According to Hakanson (1980), \( T_{r}^i \) values for Cu = 5, Mn = 1 and Ni = 5.

1.3.4 Sequential extraction of heavy metals

A modified BCR sequential extraction procedure (Rodgers et al. 2015) 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 80°C for 1h. After cooling down, 20 mL of 1.0 M ammonium acetate (pH = 2) was added at room temperature for 16h to extract the 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) (Baran et al. 2019). Previous study of river sediment showed recoveries (\( \frac{F_1+F_2+F_3+F_4}{\text{Pseudo-total}} \times 100 \)) of this method in the range of 94–106% for Cu, Mn, and Ni.

1.3.6 Toxicity risk assessment

The Risk Assessment Code (RAC) has been used to assess the environmental risks and harmful biological effects that could result from certain concentrations of metallic pollutants in sediments (Canuto et al. 2013; Nemati et al. 2011). This risk is assessed by considering the exchangeable fraction linked to carbonates (F1). This fraction represents the fraction most toxic to the environment (Canuto et al. 2013; Nemati et al. 2011). The risk rate is determined according to the following relationship:

\[ \text{RAC}(\%) = \frac{F_1}{F_1+F_2+F_3+F_4} \times 100 \]  
[5]

When the Percentage Risk (RAC) is less than 1%, the sediment does not present a risk to the aquatic environment. Percentages of 1 < RAC < 10 reflect low risk. Those of 11 < RAC < 30 and 31 < RAC < 50 indicate medium risk and high risk, respectively. Above 50%, the sediment can cause a very high risk and is considered dangerous because the metals can be easily assimilated by aquatic species.

1.3.7 Statistical analyses
Multivariate statistical analyses including principal component and cluster analyses were performed to estimate geochemical factors controlling trace metals distribution in the sediments. The One Way Analysis of variance (ANOVA) was performed 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 performed when the equal variance test failed. The difference was considered statistically significant at $p < 0.05$. Statistical analyses were performed with Sigmaplot 12.5, except cluster analysis that was performed with Statistica 7.1 Software.

Results and discussion

2. Results

2.1. Sediment texture, pH and total organic carbon

During the sampling period, the percentage of sand in sediments from artisanal mining stations varied between 62.8% and 79.8% at Korhogo with an average of 70.9 ± 5.30%, and between 73.1% and 78.1% at Tengrela with an average of 76.3 ± 1.43%. The percentage of silt and clay varied between 20.2% and 37.8% at Korhogo with an average of 29.1 ± 5.30%, and 21.9 and 26.9% at Tengrela with an average of 23.72 ± 1.43%. As for industrial stations at Korhogo, the sand fraction varied from 73.8 to 80.8% with an average 77.3 ± 3.45%, while the silt and clay fraction varied from 19.2 to 26.1% with an average of 22.7 ± 2.6%. The average sand content in sediments from industrial areas was significantly higher ($p < 0.05$) than the one in the artisanal stations. On the contrary, the average in silt and clay content was significantly higher ($p < 0.05$) in the artisanal stations than that measured in the industrial stations. The average sand content in artisanal stations in Tengrela was significantly higher than that in Korhogo. On the contrary, the average in silt and clay content was significantly higher ($p < 0.05$) in the artisanal stations at Korhogo than that measured in the artisanal stations in Tengrela. Overall, sediment texture results showed a large spatial variability, with sand being the most dominant fraction.

The average sediment pH followed the order Bevogo (7.63 ± 0.95) > Tongon (6.85±0.92) > Taoura (6.76±0.55) > Badenou (6.59±0.47) at Korhogo (6.98 ± 0.80) and the order Kanakono (7.37±0.83) > Sissingue (7.49±0.49). The average pH values at Korhogo were slightly lower than those at Tengrela. No significant statistical difference was found among the sites.

The results in Table 3 showed that TOC contents of Korhogo surface sediments varied largely from 0.79 to 7.18% with an average of 2.85 ± 1.36%, while those of Tengrela varied from 0.15 to 1.05% with an average of 0.49 ± 0.14%. Nevertheless, the Korhogo sediments recorded the highest levels. The average TOC content in artisanal stations in Korhogo was significantly higher than that in Tengrela.

2.2. Spatial distribution of heavy metals in sediments

2.2.1. Spatial distribution of total Cu

The spatial distributions of total Cu concentrations in surface sediments of Korhogo and Tengrela are shown in Figures 2c1 and 2c2. Cu concentrations ranged from 2 to 127 μg/g with an average of 23 ± 11 μg/g, 40 ± 23 μg/g, 26 ± 7 μg/g, 56 ± 42 μg/g, 15 ± 8 μg/g, 14 ± 3 μg/g at Badenou, Tongon, Taoura, Bevogo, Sissingue and Kanakono, respectively. The results of figure 2c1 showed that Cu concentrations did not vary significantly ($p < 0.05$) among artisanal mining areas (Badenou, Taoura and Bevogo) at Korhogo. However, Cu had different mapping distribution in sediments from these areas. Cu concentrations in Badenou and Taoura were the lowest (3 -52 μg/g) indicated by the red and orange colours, while were the highest (77 - 127 μg/g) in Bevogo (blue colour).
In sediments collected from industrial area at Tongon, Cu distribution varied among the stations. The highest values (77–101 µg/g) were found at stations M3 and M4 (blue colour). There was no significant difference (ANOVA, p < 0.05) between the artisanal and the industrial stations at Korhogo.

The spatial distribution mapping trend of Cu was not the same in artisanal mining areas at Tengrela. Cu concentrations in stations T1 and T10 were in the lower range 2–11 µg/g which correspond to the red and orange colours. On the contrary, those of stations T1, T3, T5, T6, T7, T8 and T9 were in the range indicated by blue colours (14 – 25 µg/g) corresponding to the highest values (figure 2c2). ANOVA analysis showed that there was no significant difference (p < 0.05) between Kanakono and Sissingue for Cu concentrations.

### 2.2.2. Spatial distribution of total Mn

As shown in Figures 2a1 and 2a1, Mn concentrations varied between 171 and 4380 µg/g. The average Mn concentrations found in Korhogo sediments were 1893 ± 1451 µg/g (Badenou), 636 ± 146 µg/g (Tongon), 1013 ± 457 µg/g (Taoura) and 603 ± 306 µg/g (Bevogo). In Tengrela sediments Mn average were 448 ± 263 µg/g and 309 ± 81µg/g at Sissingue and Kanakono, respectively. The Mn concentrations in the sediments from artisanal mining areas showed no significant spatial variability (p < 0.05) at Korhogo. On the contrary, the distribution mapping of Mn varied with the stations. The values obtained in Bevogo (171 – 527 µg/g, red colour) were lower than those (1018 – 4380 µg/g, dark blue colour) of Taoura and Badenou. The Mn concentrations in the artisanal and the industrial sediments at Korhogo did not differ significantly (p < 0.05). However, the spatial distribution mapping of Mn in the sediments at Tongon and Bevogo was the same. ANOVA analysis showed no significant spatial variability (p < 0.05) in Mn concentrations in sediments at Tengrela. On the opposite, Mn spatial mapping distributions were the same in all stations at Kanakono and Sissingue except station T1. The values of Mn concentrations in stations except station T1 were in the lower range (192 – 344 µg/g, red colour).

Significant difference (p < 0.05) of Mn concentrations was found between Kanakono and Badenou. The sediments at Badenou were found to be the most contaminated.

### 2.2.3. Spatial distribution of total Ni

Figures (b1) and (b2) showed the spatial distributions of Ni in the surface sediments of Korhogo and Tengrela, respectively. The Ni concentrations varied from 2µg/g to 97 µg/g, with average values of 23 ± 11 µg/g, 60 ± 11 µg/g, 25 ± 8 µg/g, 20 ± 4 µg/g, 15 ± 7 µg/g, 18 ± 9 µg/g at Badenou, Tongon, Taoura, Bevogo, Sissingue and Kanakono, respectively.

The distributions mapping trend of Ni in artisanal mining areas at Korhogo were the same indicated by the red and orange colours which correspond to the lowest values (3- 40 µg/g). Nevertheless, the Ni concentrations in the sediments did not vary significantly (p < 0.05) among all artisanal sites. At Tongon, an opposite spatial distribution mapping of Ni was observed. The values of Ni at stations M1 and M5 were in the lowest range (colour orange), while those of the stations M2, M3 and M4 were in the highest (colour dark blue). There was a significant difference (p < 0.05) between artisanal site (Bevogo) and industrial site (Tongon) at Korhogo. The highest concentration (60 ± 11 µg/g) was found at Tongon.

The spatial distribution mapping of Ni in the sediments of Tengrela was almost similar in all stations except the stations T10 and T3 which correspond to the lowest values (2 - 13 µg/g, red and orange colours). However, no spatial variability (p < 0.05) of Ni was observed at Tengrela.
One-way ANOVA analysis (p < 0.05) showed no significant difference between artisanal sites at Korhogo and artisanal site at Tengrela. Nonetheless, the highest concentration (25 ± 8 μg/g) was found at Taoura.

2.3. The values of pollution indices

2.3.1. Geo-accumulation index (Igeo)

Igeo proposed by Müller and Suess (1979) was applied in the beach sediments to assess the metal contamination levels above the background or baseline concentrations (Bhuiyan et al.2010; Kalender and Uçar 2013). The values of the Korhogo and Tengrela sediment geo accumulation index are shown in Table 3. The average Igeo values of Cu, Mn and Ni in the Tengrela sediments were all less than zero (class 0), indicating that sediments are uncontaminated. The sediments collected in all sites except Bevego at Korhogo were uncontaminated by Cu. At Bevego, moderate contamination level of Cu was observed. For Ni, the sediments contamination level was the same in all the artisanal areas at Korhogo. The sediments in these areas were uncontaminated by Ni, indicated by Igeo values less than 0. Uncontaminated to moderately contamination in Ni was observed in the industrial area (Tongon) at Korhogo. Sediments were uncontaminated by Mn at Tongon and Bevego. On the opposite, those collected at Badenou and Taoura were moderately and uncontaminated to moderately contaminated by Mn, respectively.

The contamination levels trend of Cu, Ni and Mn vary one site to another at Korhogo, while that at Tengrela were the same.

2.3.2. Enrichment Factor (EF)

EF values are shown in Table 3. On the Hakanson (1980) scale, EF (0.9 8± 0.3 ≤ EF ≤ 1.46 ± 0.64) values calculated using mean Cu concentrations at Korhogo and Tengrela showed that all sediments were minor enriched by Cu, except sediments in the Bevogo mining area which were moderately enriched (EF = 3.66 ± 3.06) in Cu. For Ni, EF values in the Badenou, Taoura, Bevogo, Kanakono and Sissingue sediments were less than 1, showing that the sediments were not enriched by Ni. While those of Tongon had a minor enrichment in Ni (1 < EF < 3). On the other hand, all the sediments of Kanakono, Sissingue and Tongon were not enriched (0.73 ± 0.37 ≤ EF ≤ 0.80 ± 0.38) in Mn except the Badenou, Taoura and Bevogo sediments which showed minor enrichment (1 < EF < 3) in Mn.

2.4. Geochemical control of trace metals (Cu, Mn and Ni) in sediments

Because there was no significant difference between metal concentrations between Tengrela and Korhogo, Principal Component Analysis (PCA) was applied to data from all the stations. The results are shown in Table 4. Three factors were found to account for 76.3% of the variance of the data set. Three obvious characteristics were observed. Iron and trace metals Cu, Mn, and Ni, and the fine fraction of sediments (silt and clay) along with TOC were associated with factor 1. Ni and the fine fraction as well as the sand contributed to factor 2. The third group was formed by the high contribution of pH and medium contributions trace metals Cu and Mn on factor 3.

In addition to the PCA, an Ascending Hierarchical Classification (AHC) analysis was performed on all the sampling stations at Tengrela and Korhogo. The results are shown in Fig.3. The AHC results showed a close association of TOC with Fe, trace metals Cu, Mn and Ni, and the fine fraction. The sand and the pH formed no group with any parameter.

2.5. Ecological risk assessment
The results of the ecological risk indices (Er) and (IR) for all sampling areas are shown in Table 3. It showed that all sampling areas were considered to have a very low level of ecological risk (Er< 40 and IR < 80). The highest IR was found in Tongon industrial zone sediments, and the lowest IRs was reported in Tengrela sediments.

3. Evaluation of the potential mobility of traces metals in sediments

The individual Cu, Mn and Ni speciation fractions expressed as percentages of their total concentrations are shown in Fig. 4.

3.1. Chemical Fractionation of Nickel in Sediments

The distribution of Nickel in the different fractions of sediments is shown in Figure 4. Nickel is mainly linked to the residual fraction (R) with percentages varying between 59.68 ± 3.53% (Sissingue) and 66.87 ± 7.16% (Tongon). This equivalent to 9.27 ± 3.73 - 38.19 ± 21.35 µg/g of Ni concentration. There was no significant difference (ANOVA, p<0.05) between different stations for Ni concentrations in the residual, iron/manganese oxides and organic matter fractions. For the acid-soluble fraction (F1), the concentration of Ni in the artisanal mining area of Bevogo was significant higher (p <0.05) compared to other sites. The distribution of nickel in the different phases of the sediments of M’bengue and Tengrela is as follows: Badenou, Taoura and Bevogo: residual fraction (R) > fraction linked to organic matter and sulphides (F3) > fraction linked to oxides (F2) > exchangeable fraction linked to carbonates (F1), Tongon: Residual fraction (R)> exchangeable fraction linked to carbonates (F1) > fraction linked to organic matter and sulphides (F3) > fraction linked to oxides (F2), Sissingue: residual fraction (R)> fraction linked to oxides (F2) > fraction linked to organic matter and sulphides (F3) > exchangeable fraction bound to carbonates (F1), Kanakono: Residual fraction (R)> fraction linked to organic matter and sulphides (F3) > exchangeable fraction linked to carbonates (F1) > fraction linked to oxides (F2). In the M’bengue stations, the order of distribution of nickel in the sediments is identical in the Badenou, Taoura and Bevogo stations.

3.2. Chemical Fractionation of Copper in Sediments

The percentages of Copper in the various fractions of sediments are shown in figure 4. The residual fraction (R) controls the distribution of copper in the different fractions of the sediments with percentages varying between 65.89 ± 3.40% (Kanakono) and 71.42 ± 7.20% (Tongon). This corresponds to a concentration varying from 8.96 ± 4.24 µg/g to 29.31 ± 17.63 µg/g of Cu concentration. All the proportions of the residual fractions recorded are greater than 65%, which shows that copper is less available in the Stations studied. There was no significant difference (ANOVA, p<0.05) between different stations for Ni concentrations in the residual, iron/manganese oxides and organic matter fractions, the acid-soluble fraction (F1). The decreasing order of retention of copper by the different phases of the sediments at the different stations is as follows.

Badenou, Bevogo and Kanakono: Residual fraction (R)> fraction linked to organic matter and sulphides (F3)> fraction linked to oxides (F2) > exchangeable fraction linked to carbonates (F1), Tongon: residual fraction (R) > fraction linked to the fraction linked to oxides (F2)> exchangeable fraction linked to carbonates (F1)> organic matter and sulphides (F3), Taoura and Sissingue: residual fraction (R)> exchangeable fraction linked to carbonates (F1)> fraction linked to fraction linked to oxides (F2)> organic matter and sulphides (F3), Copper
would have the same behaviour with respect to the different phases of the sediments of Badenou, Bevogo and Kanakono, then of Tongon and Sissingue. Indeed, the order of distribution in Badenou is similar to that of Bevogo and Kanakono, also those of Tongon and Sissingue are identical.

3.3. Chemical fractionation of manganese in sediments

Figure 4 shows the distribution of manganese in the different fractions of the sediments of M’bengue and Tengrela. It clearly appears that manganese is mainly linked to the residual fraction (R), with an average proportion varying between 66.36 ± 9.28% (Bevogo) and 79.22 ± 13.84% (Badenou). This proportion corresponds to a concentration varying from 422.10 ± 247.92 µg / g to 1638.78 ± 1311.81 µg/g of Mn concentration. ANOVA analysis (p <0.05) shows that no significant difference was observed between stations for Mn concentrations in the residual, iron/manganese oxides and organic matter fractions, the acid-soluble fraction (F1). The retention of manganese by the different phases of the sediments allows two types of classification to be made. The first concerns the Badenou, Touara, Sissingue and Kanakono stations: Residual fraction (R) > fraction linked to organic matter and sulphides (F3) > fraction linked to oxides (F2) exchangeable fraction linked to carbonates (F1), The second relates to the Tongon and Bevogo stations: Residual fraction (R) > fraction linked to oxides (F2) > fraction linked to organic matter and sulphides (F3) > exchangeable fraction linked to carbonates (F1).

3.4. Assessment of the risk of toxicity linked to metals Cu, Ni and Mn.

Table 6 gives the values of the toxicity risks of the metals Cu, Ni and Mn in the sediments of the various stations. In general, Manganese can cause a low risk in all the stations studied (5.25±2.32≤ RAC (%) ≤ 9.30±2.16). The results show that the sediments of Badenou, Tongon, Bevogo and Kanakono can present a low risk of toxicity by Copper with percentages varying between 5.51±1.14 and 9.84±2.58%. On the other hand, the sediments of Taoura and Sissingue may present a medium risk of toxicity (11.37 ± 5.15≤ RAC (%) ≤ 11.59 ± 2.50). The Tongon, Taoura, bevogo, Kanakono and Sissingue sediments may present an average risk of Nickel toxicity (11.52±2.23≤ RAC (%) ≤ 12.52±2.17), Apart from the Badenou sediments which present a low risk of toxicity (RAC (%) = 7.75 ± 4.50).

4. Discussion

4.1. Surface sediment characteristics

The variability of pH in sediments surrounding the mining areas is related to the variation of extrinsic factors. Acid mine drainage is expected to result in much more acidic pH values than those reported in this study (near neutral). This may be due to geological characteristic in the area such as carbonate rocks that could lead to high sedimentary pH. The lack of significant spatial variability of pH at artisanal sites could result from the buffering capacity of the sediments. Sediment grain size data from the study areas showed that all the sediments had a sandy texture. The geology of the savannah district which is essentially based on a large set of homogenous and heterogeneous biotile granitoids (Sako et al. 2018) could explain this sandy texture.

The sediment texture is an important factor which influences the TOC distribution in sediments (Kinimo et al.2018). In this study, the sediments texture varied among Korhogo and Tengrela artisanal stations. That may explain why TOC content in sediment varied between the stations at Korhogo and Tengrela.
4.2. Spatial distribution of total trace metal (Cu, Ni and Mn) concentrations

The total concentrations of metals (Cu, Mn and Ni) in artisanal sediments did not vary significantly among the stations. Trace metals accumulation into the sediment depends on many parameters such as pH, sediments texture and TOC. The acidic pH of sediments promotes the bioavailability of metals, while the basic pH increases metal adsorption (Barik et al.2018). Due to its smaller specific surface, the sand fraction accumulates less metal than clay fraction. Consequently, metal concentrations in sediments increase with finer particles. In addition, several studies reported that TOC contents in sediments increase with finer particles. The average of pH determined in this study did not vary among the artisanal sites at Korhogo and Tengrela. That may imply why trace metals concentrations did not significantly differ one site to another.

The samples collected from artisanal areas at Tengrela are located downstream the Bagoé River. Perseus Mining had not started gold extraction at Sissingue before the present study. Thus, all the sampling stations along the Bagoé River at Tengrela could be considered as artisanal mining areas. During the study period, the concentrations of trace metals Cu, Mn and Ni were comparable in all the ten stations at Tengrela. This probably indicates that the intensity of water flow, and sediment and water discharges, and anthropogenic pressures such as agricultural and urban activities may not differ significantly in the watershed of the Bagoé River during the sampling period. The Bandama River waters industrial stations at Tongon and flows downstream towards artisanal mining stations at Badenou, Taoura and Bevogo, respectively. However, no concentration gradient was found along the Bandama River for Cu, Mn, and Ni at Korhogo. Moreover, there was in general no significant metal concentration difference between the stations. This indicates that there was no sign of transported Cu, Ni, and Mn pollution from the industrial mining stations upstream the Bandama River towards the artisanal stations located downstream during the study period. One possible cause could be that the Bandama River bed was dry, or the water velocity was almost zero at many places during the sampling span time. Nevertheless, the significant difference of Mn concentration between Bevego and Kanakono, and between the artisanal site Bevego and the industrial site Tongon at Korhogo for Ni could be explained by the different affinities of the metals for the sediments and the different sources as reported by Kang et al. (2017) in the Jiaozhou Bay. Kang et al. (2017) mentioned that the different spatial distribution trend could be explained by the sediment heterogeneity in time and space. In addition, the windborne transport and atmospheric deposition of dust may play a significant role in spreading contaminants (Li et al.2017). These processes probably caused the differences in the metal spatial distributions in the sediment at Korhogo and Tengrela. Li et al. (2017) showed similar distribution of Cu concentrations in sediments from Xikuangshan mining area (China). In contrast, Toro et al. (2016) observed that the distribution of trace metals Cu, Ni and Mn varied significantly in sediments around Chico mining area (Colombia), which is in stark contrast with our observations. These findings show that the spatial variations of trace metals in sediments around the mining areas are local specific.

For comparison purposes, the trace metals concentrations in this study and in some other mining areas are summarized in Table 5. Although the different geological settings and difference in analytical methods may influence metal concentrations in sediments, it can be seen that the environmental contamination with Cu, Mn and Ni by mining activities found in the present study is consistent with previous investigations in Ghana (Klubi et al.2018; Bempah and Ewusi 2016). Moreover, compared with previous research in other mining areas in central-southern and south-eastern Côte d’Ivoire (Kinimo et al.2018), the trace metals concentrations found in the current study are low. Therefore, the concentrations of Cu, Ni and Mn determined in this study could represent the basis...
data for these areas. Nevertheless, repeated measurements over a long period of time should be carried out to better understand the spatial variability of trace metals in this study.

### 4.3. Pollution sources identification and geochemical control of traces metals

The results of Igeo indicated that low to moderate contamination of sediments by Cu, Mn and Ni were obtained at Korhogo, while sediments showed low contamination in Cu, Mn and Ni in all sites at Tengrela. This may suggest an external contribution of trace metals (Cu, Ni and Mn) in the sediments. For example, Enrichment Factor (EF) is used to assess the potential impact of human activities on trace metal concentrations in sediments (Kowalska et al. 2016; Peter and Adeniyi 2011). EF values show that the Korhogo and Tengrela sediments are slightly enriched in Cu, except sediments in the Bevogo artisanal mining area that have moderate Cu contamination. The minor and moderate enrichment in Cu in the sediments showed an external contribution of Cu in sediments through various activities practiced in these areas, such as artisanal and industrial gold mining. For Ni, the EF values in the Badenou, Taoura, Bevogo, Kanakono and Sissingue sediments showed no enrichment of sediment by Ni. This means that artisanal and industrial gold mining still is not significant source of Ni in these areas. On the contrary, the Tongon sediments have a minor Ni enrichment showing an external contribution of the metal. In addition, Mn has a natural enrichment in the sediments of Kanakono, Sissingue and Tongon, while the enrichment of the Taoura, Badenou and Bevogo sediments is minor because of the external supply of Mn. It has been reported that metals are of anthropogenic origin if EF value is higher than 1.5 (Zhang et al. 2002). The average values of EF for Cu at Bevego (EF = 3.66 ± 3.06), for Mn (EF = 2.27 ± 1.69) at Badenou and for Ni (EF = 1.71 ± 0.72) at Tongon indicated anthropogenic enrichment.

The results of PCA and AHC indicated that TOC is a key factor controlling the distribution of trace metals Cu, Mn and Ni in the study area. TOC is in general associated with finer fractions of sediments. This was confirmed by results from the present study. Due to their high surface area, finer particles in sediments represent an important carrier for organic matter (Ouattara et al. 2018). The positive contribution of TOC and finer particle (silt+clay) observed on factor 1 implies high sorption and affinity of TOC on finer particle. Thus, the association of TOC with the finer fraction makes the finer fraction another factor driving trace metal distribution in the sediments. Chen et al. (2012) have reported that Fe derives primarily from geological sources. Therefore, the association of trace metals Cu, Ni and Mn with Fe in the present study may suggests that these trace metals are mainly from a natural source. Furthermore, the EF values showed that sediments were generally not enriched in Cu, Mn, and Ni, which is consistent with a natural source of Cu, Mn and Ni. However, a part of the trace metals Cu, Mn and Ni in this study area may also derived from anthropogenic sources through unintentional contaminations from gold miners and the use pesticides and phosphate fertilizers (Rauch and Graedel 2007). The study area is dominated by agriculture focused on cash crops such as cotton, cashew, yam, corn, and vegetables crops. The production of these crops can be a source of Cu in the environment (Yapo et al. 2016). Thus, Cu, Mn and Ni would be subjected to anthropogenic contributions indicated by the contribution of Cu, Mn and Ni to factor 1. This was supported by high EF values of Cu, Mn and Ni at Bevogo, Badenou and Tongon, respectively. Therefore, factor 1 could be defined as both natural and anthropogenic sources. The results of PCA also revealed that sediment texture is an important carrier for Ni both through sand and silt and clay fractions. However further studies should be conducted to better understand high association of Ni with the sands revealed by PCA, but not by AHC in the sediments.
The grouping of pH, Cu and Ni on factor 3 suggests that pH drives the distribution of Cu and Ni. The pH has an impact on the mobility and solubility of metals in sediments. In acidic conditions, the mobility of trace metal is pronounced, while high pH leads to the metal adsorption in sediment (Halim et al. 2013). The average pH value (all stations combined) in the present study was 7.11 ± 0.77 pH units. Thus, Cu and Mn adsorption would be relatively promoted in sediments during the sampling period. According to Peng et al. (2009), there is a pH limit controlling trace metals mobility in sediments (e.g., 4.5 pH units for Cu). Trace metals would be released from sediments only if they reach such pH limit.

AHC results failed to reveal the influence of pH and sand in controlling the distribution of trace metals (Cu, Mn, and Ni). Therefore, performing two multivariate analyses to deduce geochemical behaviours or sources of trace metals could provide more meaningful information than what could do one single test.

The present study suggests that trace metals Cu, Mn and Ni concentrations are easily affected both by natural factors and human activities in the study area. The sources of Ni, Cu and Mn could therefore be divided into two groups, the sources of the first group being the geological formation of sediments and agricultural activities, the sources of the other group being transport, atmospheric deposition, waste and mining. Therefore, enrichment factor (EF), Principal component analysis (PCA) and Ascending Hierarchical Classification (AHC) can be combined to better understand the sources of trace metals (Cu, Ni and Mn).

4.4. Sediment risk assessment

In the Korhogo and Tengrela sites, the potential ecological factors Er of Cu, Ni and Mn were low because the Er values were lower than 40. The order of the potential ecological risk factor Er of the trace metals in the sediments of the different studied sites was: Badenou, Taoura, Bevogo, Sissingue and Kanakono: Cu > Ni > Mn. Tongon: Ni > Cu > Mn.

The results indicated that the potential risk was low at all sites, where the IR values were below 80. Based on the IR values (Table 3), the trend of the potential ecological risk of trace metals in surface sediments was: Tongon > Bevogo > Taoura > Badenou > Kanakono > Sissingue. This indicates that Cu, Ni and Mn in the sediments of the Tongon industrial areas could pose higher risks than those in the artisanal areas. Therefore, the monitoring of the Tongon area should be stepped up to prevent pollution of drinking water sources in the future. Local communities could be exposed through pathways such as consumption of contaminated vegetables, fish and fruits. Therefore, bioaccumulation studies are needed to understand human potential health risks.

Result from RAC show that trace metals present a low toxicity risk to the environment and biota in the areas studied. In summary, the identification of the distribution of trace metals and their relationships with organic matter in sediments were important steps in determining their mobility, potential bioavailability and toxicity to the aquatic environment.

4.5. Sequential extraction

In this study, the results of the chemical fractionation show that the trace metals (Cu, Ni and Mn) are mainly related to the residual fraction. This means that trace metals are bound to silicates and are therefore not available to the aquatic system (Saleem et al. 2015). The results of the chemical fractionation of nickel are in agreement with those of Ji et al. (2018), who showed that nickel is mainly bound to the residual fraction (60%) in the sediments of the Yongding River in China. Similarly, Compaore et al. (2019) showed that the residual fraction controls the distribution of nickel in soil fractions collected at Youga in southern Burkina Faso. On the other hand, Da Silveira Pereira et al. (2020) showed that nickel was not mainly related to the residual fraction in soils in areas influenced
by the Serra Pelada gold mine in Brazil. This is contrary to our results. However, the oxide bound fraction of nickel represents the most important reactive fraction in the Badenou and Sissingue sediments. Thus, an important part of the nickel present in the sediments of these regions can be fixed by iron and manganese oxides. Therefore, a modification of the redox conditions would lead to the solubilization of the Nickel by dissolution of these oxides. This order is different from that of Tongon. This difference could be explained by the different types of mining activities in these regions. The activities in Tongon are industrial in nature while those in Bevogo, Taoura and Badenou are artisanal in nature. The results of the copper distribution in the sediments studied show that copper is mainly related to the residual fraction. Thus our results corroborate with the studies carried out in the Yongding River in China (Li et al.2018), the mining soils studied in China (Sun et al.2018) and in Burkina Faso (Compaore et al.2019). These. On the other hand, the results of the study conducted by Aguilar-Hinojosa et al (2016) on sediments impacted by mining activities in Sonora, Mexico, are not consistent with those of the present study. Indeed, these authors observed that copper was weakly associated with the residual fraction. These different results of the distribution of the sediments studied suggest that a large part of the manganese is strongly related to the crystalline structure of the sediments. Our results are similar to those obtained by Compaore et al (2019) and Ji et al (2018) respectively in sediments and soils around a mine in Burkina Faso and China, where a high proportion of was obtained in the residual fraction. In contrast, Aguilar-Hinojosa et al. (2016) showed opposite results in stream sediments from a mining region in Mexico. Mn, Ni and Cu are more associated with the residual fractions (Figure 4), which have low solubility. As such, these trace metals are inert under natural conditions. High levels of Cu, Ni and Mn in the residual phase suggest that these trace metals are relatively insensitive to changes in the surrounding conditions. The same result is also obtained in Ji et al (2018).

5. Conclusion

Trace metals (Cu, Ni and Mn) concentrations in sediments around gold mining areas in the northern Cote d’Ivoire were investigated in this study. This research showed that the concentrations of metals (Cu, Mn, and Ni) in artisanal sediments did not vary significantly among the stations. The spatial maps of Cu and Mn indicated different distribution trends in artisanal area at Korhogo and Tengrela, while that of Ni showed similar distribution trends. The results of Igeo indicated low to moderate contamination of sediments by Cu, Mn and Ni at Korhogo, and low contamination in Cu, Mn and Ni at Tengrela. Enrichment factor showed anthropogenic contribution of Cu, Mn and Ni in sediments at Bevogo, Badenou and Tongon, respectively. These results confirm the contamination level obtained by Igeo. The results of risk assessment showed that Cu, Ni, and Mn pose low ecological risk in the surface sediments. It was concluded that, concentrations of Cu, Ni and Mn provided in this study can be used as basic data in sediments at Korhogo and Tengrela. Therefore, measurements over a longer study period as well as complementary studies including trace metals speciation and accumulation in organisms need to be conducted in order to better understand the trace metals distribution and the risks for human health. The phases of distribution and partitioning of trace metals constitute a major environmental concern with regard to chemical fractionation and ecotoxicological aspects. It can also be used as a tool to provide information on the bioavailability and mobility of trace metals in sediments. The chemical fractionation of trace metals in the collected sediments is related to the residual fraction. The RAC results suggested that Cu, Ni and Mn posed a low risk to the local environment.
Compliance with Ethical Standards

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

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References

Abdul-Wahab SA, Marikar FA (2012) the environmental impact of gold mines: pollution by heavy metals. Cent Eur J Eng, 2(2):304-313. https://doi.org/10.2478/s13531-011-0052-3
Aguilar-Hinojosa Y, Meza-Figueroa D, Villalba-Atondon AI, Encinas-Romer MA, Valenzuela-García J L, Gómez-Álvarez A (2016) Mobility and bioavailability of metals in stream sediments impacted by mining activities: the Jaralito and the Mexicana in Sonora, Mexico. Water, Air, & Soil Pollution, 227(9), 345
Atibu EK, Devarajan N, Laffite A, Giuliani G, Salumu JA, Muteb RC, Poté J (2016) Assessment of trace metal and rare earth elements contamination in rivers around abandoned and active mine areas. The case of Lubumbashi River and Tshamilemba Canal, Katanga, Democratic Republic of the Congo. ChemErde-Geochem76 (3): 353–362.https://doi.org/10.1016/j.chemer.2016.08.004
Baran A, Mierzwa-Hersztek M, Gondek K, Tarnawski M, Szara M, Gorczyca O, Koniarz T (2019) The influence of the quantity and quality of sediment organic matter on the potential mobility and toxicity of trace elements in bottom sediment. Environmental Geochemistry and Health, 41(6), 2893-2910.
Barik SK, Muduli PR, Mohanty B, Rath P, Samanta S (2018) Spatial distribution and potential biological risk of some metals in relation to granulometric content in core sediments from Chilika Lake, India. Environ Sci Pollut Res 25(1): 572-587. https://doi.org/10.1007/s11356-017-0421-4
Bempah CK, Ewusi A (2016) Heavy metals contamination and human health risk assessment around Obuasi gold mine in Ghana. Environ Monit Assess 188: 261. http://dx.doi.org/10.1007/s10661-016-5241-3.
Bettinelli M, Beone GM, Spezia S, Baffi C (2000) Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis. Anal Chim Acta424, 289-296. https://doi.org/10.1016/S0003-2670 (00)01123-5
Bhuiyan MA, Parvez L, Islam MA, Dampare SB, Suzuki S (2010) Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. J Hazard Mater 173(1-3): 384-392. https://doi.org/10.1016/j.jhazmat.2009.08.085
Biggeri A, Lagazio C, Catelan D, Pirastu R, Casson F, Terracini B, (2006) Report on health status of residents in areas with industrial, mining or military sites in Sardinia, Italy. Epidemiol Prev 30 (1): 5–95.
Boussen S, Soubrand M, Bril H, Ouerrfelli K, Abdeljaoaud S (2013) Transfer of lead, zinc and cadmium from mine tailings to wheat (Triticum aestivum) in carbonated Mediterranean (Northern Tunisia) soils. Geoderma 192: 227-236.https://doi.org/10.1016/j.geoderma.2012.08.029
Cai LM, Xu ZC, Qi JY, Feng ZZ, Xiang TS (2015) Assessment of exposure to heavy metals and health risks among residents near Tonglushan mine in Hubei, China. Chemosphere 127: 127–135. https://doi.org/10.1016/j.chemosphere.2015.01.027.
Canuto FAB, Garcia CAB, Alves JPH, Passos EA (2013) Mobility and ecological risk assessment of trace metals in polluted estuarine sediments using a sequential extraction scheme. Environmental monitoring and assessment, 185(7), 6173-6185.

Carbonell-Barrachina AA, Jugsujinda A, Burlo F, Delaune RD, Patrick WH (2000) Arsenic chemistry in municipal sewage sludge as affected by redox potential and pH. Water Res 34: 216-224. https://doi.org/10.1016/S0043-1354(99)00127-X

Chakraborty S, Chakraborty P, Nath BN (2015) Lead distribution in coastal and estuarine sediments around India. Mar Pollut Bull 97(1): 36-46. https://doi.org/10.1016/j.marpolbul.2015.05.056

Chen B, Liang X, Xu W, Huang X, Li X (2012) The changes in trace metal contamination over the last decade in surface sediments of the Pearl River Estuary, South China. Sci Total Environ 439: 141-149. http://dx.doi.org/10.1016/j.scitotenv.2012.09.025

Cheng WH, Yap CK (2015) Potential human health risks from toxic metals via mangrove snail consumption and their ecological risk assessments in the habitat sediment from Peninsular Malaysia. Chemosphere 135: 156–165. https://doi.org/10.1016/j.chemosphere.2015.04.013

Donkor AK, Bonzongo JCJ, Nartey VK, Adotey DK (2005) Heavy metals in sediments of the gold mining impacted Pra River basin, Ghana, West Africa. Soil Sediment Contam 14(6): 479-503. https://doi.org/10.1080/15320380500263675

Elias P, Gbadegesin A (2011) Spatial relationships of urban land use, soils and heavy metal concentrations in Lagos Mainland area. J Appl Sci Environ Manage 15 (2):391-399.

Garrido S, Campo GMD, Esteller MV, Vaca R, Lugo J (2002) Heavy metals in soil treated with sewage sludge composting, their effect on yield and uptake of broad bean seeds (Viciafaba L.). Water Air Soil Poll 166(1-4): 303-319. https://doi.org/10.1007/s11270-005-5269-4

Girard G, Sircoulon J, Touchebeuf P (1970) Aperçu sur les régimes hydrologiques de Côte d’Ivoire. ORSTOM Editions, Côte d’Ivoire.

Gupta S, Sharma SK, Kumar A (2019) Biosorption of Ni (II) ions from aqueous solution using modified Aloe barbadensis Miller leaf powder. Water Sci Technol 12(1): 27-36. https://doi.org/10.1016/j.wst.2019.04.003

Gwiazda R, Lucchini R, Smith D (2007) Adequacy and Consistency of Animal Studies to Evaluate the Neurotoxicity of Chronic Low-Level Manganese Exposure in Humans. J Toxicol Environ Health A 70(7): 594-605. https://doi.org/10.1080/10937400600882897

Hakanson L, (1980) Ecological risk index for aquatic pollution control. A sediment logical approach. Water Res 14 (5): 975-1001. https://doi.org/10.1016/0043-1354(80)90143-8

Halim MA, Majumder RK, Zaman MN, Hossain S, Rasul MG, Sasaki K (2013) Mobility and impact of trace metals in Barapukuria coal mining area, Northwest Bangladesh. Arab J Geosci 6(12): 4593-4605. https://doi.org/10.1007/s12517-012-0769-1

Ikem A, Egiebor NO, Nyavor K (2003) Trace elements in water, fish and sediment from Tuskegee Lake, Southeastern USA. Water Air Soil Pollut. 149, 51–75.

Islam KR, Weil RR (2000) Land use effects on soil quality in a tropical forest ecosystem of Bangladesh. Agr Ecosyst Environ 79(1):9–16. https://doi.org/10.1016/S0167-8809(99)00145-0
Ji H, Li H, Zhang Y, Ding H, Gao Y, Xing Y (2018) Distribution and risk assessment of heavy metals in overlying water, pore water, and sediments of Yongding River in a coal mine brownfield. *Journal of soils and sediments*, 18(2), 624-639.

Kalender L, Uçar SC (2013) Assessment of metal contamination in sediments in the tributaries of the Euphrates River, using pollution indices and the determination of the pollution source, Turkey. *J Geochem Explor* 134: 73–84. https://doi.org/10.1016/j.gexplo.2013.08.005

Kang J, Zhang Y, Chen J, Chen H, Lin C, Wang Q, Ou Y (2003) Nickel-Induced Histone Hypoacetylation: The Role of Reactive Oxygen Species. *Toxicol Sci* 74(2): 279–286. https://doi.org/10.1093/toxsci/kfg137

Kang X, Song J, Yuan H, Duan L, Li X, Li N, Liang X, Qu B (2017) Speciation of heavy metals in different grain sizes of Jiaozhou Bay sediments: Bioavailability, ecological risk assessment and source analysis on a centennial timescale. *Ecotox Environ Safe* 143: 296–306. http://dx.doi.org/10.1016/j.ecoenv.2017.05.036

Kinimo KC, Yao KM, Marcotte S, Kouassi NBL, 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. *J Geochem Explor* 190: 265-280. https://doi.org/10.1016/j.gexplo.2018.03.013

Klubi E, Abril JM, Nyarko E, Delgado A (2018) 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*190: 229-244. https://doi.org/10.1016/j.gexplo.2018.03.014

Kowalska J, Mazurek R, Gaśiorek M, Setlak M, Zaleski T, Waroszewski J (2016) Soil pollution indices conditioned by medieval metallurgical activity – A case study from Krakow (Poland). *Environ Pollut*, 218: 1023–1036. http://dx.doi.org/10.1016/j.envpol.2016.08.053

Li Q, Ji H, Qin F, Tang L, Guo X, Feng J (2014) Sources and the distribution of heavy metals in the particle size of soil polluted by gold mining upstream of Miyun Reservoir, Beijing: implications for assessing the potential risks. *Environ MonitAssess*186 (10), 6605-6626.https://doi.org/10.1007/s10661-014-3877-4

Li X, Yang H, Zhang C, Zeng G, Liu Y, Xu W, Lan S (2017) Spatial distribution and transport characteristics of heavy metals around an antiquity mine area in central China. *Chemosphere* 170:17-24. https://doi.org/10.1016/j.chemosphere.2016.12.011

Liu G, Wang J, Zhang E, Hou J, Liu X (2016) Heavy metal speciation and risk assessment in dry land and paddy soils near mining areas at Southern China. *Environ Sci Pollut Res*23(9): 8709-8720. https://doi.org/10.1007/s11356-016-6114-6

Lusilao-Makiese JG, Tessier E, Amouroux D, Tutu H, Chimuka L, Weiersbye I, Cukrowska EM (2016) Mercury speciation and dispersion from an active gold mine at the West Wits area, South Africa. *Environ MonitAssess*188 (1): 47.https://doi.org/10.1007/s10661-015-5059-4

Maanan M, Saddik M, Maanan M, Chaibi M, Assobhei O, Zourarah B (2015) Environmental and ecological risk assessment of heavy metals in sediments of Nador lagoon, Morocco. *Ecol Indic* 48: 616–626. https://doi.org/10.1016/j.ecolind.2014.09.034

Makinde WO, Ayodele OE, Ayodele TI, Oluremi OI, Temitope OK, Temitope FO (2017) Heavy metal contamination in stream water and sediments of gold mining areas of South Western Nigeria. *Afr J Environ Sci Technol* 10: 150–161. https://doi.org/10.5897/AJEST2015.2015

Molina-Villalba I, Marina L, Rodríguez-Barranco M, Hernández AF, Gonzalez-Alzaga B, Aguilar-Garduño C, Fernando G (2015) Biomonitoring of arsenic, cadmium, lead, manganese and mercury in urine and hair of children living near mining and industrial areas. *Chemosphere* 124:83–91. https://doi.org/10.1016/j.chemosphere.2014.11.016

Monterroso C, Rodríguez F, Chaves R, Diez J, Becerra-Castro C, Kidd PS, Macías F (2014) Heavy metal distribution in mine-soils and plants growing in a Pb/Zn-mining area in NW Spain. *Appl Geochemistry* 44: 3-11. https://doi.org/10.1016/j.apgeochem.2013.09.001
Müller G, Müller G, Putz G (1969) Index of geoaccumulation in sediments of the Rhine River. Geojournal 2: 108-118.

Müller PJ, Suess E (1979) Productivity, sedimentation rate, and sedimentary organic matter in the oceans— I. Organic carbon preservation. Deep-Sea Res 26(12): 1347–1362. https://doi.org/10.1016/0198-0149(79)90003-7

Naji A, Sohrabi T (2015) Distribution and contamination pattern of heavy metals from surface sediments in the southern part of Caspian Sea, Iran. Chem. Spec. Bioavail. 27, 29-43.

Nemati K, Bakar NKA, Abas MR, Sobhazadeh E (2011) Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sangai Buloh, Selangor, and Malaysia. Journal of Hazardous Mater. 192(1), 402-410.

Niane B, Moritz R, Guédron S, Ngom PM, Pfeifer HR, Mall I, Pote J (2014) Effect of recent artisanal small-scale gold mining on the contamination of surface river sediment: case of Gambia River, Kedougou. J Geochem Explor 144: 517–527. https://doi.org/10.1016/j.gexplo.2014.03.028

Niane B, Naresh D, John P, Robert M (2019) Quantification and characterization of mercury resistant bacteria in sediments contaminated by artisanal small-scale gold mining activities, Kedougou region, Senegal. J Geochem Explor 205: 106353. https://doi.org/10.1016/j.gexplo.2019.106353

Nilin J, Moreira LB, Aguiar JE, Abessa MRS, Lotufo TMC, Costa-Lotufo LV (2013) Sediment quality assessment in a tropical estuary: The case of Ceará River, Northeastern Brazil. Mar Environ Res 91: 89–96. https://doi.org/10.1016/j.marenvres.2013.02.009

Ouattara AA, Yao KM, Soro MP, Diaco T, Trokourey Albert (2018) Arsenic and trace metals in three West African rivers: concentrations, partitioning, and distribution in particles-size fractions. Arch Environ Con Tox 75: 449-463. https://doi.org/10.1007/s00244-018-0543-9

Peng JF, Song YL, Yuan P, Cui XY, Qiu GL (2009) The remediation of heavy metals contaminated sediment. J Hazard Mater 161: 633-640. https://doi.org/10.1016/j.jhazmat.2008.04.061

Peter E, Adeniyi G (2011) Spatial relationships of urban land use, soils and heavy metal concentrations in Lagos Mainland Area. J App Sci Environ Manage 15(2) : 391-399.https://doi.org/10.4314/jasem.v15i2.68533

Rauch JN, Graedel TE (2007) Earth’s anthrobiogeochemical copper cycle. Global Biogeochem Cy 21:1-13. https://doi.org/10.1029/2006GB002850

Ríojas-Rodríguez H, Solís-Vivanco R, Schilmann A, Montes S, Rodríguez S (2010) Intellectual function in Mexican children living in a mining area and environmentally exposed to manganese. Environ Health Perspect 118 (10): 1465–1470. https://doi.org/10.1289/ehp.0901229

Rodgers K J, Hursthouse A, Cuthbert S (2015) The potential of sequential extraction in the characterisation and management of wastes from steel processing: a prospective review. Int J Environ Res Public Health 12(9): 11724-11755. https://doi.org/10.3390/ijerph120911724

Romanowicz-Makowska H, Forma E, Bryś M, Krąjewska WM, Smolarz B (2011) Concentration of cadmium, nickel and aluminium in female breast cancer. Pol J Pathol 62(4): 257-261.

Sako A, Semdé S, Wennenga U (2018) Geochemical evaluation of soil, surface water and groundwater around the Tongon gold mining area, northern Côte d’Ivoire, West Africa, J Afr Earth Sci 145: 297-316. https://doi.org/10.1016/j.jafrearsci.2018.05.016

Saleem M, Iqbal J, Akhter G, Shah MH (2018) Fractionation, bioavailability, contamination and environmental risk of heavy metals in the sediments from a freshwater reservoir, Pakistan. J Geochem Explor 184: 199-208. https://doi.org/10.1016/j.gexplo.2017.11.002

Saleem M, Iqbal J, Shah MH (2015) Geochemical speciation, anthropogenic contamination, risk assessment and source identification of selected metals in freshwater sediments—a case study from Mangla Lake, Pakistan. Environ Nanotechnol Monit Manage 4: 27-36. https://doi.org/10.1016/j.enmm.2015.02.002
Soliman NF, El Zokm GM, Okbah MA (2017) Risk assessment and chemical fractionation of selected elements in surface sediments from Lake Qarun, Egypt using modified BCR technique. Chemosphere, doi: 10.1016/j.chemosphere.2017.10.049.

Sun Z, Xie X, Wang P, Hu Y, Cheng H (2018) Heavy metal pollution caused by small-scale metal ore mining activities: A case study from a polymetallic mine in South China. Science of the Total Environment, 639, 217-227.

Sunkari ED, Appiah-Twum M, Lermi A (2019) Spatial distribution and trace element geochemistry of laterites in Kunche area: Implication for gold exploration targets in NW, Ghana. J Afr Earth Sci 158: 103519.

Taiwo AM, Awomeso JA (2017) Assessment of trace metal concentration and health risk of artisanal gold mining activities in Ijeshaland, Osun State Nigeria— Part 1. J Geochem Explor 177:1-10.

Toro PPV, Bedoya LFV, Correa ID, Franco GRB, Alcántara-Carrió J, Baena JAP (2016) Impact of terrestrial mining and intensive agriculture in pollution of estuarine surface sediments: spatial distribution of trace metals in the Gulf of Urabá, Columbia. Mar Pollut Bull 111(1-2): 311-320.

Touch N, Hibino T, Takata H, Yamaji S (2017) Loss on Ignition-Based Indices for Evaluating Organic Matter Characteristics of Littoral Sediments. Pedosphere 27(5): 978-984. https://doi.org/10.1016/S1002-0160 (17)60487-9

Traore I W, Houhamdi M (2017) Bioassessment of Artisanal Mining’s Impact on Bagoé River Water Quality in Sikasso Region. World J Environ Biosci 6(4): 7-14.

USEPA (2007). SW-846 Test Method 3051A: Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils. 1-30.

Varrica D, Tamburo E, Dongarrà G, Sposito F (2014) Trace elements in scalp hair of children chronically exposed to volcanic activity (Mt. Etna, Italy). Sci Total Environ. 470:117-126. https://doi.org/10.1016/j.scitotenv.2013.09.058

Wedepohl KH (1996) The composition of the continental crust. Geochim Cosmochim Ac 59(7): 1217-1232. https://doi.org/10.1016/0016-7037 (95)00038-2

Xiaomin C, Hongbing J, Wen Y, Baohu Z, Huaijian D (2016) Speciation and distribution of mercury in soils around gold mines located upstream of miyun reservoir, Beijing, China. J Geochem Explor 163:1-9.

https://doi.org/10.1016/j.gexplo.2016.01.015

Yapo R I, Mambo V, Alder AC, Ohou-Yao MJ, Libgan R, Dao D, Stamm C, Bonfoh B (2016) Caractérisation saisonnière des eaux de pruits à usage maraîchère et domestique de Korhogo (Côte d’Ivoire). Int J Biol Chem Sci 10(3): 1433-1449. https://doi.org/10.4314/ijbcs.v10i3.41

Yassir B, Alain P (2015) Speciation of four heavy metals in agricultural soils around DraaLasfarmine area in Marrakech (Morocco). Pollution 1(3): 257-264.

Zahra A, Hashmi MZ, Malik RN, Ahmed Z (2014) Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah - feeding tributary of the Rawal Lake Reservoir, Pakistan. Sci Total Environ 470: 925-933. https://doi.org/10.1016/j.scitotenv.2013.10.017

Zhang J, Liu CL (2002) Riverine composition and estuarine geochemistry of particulate metals in China: weathering features, anthropogenic impact and chemical fluxes. Estuar Coast Shelf Sci54: 1051–1070. https://doi.org/10.1006/ecss.2001.0879

Zheng J, Chen KH, Yan X, Chen SJ, Hu GC, Peng XW, Yang ZY (2013) Heavy metals in food, house dust, and water from an e-waste recycling area in South China and the potential risk to human health. Ecotox Environ Safe 96: 205-212. https://doi.org/10.1016/j.ecoenv.2013.06.017