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Evaluation of Metal Contamination of Sediments around an Industrial Gold Mine in Côte d'Ivoire: The Example of Arsenic

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ABSTRACT: The Tongon gold mine produces millions of tons of waste rock and tailings which are stored in dumps around the mine. This mine waste is contaminated with arsenic. Arsenic has acutely toxic effects on aquatic life within polluted areas. The potential for contamination of the area's aquatic environment is apparent. Therefore the objective of this paper was to evaluate the arsenic contamination of the sediments around the industrial gold mine in Côte d'Ivoire using inductively coupled plasma mass spectroscopy (NexION 2000 ICP-MS, USA) after aqua regia acid digestion. In addition, the metal contamination indices were used to evaluate the degree of arsenic contamination in the sediments. The obtained results indicated that the sediments in the industrial area of the Tongon gold mine have high arsenic concentrations in the proximity of pits and dumps. The geoaccumulation index ($-0.09 < I_{geo} < 2.20$) and the pollution load index (0.93) revealed that the sediment is moderately contaminated with arsenic. These findings suggest an ecological risk and therefore the need for environmental monitoring, supported by the elaboration of an effective remedial action strategy to minimize local pollution and contamination.

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The gold mining industry has been a major contributor to the country's economy for a long time (Kone *et al.*, 2019). However, people living in gold mining areas are frequently confronted with a number of health problems associated with toxic elements including heavy metals (Sako *et al.*, 2018)**.** The environmental contamination by heavy metals from gold mining areas has been identified as one of the most serious environmental problems in many countries. This is because the extraction, the processing of the mineral and the disposal of the mine tailings are the operations which cause the contamination of the environmental by the dispersion of heavy metals (Sako *et al.*, 2018). Because metal elements are stable in the environment, they are able to enter the living system via polluted water, soil and air. Thus, they can be accumulated in the living system over a long period of time and cause adverse effects on it (Kinimo *et al.*, 2018). In gold mining areas, arsenic is a frequently present metal (Kinimo *et al.*, 2018). Arsenic in mine wastes is accumulated in water and sediments and can be problematic for the health of people living near mining

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areas (Kinimo *et al.,* 2021)**.** Arsenic present in the aquatic environment penetrates the human body through the consumption of surface water and through dermal contact with water. In addition, it can bio-accumulate in the body and cause adverse health effects such as cancer (N'goran *et al.,* 2022). Most people in rural areas use surface water for daily needs and for drinking (Kone *et al.,* 2019). It is thus necessary to assess the heavy metal content in water and particularly in sediments in mining areas, as these have been shown to be the main reservoirs of these contaminants in the aquatic environment (Kouakou *et al.,* 2021). Therefore the objective of this paper was to evaluate the arsenic contamination of the sediments around the industrial gold mine in Côte d'Ivoire.

MATERIAL AND METHODS

Sediment sampling: The Tongon industrial mine is located in northern Côte d'Ivoire (N 9°57′- 5°76′ W 5°42′- 13°68′), approximately 628 km northeast of Abidjan, the economic capital. Sediment samples were collected using a hand drag in the area of the Tongon industrial mine and its surroundings to assess the lateral dispersion of mining-related contaminants. The location of the respective sampling sites is shown in Figure 1. The collected samples are packaged in plastic bags, labelled according to the collection site. The samples were stored in a cooler for transport to the laboratory where they were placed at (-4°C) in the freezer (Kouakou et al., 2016). After drying in an oven (60°C) for 24 hours, the sample was pre-sieved on a sieve to remove coarse elements such as pieces of shells, branches and leaves before being sieved through a sieve. Fractions smaller than 2 mm were kept in sealed plastic bottles to protect them from moisture and stored in a dark, cool (20°C) cabinet for analysis.

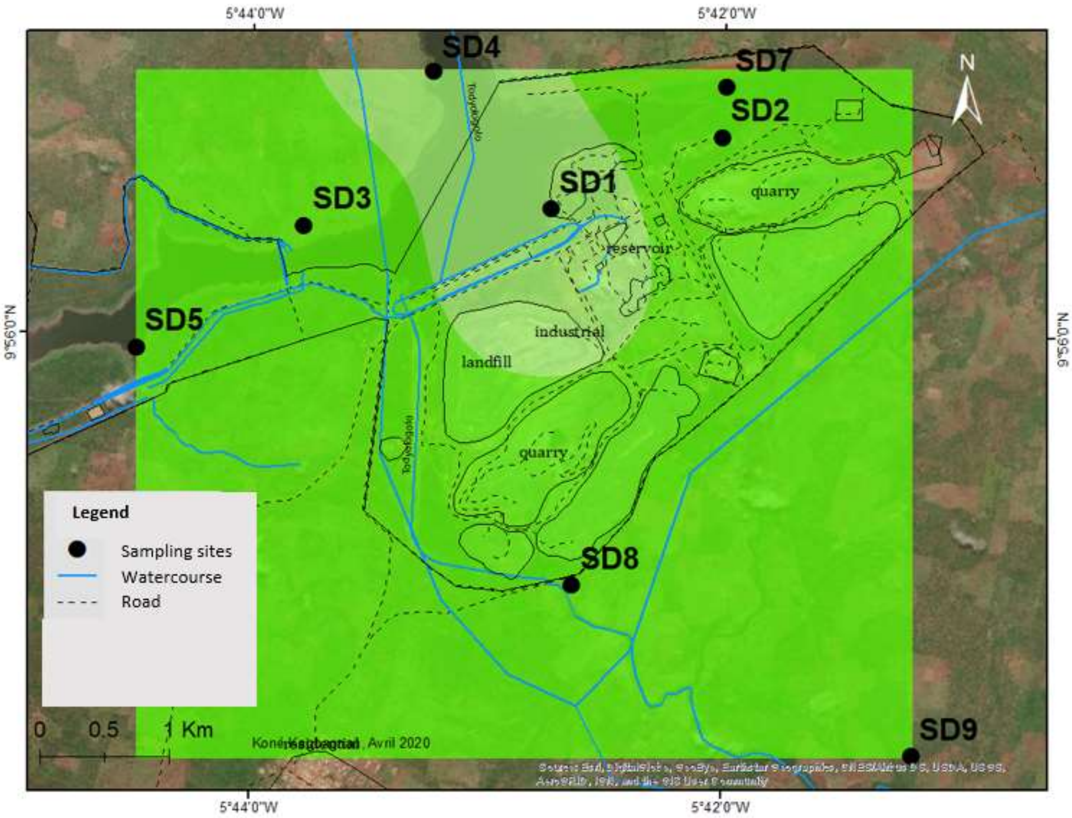

Fig 1: Sediment sampling sites

Determination of arsenic concentrations in sediment samples: The analyses for the determination of total arsenic concentration in the sediment samples required the synthesis of aqua regia. This aqua regia is synthesised from 65% pure concentrated nitric acid HNO_3 and 37% pure concentrated hydrochloric acid HCl at a 1/3 (v/v) ratio. A 48% pure concentrated hydrofluoric acid solution HF and a boric acid solution H_3BO_3 prepared from distilled water were also used for the determination of the total arsenic concentration. The sediments were mineralised using a reference method for marine pollution studies (Kouakou *et al.,* 2016). The principle of this method is based on the total dissolution of the sediments by hydrofluoric acid (HF) and aqua regia (HNO_3: HCl; 1:3, v/v) at high temperature. The use of HF is essential because it is the only acid that completely dissolves silicates and all metals (Kouakou *et al.,* 2016). 0.2 g of dry, homogeneous sediment or soil sample placed in a Teflon tube previously washed with acid underwent hot mineralisation using 1 mL of aqua regia (HNO_3 : HCl; 1:3, v/v) and 6 mL of concentrated HF (48%). Heating was carried out in a water bath at 120°C for 2 hours 30 minutes. After cooling in ambient air, the residue was taken up in a boric acid solution (2.70 g in 20 mL of distilled water). The final volume was reduced to 50 mL and left to stand for 6 hours. After the samples were concentrated and digested, the arsenic concentrations were determined by inductively coupled plasma mass spectroscopy (NexION 2000 ICP-MS, USA). The minimum detection limit (MDL) is 0.0005 mg/L for arsenic. Assessment of the level of metallic contamination of sediments. In this study, the metal concentration values of the upper continental crust (UCC) were used as reference values (Table 1) (Kouakou *et al.,* 2016)., because they were shown to be the most appropriate for the sediments of the Ivory Coast area (Kouakou *et al.,* 2016).

Table 1: Metal content of the upper continental crust (UCC)

Metal	As	Hg	Cr	Mn	Fe	Ni	Cd	Cu	Pb	Zn
Content (mg/kg)	2	0.056	35	527	30890	18.6	0.1	14.3	17	52

Geoaccumulation index: The geoaccumulation index ($I_{géo}$) is calculated from the following formula:

$$I_{géo}=\log_2\left(\frac{[\text{metal}]_s}{1,5\times[\text{metal}]_b}\right) \qquad (1)$$

Where $[\text{metal}]_s$ is the concentration of the metal in the sediment in mg/kg; $[\text{métal}]_b$ is the concentration of metal in UCC in mg/kg.

The geoaccumulation index establishes a relationship between the measured concentration of a metal in the fine fraction of sediments and the geochemical background concentration chosen as a reference for the metal under study, including a corrective factor (1.5) for lithological variations of the metal elements. I_{geo} values greater than 1 indicate moderate contamination of a sediment sample by the metal under study, while those greater than 3 indicate high contamination (Kouakou *et al.,* 2016). The I_{geo} values are used to define seven levels of contamination (Table 2).

Table 2: The different classes of sediment contamination

CF value	Levels of contamination
CF < 1	Low contamination
1 ≤ CF < 3	Moderate contamination
3 ≤ CF < 6	Considerable contamination
CF ≥ 6	Very strong contamination

Contamination Factor: The contamination factor (CF) is evaluated from the relationship 5:

$$CF=\frac{[As]_s}{[As]_b} \qquad (2)$$

Where: $[As]_s$ is the concentration of the metal in the sediment in mg/kg; $[As]_b$ is the concentration of the metal in UCC in mg/kg. The different levels of contamination according to the CF values are grouped in the table 3

Table 3: Contamination levels according to CF values

Class	Value	Levels of contamination
0	$I_{géo}$<0	Uncontaminated
1	0< $I_{géo}$<1	Uncontaminated to moderately contaminated
2	1< $I_{géo}$<2	Moderately contaminated
3	2< $I_{géo}$<3	Moderately to severely contaminated
4	3< $I_{géo}$<4	Severely contaminated
5	4< $I_{géo}$<5	Severely contaminated to extremely contaminated
6	5< $I_{géo}$	Extremely contaminated

Pollution Loading Index: Equation (6) was used to calculate the Pollution Loading Index (PLI). This index is calculated from the Contamination Factor (CF).

$$PLI=(CF_1\times CF_2\times CF_3\times\ldots\ldots\ldots\times CF_n)^{1/n} \qquad (3)$$

Where n is the number of sediments; CF is the contamination factor.

The pollution loading index gives cumulative information on metal pollution in soils or sediments. For PLI = 0, there is no deterioration; for PLI = 1, only baseline levels of pollutants are present, and PLI value > 1 indicates progressive deterioration of the sediments (Kouakou et al., 2016).

Environmental quality assessment of sediments: The approach based on the synthesis of SQG_S sediment quality guidelines (TEC-PEC) was used in this study to assess the risk of arsenic toxicity in sediments or soils in the study area. The threshold concentration (TEC) of arsenic (below which adverse effects are not likely to occur) is 9.79 mg/kg respectively. The probable effect level (PEL) (above which adverse effects are more likely to occur) is 33 mg/kg (Kouakou *et al.,* 2016).

Quality of the analyses: The quality of the analyses was controlled by using blanks and by performing duplicates. To prevent uncertain contamination, all laboratory equipment used was washed with phosphate-free soap, double rinsed with distilled water and soaked in 10% nitric acid for 24 hours. They were then rinsed twice with distilled water and dried at room temperature.

The limits of detection (LOD) for the elements were calculated as follows:

$$LOD = 3\times\frac{s}{m} \qquad (4)$$

Where "s" is the standard deviation of 10 blank measurements and "m" is the slope of the resulting calibration curve. The prepared blanks are analyzed at the same time as each batch of 10 samples.

Statistical methods and representations: Analysis of variance (one-way ANOVA) was used to assess the difference between the sampling sites. The difference was considered significant at $P < 0.05$. Whenever the difference was significant, Tukey's test was performed to identify groups that were particularly different from each other. The statistical analyses (mean value, minimum, maximum, standard deviation, analysis of variance and Pearson's correlation) were carried out with the STATISTICA 2005 software (version 7.1). Spatial distribution maps were produced using ArcGIS- 10.2. 2.

RESULTS AND DISCUSSION

Spatial distribution of arsenic concentrations in the sediments of the study area: Figure 2 and Figure 3 present the concentrations and spatial distribution of arsenic in the sediments of the Tongon industrial mine area respectively. The average arsenic concentrations in the sediments range from 1.227 ± 0.535 mg/Kg to 236.681 ± 85.063 mg/Kg (Figure 2). With the exception of sampling sites SD1, SD3 and SD8, a zone of high concentration was observed in the vicinity of the quarries, especially the northern quarry and the landfills, with a range of average concentrations between 9.8 and 236.67 mg/Kg (Figure 3). These mean concentrations are very high and well above the threshold effect concentration TEC (9.79 mg/kg) below which adverse effects are not likely to occur; and the probable effect concentration PEC (33 mg/kg) above which adverse effects are more likely to occur (Figure 2).

Table 4: Comparison of arsenic concentrations in the Tongon gold mine zone sediments with other zones in different gold mining operations.

Location	Bonikro gold mine (Côte d'Ivoire)	Agbaou gold mine (Côte d'Ivoire)	Afema Gold mine (Côte d'Ivoire)	Tongon gold mine (Côte d'Ivoire)
Arsenic concentration (mg/kg)	1,0 – 41,0	1,0 – 48,0	2,0 – 561,0	1,23 – 236,67
Reference	(Kinimo *et al.,* 2018).	(Kinimo *et al.,* 2018).	(Kinimo *et al.,* 2018).	the present study

Arsenic concentrations in the sediments from this study were compared with those from other areas of different gold mining operations in Côte d'Ivoire (Table 4).

The range of average arsenic concentrations obtained in this study is higher than those determined in the Bonikro and Agbaou mining areas. It is lower than that determined in the mining areas of Afema. This comparison shows that the Tongon gold mine area is one of the most arsenic contaminated gold mining areas. However, the arsenic concentrations in the sediments do not provide any information on the level of contamination. Therefore, in the following paragraph, the level of metallic contamination of the sediments is assessed.

Assessment of the level of arsenic contamination of sediments in the Tongon mine area: Geoaccumulation index : The geoaccumulation index ($I_{géo}$) takes into account natural fluctuations in metal concentration. Table 5 shows the geoaccumulation index values for sediments. For arsenic, the geoaccumulation index values range from -0.09 to 2.2. All these values indicate that the sediments belong to the Müller class of 0 to 3, highlighting their severe arsenic contamination in the vicinity of the northern quarry (SD2, SD7) and the sampling site SD5.

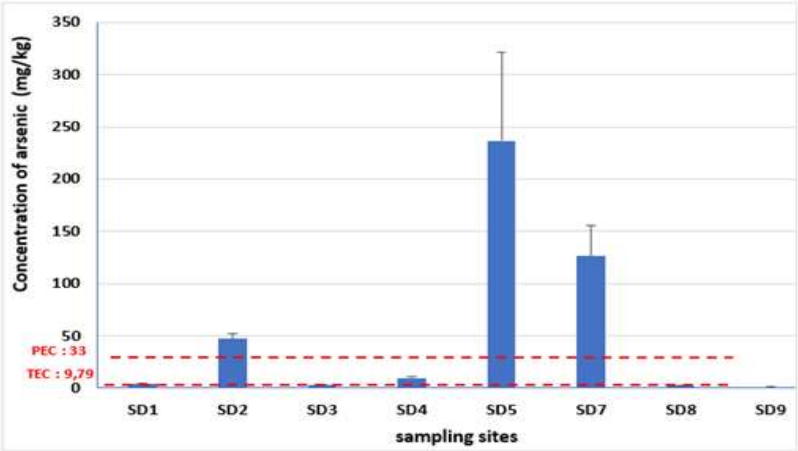

Fig 2: Concentrations of arsenic in sediments in the Tongon industrial mine area

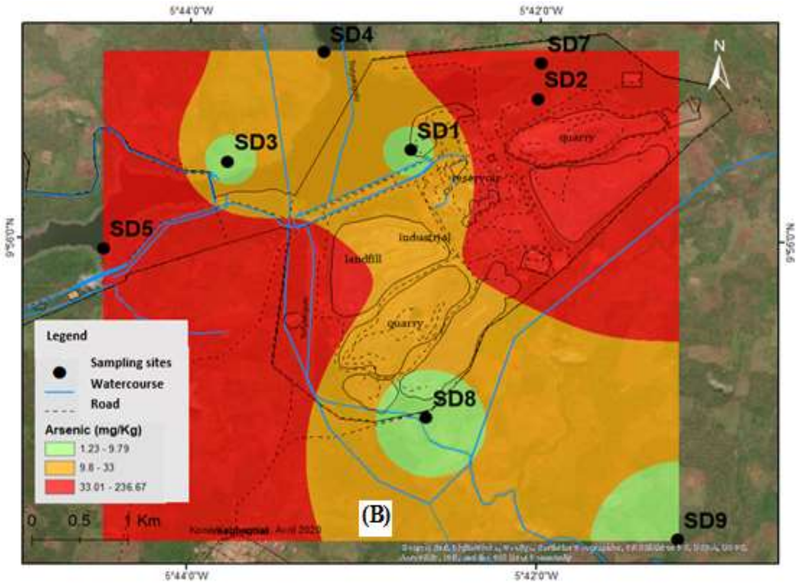

Fig 3: Spatial distribution (B) of arsenic in sediments in the Tongon industrial mine area

Table 5: Arsenic geoaccumulation index of sediments

SITE	SD1	SD2	SD3	SD4	SD5	SD7	SD8	SD9
$I_{géo}$	0,45	1,50	0,27	0,82	2,20	1,92	0,17	-0,09

Table 6: CF and sediment values

SITE	SD1	SD2	SD3	SD4	SD5	SD7	SD8	SD9
CF	2,14	2,78	0,17	0,59	13,92	7,42	0,13	0,07

Contamination factor and pollution loading index: Table 6 summarises the contamination factor (CF) values of the sediments and the pollution loading index (PLI) value. Different levels of contamination were observed depending on the sampling sites. For arsenic, the CF values range from 0.07 to 13.92. The values for sites SD3, SD4, SD8 and SD9 are lower than 1, indicating low arsenic contamination in the sediments. The values for sites SD1 and SD2 are between 1 and 3, indicating moderate arsenic contamination of the sediments. For sites SD5 and SD7, they are well above 6, indicating high arsenic contamination of sediments.

To assess the impact of mining activities on sediment quality, the pollution load index (PLI) was determined. The PLI value for all the sediments concerned is 0.93. This value is is nearly 1. This value indicates that the sediments in the Tongon mine area have a moderate arsenic pollution load. It should be remembered that the pollution load is due to the quantity of wastewater discharged, and therefore to anthropogenic activities. It should be noted that for efficient gold extraction, the Tongon mine uses sodium cyanide at a high pH (up to 10), obtained by adding lime to the cyanide solution. Thus, alkaline tailings sludge with a high heavy metal content is pumped into the tailings dam. In addition, the dissolution of solid waste by rainwater infiltrating the tailings is a potential source of many contaminants, including arsenic.

Conclusion: In this study an assessment of the level of arsenic contamination in sediments in the Tongon gold mine area was done. The sediments in the industrial zone of the Tongon gold mine had high arsenic concentrations in the vicinity of the quarries and dumps. The geo-accumulation index and the pollution loading index showed that the sediments are moderately contaminated with arsenic.

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