



RESEARCH ARTICLE

ASSESSMENT OF THE ENVIRONMENTAL IMPACT OF MERCURY AND CYANIDE IN ILLEGAL GOLD MINING IN DJEKANOU (CÔTE D'IVOIRE)

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ABSTRACT

Gold panning is an illicit gold mining activity that involves the uncontrolled use of toxic chemicals such as cyanide and mercury. The pollution generated by these two chemicals has negative repercussions on the environment and the health of populations living near illegal mining sites. The objective of this study is to assess the environmental impact of the use of mercury and cyanide in illegal gold panning in Djékanou. To this end, four (04) quarterly water, sediment, and soil sampling campaigns were conducted. The pH, temperature, electrical conductivity, and dissolved oxygen levels of the water were measured in situ. Mercury concentrations were determined in the water, sediment, and soil using atomic absorption spectrophotometry (AAS). Cyanide contents in different matrices were determined using a UV-visible photospectrometer (WFJ-752, China). Mercury and cyanide concentrations in surface water of the gold mining area range from 0.015 to 0.063 mg/L and from 0.04 to 0.08 mg/L, respectively. Mercury contents in sediments and soils range from 0.94 to 4.25 and from 0.96 to 4.71, respectively. As for cyanide, concentrations in sediments and soils range from 0.11 to 3.96 and from 0.96 to 4.71, respectively. The results obtained show that water, sediments and soils are contaminated by mercury and cyanide due to waste sludge released into the environment during ore washing. Mercury concentrations in water, sediments, and soils sometimes exceed WHO guideline values, thus constituting real sources of exposure for local populations and animal and plant species.

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INTRODUCTION

Illegal gold mining is a common problem in almost all gold-mining areas around the world. It is a largely informal activity carried out without planning, often using ancestral and rudimentary methods and tools (Jacques *et al.*, 2005). Long criticized for its devastating social and environmental impacts, illegal gold mining continues to spread throughout the world, especially in Africa. The expansion of this activity in West Africa is due to its financial source and, above all, the lack of employment for the working-age population (Joseph Bohbot, 2017). Illegal gold mining is a real scourge that the government is struggling to eradicate despite the adoption of the 2014 Mining Code, which regulates the prospecting, research, exploitation, possession, processing, transportation, and transformation of gold. Gold mining has been widely considered by governments and donors as a factor in

environmental degradation (deforestation, water and soil pollution) (Hilson, 2002). Physical degradation of the environment is observable on the sites due to the installation and activities of gold miners. The Djékanou department, located in central Côte d'Ivoire, is not immune to this scourge. The entire natural ecosystem is impacted, with its attendant consequences: the devastation of plantations, the discoloration and pollution of water bodies, and the destruction of habitats for terrestrial and aquatic wildlife.

Consequently, few surface waters are free from pollution linked to the exploitation of mining resources (Yapi *et al.*, 2014). To date, few studies have been conducted on the potential contamination of water and soil by mercury and cyanide used by gold miners in the Djékanou department. Therefore, this study aims to assess the environmental impact of the use of mercury and cyanide in illegal gold mining in Djékanou.

MATERIALS AND METHODS

Site description : The study area is located in Djékanou city (6°29'N, 5°07'N and 7°W, 6°W). Djékanou is located in central of Côte d'Ivoire, approximately 45 km from Yamoussoukro.

Water, sediment and soil sampling: Four sampling campaigns were conducted, one per quarter. Water, sediment, and soil samples were collected from three gold mining sites: Yobouekro (Site 1), Taffissou (Site 2), and Groudji (Site 3). For each matrix (water, sediment, and soil), nine (9) samples were collected per campaign, for a total of 36 samples per matrix for the four campaigns. For the water sampling, a Niskin bottle was armed and its bait was lowered into the water to 0.5m. The water sampled was poured into polyethylene bottles of 1L volume each. Each bottle was first rinsed twice with the water to be analyzed to ensure its consistent characteristics. The water-filled bottle was immediately closed and stored in a cool, dark place (4°C) in a cooler to prevent any potential photochemical reaction. For water intended for cyanide analysis, 1 mL of a NaOH solution with a concentration of $C_b = 10 \text{ mol/L}$ was added to each 1L sample box to bring the pH of the final solution to 12 or at least above 11 to prevent HCN loss through volatilization and biological degradation. This allowed the cyanide to be preserved in the CN⁻ form until analysis. The sediment samples were collected in polyethylene bottles using a Van Veen bucket. Regarding soil samples, homogeneous 20 cm soil cores were randomly collected using a hand auger and stored in soil bags. All sediment and soil samples were kept cool (4°C) in a cooler before being transported to the laboratory for analysis as soon as possible.

Water analysis

In Situ measurements : pH, water temperature, dissolved oxygen level, and electrical conductivity were measured using a LOVIBON SENSO-DIRECT 150 multi-parameter meter.

Suspended Solids (SS) measurement : To measure suspended solids (SS), the filter disc filtration method (AFNOR NF T 90-105) was used. A volume $V = 10 \text{ mL}$ of water sample was collected and filtered through 0.45 μm Whatman filter paper. Before filtration, the empty mass of the filter, i.e., **M1**, was determined after passing through a desiccator (muffle furnace at 105°C) for two (2) hours and weighed after cooling. After passing the sample through the filter, the assembly undergoes the same operating procedure as the vacuum filter. Let **M2** be its mass. The MES are obtained by the formula given by the following equation:

$$\text{MES (g/L)} = \frac{M2 - M1}{V}$$

M1: mass of the filter before filtration (mg),

M2: mass after passage of the sample on the filter and drying (mg),

V: volume of the filtered sample (mL).

Turbidity measurement (NTU): Turbidity was determined turbidimetrically using a HACHLANGE 2100Q turbidimeter $\pm 2\%$. After homogenizing the sample to be analyzed, a volume V of the sample was transferred to a cell up to the gauge line and then hermetically sealed. This cell was placed in a turbidimeter to measure the concentration of suspended particles in the sample to be analyzed. A turbidimeter measures

suspended particles with a light beam (beam source) and a light detector set at 90° to the original beam. Particle density is a function of the light reflected by the suspended particles in the detector.

Mercury measurement in water : The water samples were filtered and then measured using a VARIAN AA240FS flame atomic absorption spectrometer coupled with a VARIAN EL0608 hydride furnace in accordance with standard NF EN 1483.

Cyanide measurement in water: Cyanide analysis in water samples was performed by the pyridine-pyrazalone method, using HACH cyanide powder reagents in sealed sachets (100 tests). A 10 mL volume of filtered water sample underwent complexation steps using cyanide reagents 3, 4, and 5 (cyaniver 3, cyaniver 4, and cyaniver5). First, one sachet of cyaniver 3 was added to 10 mL of filtrate collected in a test tube. The tube was covered with Parafilm, shaken vigorously by hand for 30 seconds, and allowed to stand for 30 seconds. Next, the contents of cyanide 4 were added and shaken for 10 seconds, and finally, the contents of cyanide 5 were added to the mixture and shaken again for 10 seconds. The mixture was allowed to stand for 30 minutes, during which time a blue color appeared, indicating cyanide complexation. The same procedure was used with distilled water as a control sample. Optical densities (absorbances) were measured at 612 nm using a UV-visible photospectrometer (WFJ-752, China). The various concentrations were determined using the calibration curve generated with a potassium cyanide solution in distilled water.

Sediment and soil analysis

Mercury measurement in soil and sediment samples: The sediment and soil samples were air-dried in the laboratory, then finely ground before being dissolved in hydrofluoric and perchloric acid according to the NF X 31-147 standard. The principle of the digestion method is based on the decomposition of sediments and soils using hydrofluoric acid (HF) in combination with aqua regia ($\text{HNO}_3:\text{HCl}$; 1:3, v/v) under hot conditions. The use of HF is essential because it completely dissolves silicate lattices and all metals (UNEP, 2007). For each sample of sediment or soil, 0.1 g of ground material was weighed and placed in Teflon boxes or bombs, then 1 mL of aqua regia (HNO_3 , HCl , 1.3 v/v) and 6 mL of hydrofluoric acid (HF) were slowly added to each bomb. The bombs were first tightly sealed using a twisting torque and then left to stand for one (1) hour under a fume hood. Then, they were placed in a water bath for 2 h 30 min at 120°C. During this time, 2.7 g of boric acid were weighed into 50 mL propylene tubes to which 20 mL of distilled water was added and then homogenized. Once the bombs were removed from the water bath, they were first allowed to cool to room temperature for 3 hours. They were opened to transfer the contents into 50 mL propylene tubes containing the previously prepared boric acid solution. Finally, the bombs were rinsed with distilled water and then added to the propylene tubes until the volume reached the mark (50 mL). After solution, the samples were filtered through Whatman filter paper (porosity 0.45 μm). The collected filtrates were placed in 100 mL flasks and then filled to the mark with distilled water. The filtered samples were analyzed using VARIAN AA240FS flame atomic absorption spectrometry coupled with a VARIAN EL0608 hydride furnace in accordance with standard NF EN 1483.



Figure 1. Map of the study area

Table 1. *In situ* measurements of the physicochemical parameters of the water

	Sites				
Parameters	Yobouékro (n=36)	Taffissou (n=36)	Groudji (n=36)	WGVDW	WGVWAF
Chemical parameters					
pH	6,65±0,11	6,66±0,07	6,61±0,09	6,5 - 9,5	pH > 5
Temperature T(°C)	29,33±0,47	29,05±0,36	29,34±0,31	T > 30°C	T > 20°C
Turbidity (NTU)	77,972±5,538	70,706±1,242	72,1 ±1,16	0,5	nd
Electrical conductivity (µS/cm)	72,1±34,267	103,36±11,33	94,52±14	< 2500	nd
Dissolved oxygen (mg/L)	3,98±0,60	3,981±0,52	3,85±0,48	9	> 5
Physical parameters					
Suspended matter (MES) (mg/L)	49,33±5,70	45,75±3,58	59,36±4,7	0,5	nd
Ammonium (NH ₄ ⁺) (mg/L)	0,05±0,02	0,059±0,02	0,14±0,12	0,2	< 0,2
Nitrites (NO ₂ ⁻) (mg/L)	0,006±0,002	0,006±0,002	0,003±0,001	3	< 0,5
Nitrates (NO ₃ ⁻) (mg/L)	4,24±1,3	3,69±0,80	4,04±0,59	50	nd
Orthophosphates (PO ₄ ³⁻) (mg/L)	0,544±0,121	0,548±0,094	0,565±0,048	0,05	< 0,5

WGVDW: WHO (2017) Guideline Value for Drinking Water; WGVWAF: WHO (2017) Guideline Value for Water for Aquaculture and Fish farming; nd: not determined; n: number of samples

Table 2. Mercury and cyanide concentrations (mg/L) in water

Chemical parameters	Sites			VGEP	WGVWAF
	Yobouékro (n=36)	Taffissou (n=36)	Groudji (n=36)		
Hg (mg/L)	0,063±0,097	0,005±0,003	0,015±0,011	0,006	nd
CN ⁻ (mg/L)	0,08±0,02	0,04±0,01	0,07±0,04	0,03	0,05

WGVDW: WHO (2017) Guideline Value for Drinking Water; WGVWAF: WHO (2017) Guideline Value for Water for Aquaculture and Fish farming; nd: not determined; n: number of samples

Table 3. Mercury and cyanide concentrations (mg.kg⁻¹) in sediments

	Sites				
Chemical parameters	Yobouékro (n=36)	Taffissou (n=36)	Groudji (n=36)	ACEC	PSRV
Hg	4,25 ± 1,53	3,95 ± 1,03	2,15 ± 0,14	0,02-0,1	3,5
CN ⁻	0,11 ± 0,10	3,96 ± 1,16	1,06 ± 0,13	nd	nd

ACEC: Average Concentration (mg.Kg⁻¹) of TMEs in the Earth's Crust (Baize, 1997); PSRV: Pollution Source Reference Values; nd: not determined, n: number of samples

Table 4: Mercury and cyanide concentrations (mg.kg⁻¹) in soils.

	Sites				
Chemical parameters	Yobouékro (n=36)	Taffissou (n=36)	Groudji (n=36)	ACEC	PSRV
Hg	4,71 ± 2,21	3,86 ± 1,62	1,61 ± 0,97		3,5
CN ⁻	0,48 ± 0,16	3,34 ± 1,23	1,65 ± 1,03	nd	nd

ACEC: Average Concentration (mg.Kg⁻¹) of ETM in the Earth's Crust (Baize, 1997); PSRV: Pollution Source Reference Values; nd: not determined, n: number of samples; n: number of samples

Cyanide measurement in soil and sediment samples: 40 g of sample, previously dried at 60°C and ground, was placed in a Teflon bottle. Distilled water at pH 7 was added to obtain a solid:liquid ratio of 1:4 (e.g., 40 g of solid and 160 mL of water). The bottle was capped and placed on a leaching apparatus. It was shaken for 7 days ± 2 hours at a rotation speed of approximately 30 ± 2 rpm. The sample was filtered through a 0.45 µm membrane. The pyridine-pyrazalone method was used to determine the various cyanide contents in soil and sediment samples, using HACH cyanide powder reagents in sealed sachets (100 tests). A 10 mL volume of filtered water sample underwent complexation steps using cyanide reagents 3, 4 and 5 (cyaniver 3, cyaniver 4 and cyaniver 5). First, one sachet of cyaniver 3 was added to 10 mL of filtrate collected in a test tube. The tube was covered with Parafilm, shaken vigorously by hand for 30 seconds and let stand for 30 seconds. Next, the contents of cyanide 4 were added and stirred for 10 seconds, and finally, the contents of cyanide 5 were added to the mixture and stirred again for 10 seconds. The mixture was allowed to stand for 30 minutes, during which time a blue color appeared, indicating cyanide complexation. The same procedure was used with distilled water as a control sample. Optical densities (absorbances) were measured at 612 nm using a UV-visible photospectrometer (WFJ-752, China). The various concentrations were determined using the calibration curve generated with a solution of potassium cyanide in distilled water.

RESULTS AND DISCUSSION

RESULTS

Physicochemical analysis of surface water from the Djékanou gold mining area

The results of the analysis of the physicochemical parameters of the water are presented in Table 1. The concentrations obtained were compared to the WHO Drinking Water Guidelines (WWG) (2017) and the WHO Aquaculture and Fish Farming Guidelines (AWFG) (2017) to ensure the suitability of these waters for domestic, agricultural, and fish farming purposes. The pH values of the resulting waters range from 6.50 to 6.80. These acidic waters, which tend toward neutrality, represent no danger for consumption or use in aquaculture and fish farming. Dissolved oxygen values range from 3.28 to 4.85 mg/L. They are less than 5 mg/L, making them unsuitable for consumption, aquaculture, and fish farming. The turbidity of the waters ranges from 66 to 83.4

NTU. These values are well above the WHO (2017) drinking water guideline value of 0.5 NTU. These waters are therefore unsuitable for drinking or domestic use. Turbidity in waterways is generally caused by suspended solids and colloidal particles that absorb, scatter, or reflect light. Phosphate levels range from 0.27 to 0.67 mg/L. Some recorded concentrations are higher than the phosphate guideline value recommended by the WHO (2017) for drinking water and water for aquaculture and fish farming, which is less than 0.5 mg/L. These waters are therefore unsuitable for consumption and for fish farming. The waters have ammonium concentrations ranging from 0.015 to 0.29 mg/L. These values are higher than the WHO guideline values for drinking water and water intended for fish farming and aquaculture, which are 0.2 mg/L, respectively. Thus, the ammonium concentrations in these waters could constitute a nuisance for human consumption, aquaculture, and fish farming. However, these waters could be used for irrigating market gardening and rice crops because nitrogen is an essential nutrient for plant life. Suspended solids (SS), which consist of all non-sedimented solids discharged into the receiving waters and consist of organic debris, clays, and microscopic organisms, have values ranging from 40 to 65 mg/L.

These relatively low values indicate water with a low SS content. The concentrations obtained were compared with the WHO (2017) guide values for water in order to consider the possibilities of using these waters for domestic, agricultural and fish farming purposes. Mercury concentrations in surface water in the gold mining area range from 0.015 to 0.063 mg/L. These concentrations are higher than the WHO guideline value for drinking water, which is 0.006 mg/L. These mercury concentrations in water are unacceptable for any domestic use. However, in Taffissou, the concentrations obtained are relatively lower than the WHO guideline values. Cyanide levels in the water range from 0.04 to 0.08 mg/L. These concentrations are higher than the WHO guideline values for drinking water, which is 0.03 mg/L, and for water intended for aquaculture and fish farming, which is 0.05 mg/L. These cyanide concentrations in water can pose a risk for any domestic or fish farming use. Furthermore, the Groudji site is less affected by ETM and cyanide compared to the Yobouékro and Taffissou sites. Table 3 presents the results of mercury and cyanide analyses in the sediments. The results show that the samples collected in the study area are affected by existing anthropogenic activities. Indeed, this pollution is more noticeable with mercury and cyanide due to their significant involvement in gold mining.

Mercury and cyanide levels in soils at the Djékanou gold mining sites: Table 4 presents the results of mercury and cyanide analyses in the soils. The mercury levels in soil samples collected in Yobouékro and Taffissou are higher than the average concentration of each trace metal element in the Earth's crust (CMCT). The mercury concentration in the soils is higher than the reference pollution source value (VRSP) due to their heavy involvement in gold mining. However, in Grouji, the mercury concentration is lower than the Reference Pollution Source Values (VRSP).

DISCUSSION

The Grouji site is minimally affected by mercury and cyanide because semi-industrial mining companies are located on the Grouji village sites. To this end, mining administration officials regularly patrol the sites alongside law enforcement officers to prevent the recolonization of these sites by illegal gold miners. However, the Yobouékro and Taffissou sites where no legal mining companies are located, are polluted by mercury and cyanide. Mercury concentrations in sediments and soils are higher than the average concentration of each trace metal in the Earth's crust (ACEC). This is consistent with the results of other authors who have shown that gold mining activities are highly polluting and are potential sources of toxic trace metals (Jung, 2001; Navarro *et al.*, 2008).

Chemicals used in gold panning can cause the disappearance of certain animal and/or plant species and consequently lead to the malfunctioning of the trophic chain (Gold, 2002). Regarding mercury (Hg) in particular, small-scale artisanal gold mining using mercury smelting for gold recovery has been identified as one of the largest contributors to mercury pollution, contaminating the atmosphere, water and people (Niane *et al.*, 2019). Indeed, mercury forms alloys called amalgams with other metals such as gold, silver and tin, hence its use in the mining and metallurgical industries. This method is used by communities practicing gold panning because it is less expensive and is within the reach of a single operator. The uncontrolled disposal of waste from mercury use is the source of mercury pollution in the environment. Therefore, its use has negative impacts on the environment, the population and human health.

Furthermore, in aquatic environments, mercury undergoes transformations under the action of microorganisms to produce organic compounds such as methylmercury (MeHg), which is more toxic than mercury (Risher *et al.*, 2002). Methylmercury is absorbed by most biological organisms. It thus accumulates in certain aquatic organisms and ends up in the food chain via predatory fish. The cyanidation method used in Djékanou is the same as that practiced in Burkina Faso. It consists of extracting gold from ores in basins using a cyanide solution accompanied by sulfuric and nitric acid and then zinc shavings. Given its gold precipitation characteristics and its high recovery rate from other ores, cyanide remains a chemical product that can be used on a large scale. Indeed, the discharge of cyanide into nature leads to the death and poisoning of a large part of the aquatic life in rivers as well as the predators that depend on them and makes the water unfit for consumption. The limit concentration of cyanide in the aquatic environment is approximately 5 µg/L. At this concentration, the metabolism of living species in the water is inhibited (Logsdon *et al.*, 1999).

CONCLUSION

Gold panning is a lucrative activity that employs young people of working age, thus reducing the unemployment rate. However, this activity has disastrous environmental and health consequences due to the degradation of water and soil quality. The results of analyses revealed the contamination of the Djékanou gold panning area by mercury and cyanide, two dangerous chemicals used by illegal gold miners to extract gold from ores. In addition to the elemental mercury used to form the gold-mercury alloy (amalgam), the population is potentially exposed to methylmercury through the consumption of aquatic species contaminated by mercury discharges. Furthermore, the mercury concentrations, sometimes higher than WHO guideline values, in the sediments of the Djékanou gold panning sites constitute real sources of exposure for local populations and the species that live there. Furthermore, the possibility of accumulation of mercury and cyanide along the food chain in aquatic organisms, plants, animals and humans is to be feared, due to the bioaccumulative capacities of these elements. Measures should be taken by the authorities and the population to resolve this environmental problem linked to illegal gold mining.

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