

# Assessment of Health Risks Related to Contamination of Groundwater by Trace Metal Elements (Hg, Pb, Cd, As and Fe) in the Department of Zouan-Hounien (West Côte d'Ivoire)

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## Abstract

In the department of Zouan-Hounien, gold mining is booming. This activity, marked by the excavation of rocks and the use of chemicals such as mercury, is likely to contaminate the region's groundwater resources and expose populations to serious diseases. This study aims to assess the health risks associated with the consumption of this water by the population. To this end, 72 groundwater samples were taken in eight (08) villages of the department at the rate of forty-six (46) well water samples and twenty-six (26) borehole water samples. A total of twenty-two wells and thirteen boreholes were sampled during two campaigns. An atomic absorption spectrometer (AAS) was used to determine the concentrations of metallic trace elements (MTEs), such as mercury (Hg), lead (Pb), cadmium (Cd), Arsenic (As), and iron (Fe) in the different samples. The daily exposure doses for oral ingestion (CDI<sub>ing</sub>) and skin contact (Exp<sub>derm</sub>) were calculated. The non-carcinogenic (HQ) and carcinogenic risks (CR) were estimated. The results show that the mean concentrations of Fe, Pb, Hg, As and Cd are respectively  $2233.48 > 3.10 > 0.60 > 1.18 > 0.08 \mu\text{g}\cdot\text{L}^{-1}$  in the wells and  $2427.94 > 4.08 > 1.27 > 1.76 > 0.08 \mu\text{g}\cdot\text{L}^{-1}$  in boreholes. Evaluating the risks to human health reveals that the mean values of hazard quotient (HQ) and cancer risk (CR) for all the elements in the wells and boreholes are lower than 1 and  $10^{-4}$  respectively in children and adults for oral and dermal exposure. However, at the oral exposure level, 9 wells and 6 boreholes recorded HQ and CR above the defined critical limits. These values indicate that the occurrence of non-cancerous and cancerous diseases in

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populations consuming these waters by contamination with mercury and arsenic is not excluded. Dermal exposure to MTEs also poses no potential health risk to the population.

## Keywords

Groundwater, MTEs, Health Risks, Contamination, Zouan-Hounien

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## 1. Introduction

As a vital component of the environment and water resource systems, groundwater is important for the global hydrological cycle and water supply (Lou et al., 2016). In Côte d'Ivoire, groundwater is the main source of drinking water for the population. Unfortunately, groundwater quantity is very low due to the crystalline and crystallophyllized soils that occupy most (97.5%) of the Ivorian territory (Ahoussi et al., 2012). And yet, groundwater contamination has become one of the most important environmental problems today (Lou et al., 2016; Qu et al., 2018). Among the great diversity of contaminants affecting water resources, metallic trace elements are of particular concern due to their high toxicity even at low concentrations in the environment (Marcovecchio et al., 2007). They are classified as environmental pollutants because of their toxic effects on plants, animals, and humans (Lou et al., 2016). Metallic trace elements (MTEs) are substances naturally present in water (minerals eroded from sediments, leaching from ore deposits, and extruded products of volcanism). However, some anthropogenic activities such as mining, agriculture, waste dumps, domestic discharges, etc., can locally increase their concentrations in groundwater. Moreover, they are non-degradable in the water table to be enriched via the food chain, from low to high levels of organisms (Prasad et al., 2014). Such enrichment leads to an accumulation of MTEs in the human body, causing chronic poisoning and threatening human health or even life (Sobhanardakani, 2018). Trace elements are considered to be systemic toxic substances that can lead to multi-organ damage, as well as teratogenic and carcinogenic effects (Qu et al., 2018). Long-term or chronic exposure to trace elements can pose serious threats to health, such as permanent intellectual and developmental impairments, behavioral problems, hearing loss, disturbance of visual and motor function, pulmonary fibrosis, cardiovascular and renal diseases, abdominal pain, hypertension, liver disorders, irregular blood composition, anorexia (Tchounwou et al., 2012; Al-Khatib et al., 2019). Several studies (Sarkar, 2002; Masok et al., 2017; Al-Khatib et al., 2019) have also shown that exposure to MTEs is involved in degenerative physical, muscular and neurological processes that can develop into Alzheimer's disease, Parkinson's disease (progressive loss of neurons). Arsenic (As), a metalloid, and certain trace elements (Hg, Pb, Cd, and Cr) are considered known or probable carcinogens (Al-Khatib et al., 2019).

The department of Zouan-Hounien, located in western Côte d'Ivoire, about

680 km from the city of Abidjan, is marked by intense mining activities (modern and traditional).

However, gold panning activities are carried out in some villages and even near some water points. This is likely to lead to contamination of groundwater by metallic trace elements through infiltration and atmospheric deposits. Water from wells and boreholes is the only source of supply for the population of the different localities for their domestic needs (cooking, washing up, laundry, bathing, etc.).

Consequently, dermal and oral exposure to MTEs is the main probable routes for human exposure to these substances in the area. Work was undertaken by (Gbamélé et al., 2020) in the area that found concentrations of Pb, As, Cd, and Fe above the (WHO, 2017) recommended threshold limit in some wells. At low concentrations, MTEs in groundwater can pose serious dangers to the population consuming them over the long term. However, the health risk assessment was not taken into account by (Gbamélé et al., 2020), despite the high concentrations of MTEs found in some places. They were limited to the dosage of MTEs in the water and their probable sources. Above all, As and Cd are known to be responsible for various types of cancer following excessive consumption of contaminated water. Therefore, the consumption of contaminated water causes a serious risk to human life. This has led to the conduct of this study which aims to assess the health risks linked to the consumption of this water by the population. Five (05) MTEs were taken into account in this study. These are mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As), and iron (Fe).

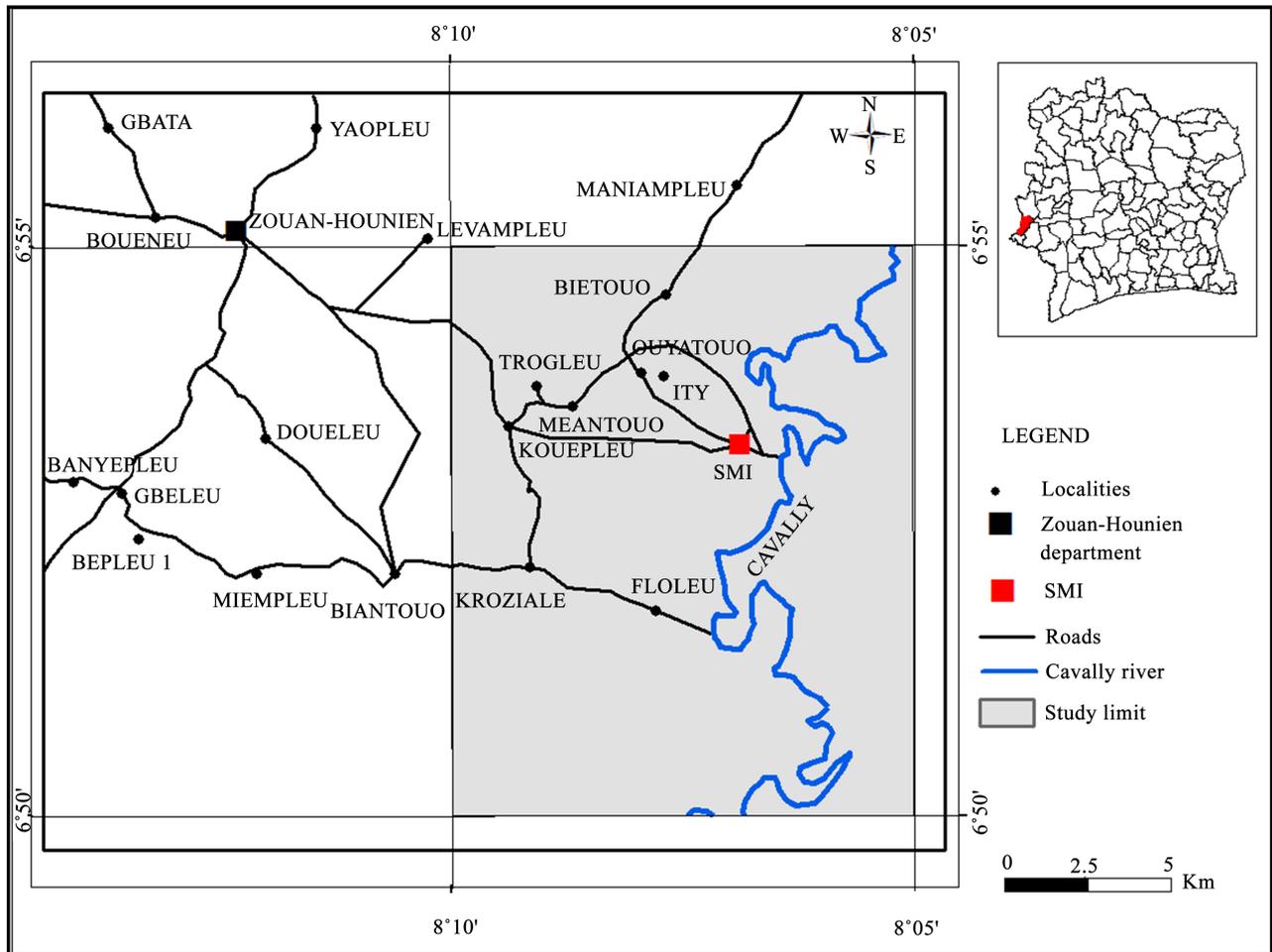
## 2. Material and Method

### 2.1. Presentation of the Study Area

Located in the west of Côte d'Ivoire, more precisely in the department of Zouan-Hounien, between latitudes 06°50' and 06°55' North and longitudes 08°05' and 08°10' West (Figure 1), it contains eight (8) villages bordering the Ity mining company (SMI). They are Kouèpleu, Trogleu, Méantouo, Ouyatouo, Ity, Krozialé, Floleu and Biétouo. These villages have the main players of mining and, for some of them, mining activities. The study area is under the mountain climate, which includes two main seasons, one rainy and one dry. The rainy season extends from May to October and the dry season from November to March (Brou et al., 2017). Annual rainfall averages 1866 mm, with an average annual temperature in Zouan-Hounien of 25.6°C. This zone is characterized by ferritic soils formed on the amphibole substratum (Dabin et al., 1960; Naho, 1988). The geological formations of the department of Zouan-Hounien are composed of ortho-amphibolites, amphibolite schists, sericite tuffs and quartzites and rare corneal and skarn histories (Naho, 1988; Ettien, 2005).

### 2.2. Sampling Campaign

Groundwater samples were taken from twenty-three (23) farmers' wells and



**Figure 1.** The geographical location of the study area (Ettien, 2010).

thirteen (13) boreholes during two sampling campaigns in eight villages bordering the Mining company of Ity (SMI) (Figure 2). The first campaign took place in March, during the dry period, and the second in October, during the rainy season of 2018. Water samples were taken using a water dipper and collected in polyethylene bottles with a volume of 250 ml. For boreholes equipped with a hand pump, water samples were taken directly from the pump after emptying the water remaining in the bladders. Before filling, the bottles were rinsed several times with the water to be analyzed, filled to the brim, and sealed tightly to avoid any air bubbles. The samples were acidified with ultrapure 6M nitric acid (HNO<sub>3</sub>) at pH ≤ 2.

All these samples were kept in coolers and then sent to the Central Laboratory for Food Hygiene and Agro-industry (LCHAI) of the National Laboratory for Support to Agricultural Development (LANADA) for various analyses. The mercury was determined by the method of flameless Atomic Absorption Spectrometry according to the NF T90-113 (1986) standard. As for the other MTEs, they were determined by the Flame Atomic Absorption Spectrometry method according to the NF T90-112 (1986) standard (AFNOR, 2008a).

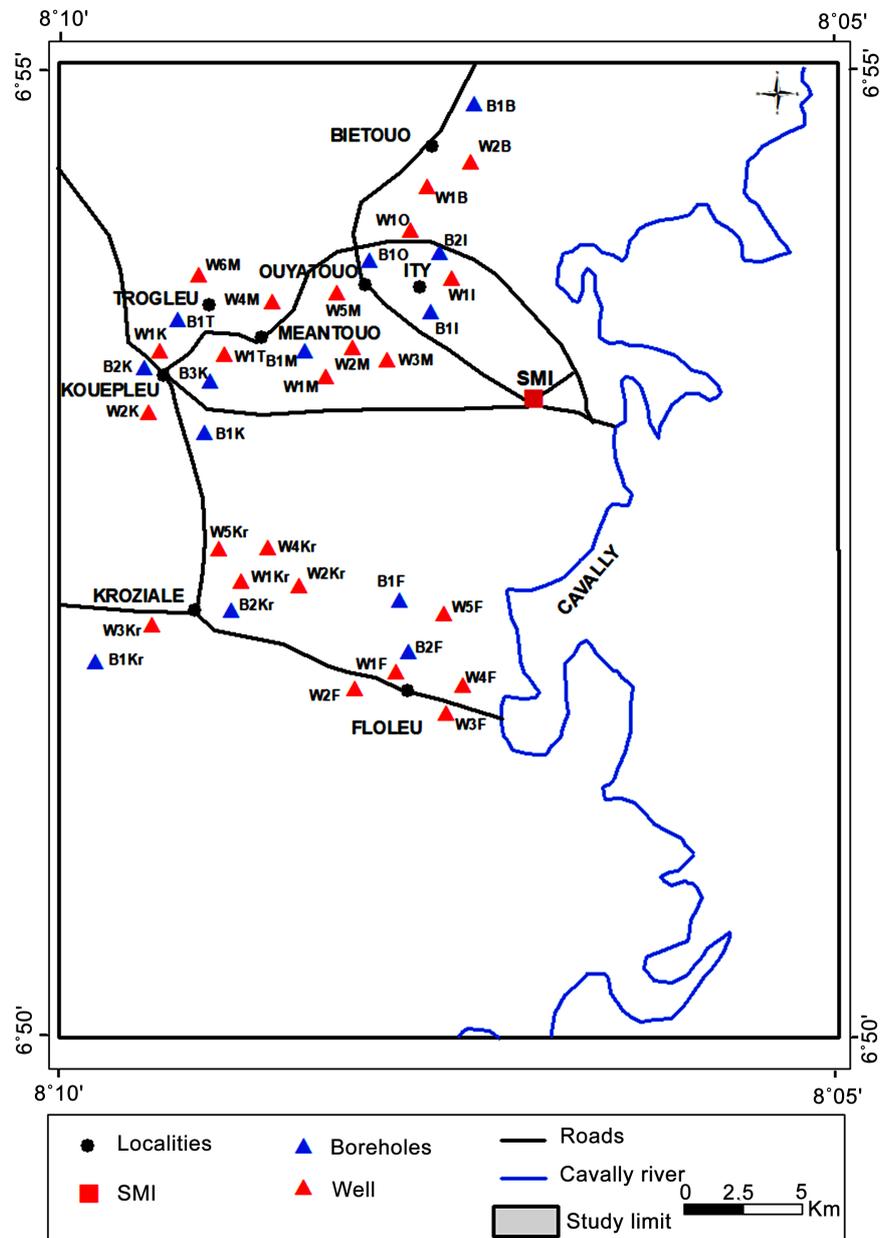


Figure 2. Groundwater sampling map in the study area.

### 2.3. Human Health Risk Assessment

Health risk assessment is a method developed by the National Research Council of Canada (NRC). It is defined as the probability of an incident or adverse health effects from exposure of humans or other animals to environmental hazards (Liang et al., 2017; Al-Khatib et al., 2019). The method contains four main steps: 1) Hazard identification; 2) Dose-response assessment; 3) Population exposure assessment; 4) Risk characterization (NRC, 1983). Hazard identification is selecting substances that should be considered in the assessment study and identifying health effects that may be derived from them (INERIS, 2009). The evaluation of the dose-response relationship makes it possible to establish the rela-

tionship between the quantity of chemical pollutants and possible undesirable effects. Exposure assessment determines the pathways of the test substance from the source to the human receptor and estimates the frequency, duration, and magnitude of exposure (Wang et al., 2017; Gbogbo et al., 2018; Shil & Singh, 2019). Risk characterization involves cancer risks or not in different populations (Obiri et al., 2016). The methods proposed for estimating the health risks associated with the five trace elements have been divided into non-carcinogenic and carcinogenic substances.

The assessment of health risks related to MTEs in well and borehole water used for consumption was carried out orally and dermally in adults and children based on the risk assessment methodology of the U.S. Environmental Protection (Agency, 2004). Based on this theory, the human health risk assessment equations were calculated, using the simplified formula of (Tanouayi et al., 2015) for oral water exposure and the (USEPA, 2004) for dermal exposure.

### 2.3.1. Hazard Identification

The substances considered in the risk assessment are Hg, Pb, Cd, As, and Fe. The choice of these substances is because mercury is the main substance used in extraction processes. Lead, Cadmium, and Arsenic are elements commonly associated with gold deposits. Besides, due to their high degree of toxicity, mercury, lead, cadmium, and arsenic are among the priority trace elements of importance for public health and pollution control (Tchounwou et al., 2012; Fu et al., 2017). Iron is a very abundant element in the subsoils of the area. It is essential for life but toxic in high doses.

### 2.3.2. Evaluation of the Dose-Response Relationship

This second step allows establishing reference doses (RfD) or toxicological reference values (TRV). These values reflect the relationship between the admissible dose of the toxic substance and the occurrence or severity of the effect studied in the population. They are values above which concentrations of certain substances could have adverse health effects. Here, RfD is for threshold chemical effects. Reference dose values for oral and dermal exposure are given in **Table 1**.

**Table 1.** RfD values for both routes of exposure.

MTE	RfD ( $\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$ )		Sources
	Oral	Dermal	
Hg	0.1	0.3	
Cd	0.5	0.5	(INERIS, 2009;
Pb	3.5	0.52	Johnbull et al., 2019;
As	0.3	0.3	Masok et al., 2017;
Fe	700	140	Shil & Singh, 2019)

### 2.3.3. Exposure Assessment (CDI)

This step consists of determining the doses of the substances that met or entered the body. The exposure scenario implemented in this study concerns eight villages without taps, whose populations only use water from wells and boreholes for their daily needs. Thus, two main routes of exposure were considered in this study. Oral ingestion and dermal contact are considered the routes by which mercury, lead, cadmium, arsenic, and iron could reach the human body. The populations involved in this study are children from 0 to 15 years old and adults older than 15 years old. It was considered that the population consumes water from wells or boreholes and is in contact with it seven days a week (7 days a week). The average drinking water consumption is estimated at 2 liters per day (or 2 kg·d<sup>-1</sup>) for adults and 1.5 liters per day (or 1.5 kg·d<sup>-1</sup>) for children (ASTEE, 2003). These scenarios result in the calculation of the chronic daily intake (CDI) for water intake and exposure for skin contact using Equations (1) and (2), used respectively by (Tanouayi et al., 2015) and the United States Environmental Protection Agency (USEPA, 2004) are used in the calculation of oral (I) and dermal (II) exposures, respectively.

$$CDI(ing) = \frac{C * IR * F}{BW} \quad (1)$$

With:

**CDI (ing):** Chronic daily intake related to the consumption of polluted water (µg·L<sup>-1</sup>·d<sup>-1</sup>);

**C:** Average concentration of each MTE measured in groundwater (µg·L<sup>-1</sup>);

**I.R.:** Daily water ingestion rate that a person consumes per day (l·d<sup>-1</sup>);

**F:** Frequency or rate of exposure (without unit). As water is consumed 7 d/7 d, F = 1;

**BW:** Bodyweight.

$$Exp(derm) = \frac{C * SA * ET * EF * ED * Kp * CF}{BW * AT} \quad (2)$$

With, C and B.W. are defined in Equation (1).

**Exp (derm):** Daily Dermal Exposure Dose;

**SA:** Skin area (cm<sup>2</sup>);

**ET:** Exposure time (h·d<sup>-1</sup>);

**Kp:** Dermal permeability coefficient (cm·h<sup>-1</sup>);

**CF:** Conversion factor (10<sup>-3</sup>);

**ED:** Exposure duration (year);

**EF:** Exposure frequency (days per year);

**AT:** Average exposure time.

The different values of these parameters used in the (USEPA, 2004) and (Tanouayi et al., 2015) health risk assessment are shown in **Table 2**.

### 2.3.4. Risk Characterization

The risk characterization combines the information from the previous three

**Table 2.** Parameters used to calculate exposure doses.

Parameters	Meaning	Units	Values		Sources
			children	Adults	
<b>I.R.</b>	Daily water ingestion rate	l·d <sup>-1</sup>	1.5	2	(ASTEE, 2003)
<b>ET</b>	Exposure time	h·d <sup>-1</sup>	1	0.58	
<b>E.F.</b>	Exposure frequency	d·year <sup>-1</sup>	350	350	
<b>E.D.</b>	Exposure duration	year	6	30	
<b>BW</b>	Body weight	kg	28	70	
<b>AT</b>	Average exposure time	d	2190	10,950	(USEPA, 2004)
<b>SA</b>	Skin area	cm <sup>2</sup>	6600	18,000	
<b>Kp</b>	Dermal permeability coefficient	cm·h <sup>-1</sup>	10 <sup>-4</sup> (Pb) and 10 <sup>-3</sup> (Hg, Cd and As)		
<b>Fc</b>	Conversion factor	l·cm <sup>-3</sup>	10 <sup>-3</sup>		

steps. It calculates the non-carcinogenic risk for substances for which a hazard and associated RfD exist and exposure has been determined. The non-carcinogenic risk effects were used to establish the hazard quotient (HQ). This is a parameter used by several authors to determine the dose of exposure to a pollutant called the reference dose (RfD) (Obiri et al., 2016; Rehman et al., 2018). It is calculated by dividing the chronic daily dose by the reference dose, as shown in Equations (3) and (4). When the RfD is composed of n trace elements, non-carcinogenic risk effects are estimated for the sum of all RfDs due to individual elements, resulting in the hazard index (HI) (Masok et al., 2017). This is the sum of the HQ of each trace element for each route of exposure (Equations (5) and (6)).

$$HQ(\text{ing}) = \frac{CDI(\text{ing})}{RfDo} \quad (3)$$

where HQ(ing) RfDo: are hazard quotient and reference dose via water ingestion, respectively.

$$HQ(\text{derm}) = \frac{Exp(\text{derm})}{RfDd} \quad (4)$$

where HQ (derm) and RfDd are the hazard quotient and reference dose via dermal exposure, respectively.

If the HQ is less than one (HQ < 1): The occurrence of a toxic effect is very unlikely. Conversely, if HQ is greater than one (HQ > 1): the occurrence of a toxic effect cannot be excluded.

$$HI_{\text{ing}} = \sum_{i=1}^n HQ_{(\text{ing})n} \quad (5)$$

$$HI_{\text{derm}} = \sum_{i=1}^n HQ_{(\text{derm})n} \quad (6)$$

With:

HI<sub>ing</sub>: Index of danger by oral exposure;

HI<sub>derm</sub>: Index of danger by dermal exposure.

When  $HI > 1$ : The occurrence of a non-carcinogenic toxic effect is probable;  
 When  $HI < 1$ : The occurrence of non-carcinogenic toxic effects is not probable.

### 2.3.5. Estimation of Carcinogenic Risk (CR)

The carcinogenic risk determines the probability calculated as a proportion (of the population) in  $\text{mg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$  (Rehman et al., 2018). It is estimated as the lifetime probability of developing cancer as a result of exposure to a potentially carcinogenic contaminant (Johnbull et al., 2019; Liang et al., 2017). For oral exposure, this risk has been estimated for As and Cd classified as known human carcinogens, and Hg and Pb, which are potentially carcinogenic to humans (IARC, 2012; Mishra et al., 2019). For dermal exposure, cancer risk has been estimated for arsenic and lead, for which cancer slope factor (CSF) values are available. According to USEPA guidelines for both age groups, when the CR is below  $10^{-6}$ , there is no risk; if the CR values are between  $10^{-6}$  and  $10^{-4}$ , the carcinogenic risk is acceptable, and if the CR values are above  $10^{-4}$ , the risk is not acceptable (Shil & Singh, 2019; USEPA, 2012).

According to these authors, this is expressed by Equations (7) and (8). The slope factor values are given in Table 3 below.

$$CR_{\text{ing}} = \text{CDI}_{\text{ing}} \times \text{CSF} \quad (7)$$

$$CR_{\text{derm}} = \text{Exp}_{\text{derm}} \times \text{CSF} \quad (8)$$

where CSF is the cancer slope factor.

## 3. Results and Discussion

### 3.1. Results

#### 3.1.1. Estimation of Groundwater Contamination

The average concentrations of the various elements in wells and boreholes are shown in Table 4. The average well concentrations of Hg, Pb, Cd, As and Fe are 1.67, 3.10, 0.08, 0.60, and 2233.48  $\mu\text{g}\cdot\text{L}^{-1}$ , respectively. In boreholes, they are 1.76, 4.08, 0.08, 1.27 and 2427.94  $\mu\text{g}\cdot\text{L}^{-1}$ . These elements are abundant in water according to the order:  $\text{Fe} > \text{Pb} > \text{Hg} > \text{As} > \text{Cd}$ . The concentrations of trace elements recorded in the boreholes are slightly higher than in the wells.

**Table 3.** Values of slope factors of the different elements by oral and dermal exposure.

MTE	CSF ( $\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ ) <sup>-1</sup>		Sources
	Oral	Dermal	
Hg	1	-	
Cd	0.38	-	(USEPA IRIS, 2017;
Pb	1.5	$8.50 \times 10^{-6}$	Shil & Singh, 2018;
As	$8.50 \times 10^{-3}$	3.66	Johnbull et al., 2019)
Fe	-	-	

**Table 4.** Statistical units of MTEs ( $\mu\text{g}\cdot\text{L}^{-1}$ ) in groundwater and WHO guideline value.

Matrix	statistic Parameters	Hg	Pb	Cd	As	Fe
well Boreholes	Min	0.41	0.05	0.00	0.00	775.19*
	Max	4.63	6.56	0.18	5.64	3551.46*
	Aveg	1.67	3.10	0.08	0.60	2233.48*
	Ecart-type	0.88	1.75	0.04	1.18	629.89
	Cv (%)	52.69	56.50	48.30	198.15	28.20
	Min	0.55	0.12	0.00	0.14	1167.06*
	Max	3.70	9.31	0.17	8.67	3944.44*
	Aveg	1.76	4.08	0.08	1.27	2427.94*
	Ecart-type	0.95	0.91	0.04	2.36	628.88
	Cv (%)	58.89	22.36	52.67	185.85	25.90
<b>(WHO, 2017)</b>		<b>6</b>	<b>10</b>	<b>3</b>	<b>10</b>	<b>300</b>

\*: Concentrations above the WHO guide value.

The concentrations of Hg, Pb, Cd, and As obtained in all the works (23 wells and 13 boreholes) are under the values recommended by the WHO for water intended for human consumption. On the other hand, iron has concentrations above the threshold value of  $300 \mu\text{g}\cdot\text{L}^{-1}$ , authorized for drinking water, in all the works.

### 3.1.2. Human Health Risk Assessments

#### 1) Oral exposure

##### • Daily Exposure Dose, Hazard Quotient and Hazard Index

The average CDI, HQ, and HI values for all MTEs are given in **Table 5**. Analysis of this table reveals that the CDI and HQ values for children are significantly higher than those for adults. Therefore, all HI values for children are higher than those for adults.

The average hazard quotient (HQ) values for Hg, Pb, Cd, As, and Fe is less than one ( $\text{HQ} < 1$ ) for both children and adults. These mean values indicate that the occurrence of a toxic effect is very unlikely. Nevertheless, mercury is the metal that contributes most to water toxicity, with average HQ values higher than those of other MTEs. They are 0.90 and 0.48 for children and adults, respectively. Taken individually, 9 wells out of 23 (W1F, W4F, W1Kr, W3Kr, W4Kr, W2K, W6M, W1O, and W1I), *i.e.*, 39.13% and 1 well (W5F), *i.e.*, 4.35%, have HQ respectively in Hg and As greater than one ( $\text{HQ} > 1$ ) in children. In adults, only 1 well (W1Kr) has Hg HQ greater than one.

In boreholes, the average value of HQ (Hg) is 0.98 and 0.52 for children and adults, respectively. Only mercury has HQ values greater than one for both children and adults. This was observed in 6 boreholes (B1F, B2Kr, B1T, B1O, B1I, and B1B) (46.15%) in children and 1 borehole (B1I) (7.69%) in adults.

The hazard index (HI), calculated for well water (1.22) and borehole water

**Table 5.** Mean values of daily exposure dose, hazard quotient and hazard index in well and borehole water.

Structures	MTE	Children		Adults	
		CDI ( $\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{BW}^{-1}\cdot\text{d}^{-1}$ )	HQ	CDI ( $\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{BW}^{-1}\cdot\text{d}^{-1}$ )	HQ
Wells	Hg	0.09	0.90	0.05	0.48
	Pb	0.17	0.50	0.09	0.03
	Cd	0.00	0.01	0.00	0.01
	As	0.03	0.11	0.02	0.08
	Fe	123.03	0.15	65.62	0.08
	HI = $\Sigma$ HQ	-	<b>1.22</b>	-	0.65
Boreholes	Hg	0.10	0.98	0.05	0.52
	Pb	0.23	0.07	0.12	0.04
	Cd	0.01	0.01	0.00	0.01
	As	0.05	0.17	0.02	0.08
	Fe	135.73	0.17	72.39	0.10
	HI = $\Sigma$ HQ	-	<b>1.39</b>	-	0.74

(1.39), reveals non-carcinogenic toxicity risks in the population, with values greater than one. Overall, 60.86% of well water (14/23) shows hazard indices above the critical value of 1 in children. These are W1F, W2F, W4F, W5F, W1Kr, W3Kr, W4Kr, W2K, W4M, W5M, W6M, W1O, W1I, and W2B. In adults, 4.35% or one well out of 23 (W1Kr) has an HI greater than one (**Table 6**).

In boreholes, 76.92% (10/13) and 23.08% (3/13) have above-unit HI in children and adults, respectively. These are B1F, B2F, B2Kr, B1K, B1T, B1M, B1O, B1I, B2I, and B1B in children and B2Kr, B1I, and B1B in adults.

These values reveal that the consumption of these waters is not without non-carcinogenic toxic effects for local populations, especially children. The HI values (children) are higher than those of adults, indicating that children are more vulnerable than adults. Mercury is the main contributor to the population's risk of toxicity. Its HQ and HI values in well and borehole water are reported in **Table 7**.

The involvement of MTEs in water toxicity is in descending order: Hg > Fe > As > Pb > Cd, in both well and borehole water, in both population groups. Moreover, the consumption of borehole water presents a higher risk than the consumption of well water.

#### • Cancer risk (CR) by oral ingestion

The average CR values recorded in wells and boreholes are on average within the defined allowable limit ( $10^{-6}$  to  $10^{-4}$ ).

In wells, the average CR is  $9.01 \times 10^{-5}$  and  $1.19 \times 10^{-5}$  for children and adults. The average CR values are  $4.81 \times 10^{-5}$  for children and  $6.37 \times 10^{-6}$  for adults in boreholes. These values show that children are more exposed to the risk of

**Table 6.** Values of Hazard Quotient (HQ) and Hazard Index (HI) in well water.

N°	Wells	Children		Adults	
		HQ	HI	HQ	HI
1	W1F	<b>1.28</b>	<b>1.47</b>	0.68	0.78
2	W2F	0.95	<b>1.39</b>	0.51	0.74
3	W3F	0.70	0.91	0.37	0.48
4	W4F	<b>1.28</b>	<b>1.77</b>	0.68	0.94
5	W5F	0.42	<b>1.62</b>	0.22	0.86
6	W1Kr	<b>2.48</b>	<b>2.72</b>	<b>1.32</b>	<b>1.45</b>
7	W2Kr	0.64	0.89	0.34	0.47
8	W3Kr	<b>1.02</b>	<b>1.45</b>	0.54	0.77
9	W4Kr	<b>1.06</b>	<b>1.16</b>	0.57	0.62
10	W5Kr	0.84	0.95	0.45	0.51
11	W1K	0.69	0.93	0.37	0.50
12	W2K	<b>1.12</b>	<b>1.35</b>	0.60	0.72
13	W1T	0.22	0.48	0.12	0.26
14	W1M	0.65	0.90	0.35	0.48
15	W2M	0.39	0.61	0.21	0.33
16	W3M	0.48	0.81	0.25	0.43
17	W4M	0.81	<b>1.14</b>	0.43	0.61
18	W5M	0.83	<b>1.12</b>	0.44	0.60
19	W6M	<b>1.02</b>	<b>1.24</b>	0.54	0.66
20	W1O	<b>1.10</b>	<b>1.46</b>	0.59	0.78
21	W1I	<b>1.55</b>	<b>1.77</b>	0.83	0.94
22	W1B	0.57	0.79	0.30	0.42
23	W2B	0.64	<b>1.06</b>	0.34	0.57
<b>Average</b>		0.90	<b>1.22</b>	0.48	0.65

Values in bold are values greater than one.

**Table 7.** Values of the Hazard Quotient (HQ) and Hazard Index (HI) in borehole water.

N°	Boreholes	Children		Adults	
		HQ	HI	HQ	HI
1	B1F	<b>1.03</b>	<b>1.37</b>	0.55	0.73
2	B2F	0.81	<b>1.23</b>	0.43	0.65
3	B1Kr	0.60	0.86	0.32	0.46
4	B2Kr	<b>1.75</b>	<b>1.90</b>	0.94	<b>1.01</b>
5	B1K	0.93	<b>1.17</b>	0.49	0.62
6	B2K	0.48	0.71	0.25	0.38
7	B3K	0.29	0.61	0.16	0.33

**Continued**

8	B1T	<b>1.03</b>	<b>1.28</b>	0.55	0.68
9	B1M	0.37	<b>1.24</b>	0.20	0.66
10	B1O	<b>1.32</b>	<b>1.67</b>	0.70	0.89
11	B1I	<b>1.98</b>	<b>2.41</b>	<b>1.06</b>	<b>1.29</b>
12	B2I	0.78	<b>1.04</b>	0.42	0.55
13	B1B	<b>1.39</b>	<b>2.59</b>	0.74	<b>1.38</b>
Average		0.98	<b>1.39</b>	0.52	0.74

Values in bold are values greater than one.

developing cancer than adults, with higher CR values (children) than adults in both boreholes and wells. However, 9 individual wells and 6 boreholes recorded CR greater than  $10^{-4}$ , defined as an unacceptable limit for cancer risk by the U.S. Environmental Protection Agency.

In children, 9 wells (39.13%) for mercury (P1F, W4F, W1Kr, W3Kr, W4Kr, W2K, W6M, W1O, and W1I) and only 1 well for arsenic (W5F), 4.35%, recorded CR values above the USEPA critical value. Only one well (W1Kr) has a CR (Hg) above the critical threshold in adults.

In boreholes, the CR for mercury and arsenic is higher than the critical value in 6 boreholes (B1F, B2Kr, B1T, B1O, B1I, and B1B) respectively, *i.e.*, 46.15% and two boreholes (B1M and B1B), *i.e.* 15.28% in children. As for adults, one borehole for mercury (P1Kr) (7.69%) and two for arsenic (B1M and B1B), (15.28%) have CR above the limit defined by the USEPA.

The possibility of developing cancer in populations following consumption of this well and borehole water is proven for some mercury and arsenic. As for Pb and Cd, the CR values obtained for them are below  $10^{-6}$ , indicating that the risk of developing cancer related to these elements is very unlikely.

The contribution of MTEs to the risk of cancer in groundwater is given in the following order: Hg > As > Cd > Pb in children and adults. Since mercury and arsenic are the main elements involved in cancer risk in the population, their CR values in wells and boreholes are reported in **Table 8** and **Table 9**, respectively.

## 2) Dermal exposure

### • Daily Exposure Dose (CDI), Hazard Quotient (HQ), Hazard Index (HI), and cancer risk (CR)

The average daily exposure dose, hazard quotient, hazard index, and cancer risk values of Hg, Pb, Cd, As in wells and boreholes are reported in **Table 10**. Analysis of this table shows that all hazard quotients obtained for children and adults are well below 1, which means that the occurrence of non-carcinogenic toxic effects by MTEs is not likely. The resulting hazard index values are  $1.86 \times 10^{-3}$  and  $1.26 \times 10^{-3}$  respectively for children and adults in well water. In boreholes, the resulting hazard index values are  $2.25 \times 10^{-3}$  and  $1.42 \times 10^{-3}$  in children and adults, respectively. These different values indicate that the likelihood of MTEs inducing non-carcinogenic toxic effects on the skin is not possible.

**Table 8.** Oral cancer risks of mercury and arsenic in well water in children and adults.

N°	Wells	Children		Adults	
		CR (Hg)	CR (As)	CR (Hg)	CR (As)
1	W1F	$1.28 \times 10^{-4}$	$3.83 \times 10^{-6}$	$6.83 \times 10^{-5}$	$2.04 \times 10^{-6}$
2	W2F	$9.54 \times 10^{-5}$	$1.30 \times 10^{-5}$	$5.09 \times 10^{-5}$	$6.91 \times 10^{-6}$
3	W3F	$6.99 \times 10^{-5}$	$2.76 \times 10^{-6}$	$3.73 \times 10^{-5}$	$1.47 \times 10^{-6}$
4	W4F	$1.28 \times 10^{-4}$	$3.77 \times 10^{-5}$	$6.83 \times 10^{-5}$	$2.01 \times 10^{-5}$
5	W5F	$4.18 \times 10^{-5}$	$1.15 \times 10^{-4}$	$2.23 \times 10^{-5}$	$6.12 \times 10^{-5}$
6	W1Kr	$2.48 \times 10^{-4}$	$3.93 \times 10^{-6}$	$1.32 \times 10^{-4}$	$2 \times 10 \times 10^{-6}$
7	W2Kr	$6.44 \times 10^{-5}$	$3.34 \times 10^{-6}$	$3.43 \times 10^{-5}$	$1.78 \times 10^{-6}$
8	W3Kr	$1.02 \times 10^{-4}$	$2.28 \times 10^{-5}$	$5.42 \times 10^{-5}$	$1.21 \times 10^{-5}$
9	W4Kr	$1.07 \times 10^{-4}$	$5.39 \times 10^{-6}$	$5.68 \times 10^{-5}$	$2.88 \times 10^{-6}$
10	W5Kr	$8.35 \times 10^{-5}$	$5.96 \times 10^{-6}$	$4.46 \times 10^{-5}$	$3.18 \times 10^{-6}$
11	W1K	$6.86 \times 10^{-5}$	$3.13 \times 10^{-6}$	$3.66 \times 10^{-5}$	$1.67 \times 10^{-6}$
12	W2K	$1.12 \times 10^{-4}$	$4.02 \times 10^{-6}$	$5.98 \times 10^{-5}$	$2.14 \times 10^{-6}$
13	W1T	$2.20 \times 10^{-5}$	$2.71 \times 10^{-6}$	$1.17 \times 10^{-5}$	$1.45 \times 10^{-6}$
14	W1M	$6.54 \times 10^{-5}$	$3.41 \times 10^{-6}$	$3.49 \times 10^{-5}$	$1.82 \times 10^{-6}$
15	W2M	$3.87 \times 10^{-5}$	$4.39 \times 10^{-6}$	$2.06 \times 10^{-5}$	$2.34 \times 10^{-6}$
16	W3M	$4.76 \times 10^{-5}$	$5.64 \times 10^{-6}$	$2.54 \times 10^{-5}$	$3.01 \times 10^{-6}$
17	W4M	$8.07 \times 10^{-5}$	$0.00 \times 10^{+00}$	$4.31 \times 10^{-5}$	$0.00 \times 10^{+00}$
18	W5M	$8.26 \times 10^{-5}$	$3.14 \times 10^{-6}$	$4.40 \times 10^{-5}$	$1.67 \times 10^{-6}$
19	W6M	$1.02 \times 10^{-4}$	$3.04 \times 10^{-6}$	$5.42 \times 10^{-5}$	$1.62 \times 10^{-6}$
20	W1O	$1.10 \times 10^{-4}$	$0.00 \times 10^{+00}$	$5.87 \times 10^{-5}$	$0.00 \times 10^{+00}$
21	W1I	$1.55 \times 10^{-4}$	$3.45 \times 10^{-6}$	$8.26 \times 10^{-5}$	$1.84 \times 10^{-6}$
22	W1B	$5.70 \times 10^{-5}$	$4.38 \times 10^{-6}$	$3.04 \times 10^{-5}$	$2.34 \times 10^{-6}$
23	W2B	$6.38 \times 10^{-5}$	$2.39 \times 10^{-5}$	$3.40 \times 10^{-5}$	$1.27 \times 10^{-5}$
<b>Average</b>		$9.01 \times 10^{-5}$	$1.19 \times 10^{-5}$	$4.81 \times 10^{-5}$	$6.37 \times 10^{-6}$

**Table 9.** Oral cancer risks of mercury and arsenic in borehole water for children and adults.

N°	Borehole	Children		Adults	
		CR (Hg)	CR (As)	CR (Hg)	CR (As)
1	B1F	$1.03 \times 10^{-4}$	$7.02 \times 10^{-5}$	$5.47 \times 10^{-5}$	$3.74 \times 10^{-5}$
2	B2F	$8.07 \times 10^{-5}$	$3.98 \times 10^{-5}$	$4.31 \times 10^{-5}$	$2.12 \times 10^{-5}$
3	B1Kr	$5.96 \times 10^{-5}$	$1.76 \times 10^{-5}$	$3.18 \times 10^{-5}$	$9.37 \times 10^{-6}$
4	B2Kr	$1.75 \times 10^{-4}$	$3.04 \times 10^{-5}$	$9.36 \times 10^{-5}$	$1.62 \times 10^{-5}$
5	B1K	$9.27 \times 10^{-5}$	$1.09 \times 10^{-5}$	$4.95 \times 10^{-5}$	$5.82 \times 10^{-6}$
6	B2K	$4.77 \times 10^{-5}$	$1.28 \times 10^{-5}$	$2.54 \times 10^{-5}$	$6.84 \times 10^{-6}$
7	B3K	$2.93 \times 10^{-5}$	$6.56 \times 10^{-5}$	$1.56 \times 10^{-5}$	$3.50 \times 10^{-5}$

## Continued

8	B1T	$1.03 \times 10^{-4}$	$1.46 \times 10^{-5}$	$5.50 \times 10^{-5}$	$7.78 \times 10^{-5}$
9	B1M	$3.67 \times 10^{-5}$	$2.44 \times 10^{-4}$	$1.96 \times 10^{-5}$	$1.30 \times 10^{-4}$
10	B1O	$1.32 \times 10^{-4}$	$0.00 \times 10^{+00}$	$7.05 \times 10^{-5}$	$0.00 \times 10^{+00}$
11	B1I	$1.98 \times 10^{-4}$	$9.58 \times 10^{-5}$	$1.06 \times 10^{-4}$	$5.11 \times 10^{-5}$
12	B2I	$7.85 \times 10^{-5}$	$1.61 \times 10^{-5}$	$4.19 \times 10^{-5}$	$8.60 \times 10^{-6}$
13	B1B	$1.39 \times 10^{-4}$	$3.48 \times 10^{-4}$	$7.44 \times 10^{-5}$	$1.86 \times 10^{-4}$
<b>Average</b>		$9.82 \times 10^{-5}$	$7.43 \times 10^{-5}$	$5.24 \times 10^{-5}$	$3.96 \times 10^{-5}$

**Table 10.** Average Exp, HQ, HI and CR values in well and borehole water by dermal exposure.

		Hg	Pb	Cd	As	HI ( $\Sigma$ HQ)	
<b>Wells</b>	Children	Exp ( $\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{BW}^{-1}\cdot\text{d}^{-1}$ )	$0.38 \times 10^{-3}$	$0.70 \times 10^{-4}$	$2.38 \times 10^{-5}$	$1.35 \times 10^{-4}$	-
		HQ	$1.26 \times 10^{-3}$	$1.33 \times 10^{-4}$	$3.44 \times 10^{-5}$	$4.49 \times 10^{-4}$	$1.86 \times 10^{-3}$
		CR	-	$5.95 \times 10^{-13}$	-	$4.34 \times 10^{-7}$	-
	Adults	Exp ( $\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{BW}^{-1}\cdot\text{d}^{-1}$ )	$0.34 \times 10^{-3}$	$0.44 \times 10^{-4}$	$1.09 \times 10^{-5}$	$0.85 \times 10^{-4}$	-
		HQ	$0.79 \times 10^{-3}$	$0.84 \times 10^{-4}$	$2.18 \times 10^{-5}$	$2.84 \times 10^{-4}$	$1.26 \times 10^{-3}$
		CR	-	$3.76 \times 10^{-13}$	-	$3.55 \times 10^{-7}$	-
<b>Borehole</b>	Children	Exp ( $\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{BW}^{-1}\cdot\text{d}^{-1}$ )	$0.41 \times 10^{-3}$	$0.92 \times 10^{-4}$	$1.91 \times 10^{-5}$	$2.12 \times 10^{-4}$	-
		HQ	$1.33 \times 10^{-3}$	$1.76 \times 10^{-4}$	$3.81 \times 10^{-5}$	$7.05 \times 10^{-4}$	2.25
		CR	-	$7.84 \times 10^{-13}$	-	$7.75 \times 10^{-7}$	-
	Adults	Exp ( $\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{BW}^{-1}\cdot\text{d}^{-1}$ )	$0.25 \times 10^{-3}$	$0.58 \times 10^{-4}$	$1.21 \times 10^{-5}$	$1.34 \times 10^{-4}$	-
		HQ	$0.84 \times 10^{-3}$	$1.11 \times 10^{-4}$	$2.10 \times 10^{-5}$	$4.46 \times 10^{-4}$	1.42
		CR	-	$4.93 \times 10^{-13}$	-	$4.90 \times 10^{-7}$	-

The CR values in well and borehole water in both children and adults are below  $10^{-6}$ , a value for which there is no risk according to the USEPA. These values are in the order of  $10^{-6}$  for arsenic and  $10^{-12}$  for the lead. These different values indicate that risks of skin cancer linked to arsenic and lead contamination are excluded.

### 3.2. Discussion

In this study, the health risk assessment considered the different routes by which chemicals are likely to reach the human body. These are the oral and dermal routes via the use of well and borehole water.

Apart from the health risks, iron recorded concentrations above the guideline values (WHO, 2017) for all structures. These high concentrations would be

linked to the decomposition of ferromagnesian minerals such as biotite and amphiboles. This hypothesis is confirmed by the geology of the study area. In fact, the geological formations of the Zouan-Hounien department consist of metamorphic rocks containing amphibole. The weathering of these rocks releases, among other things, ferrous ions ( $\text{Fe}^{2+}$ ) in the soils, giving way to ferritic soils. (Dabin et al., 1960; Naho, 1988) reported the ferritic nature of the soils in the area. Since the study area is abundantly watered, rainfall and leaching of soils lead to infiltration and accumulation of this element in groundwater. Similar iron concentrations have been reported by (Ahoussi et al., 2013) in well water from the Biankouma sub-prefecture, located in the mountainous west of Côte d'Ivoire. This abundance of iron observed in the groundwater has been attributed to the geological nature of the area, as indicated by (Ahoussi et al., 2013) on work carried out in the west of the country. In addition, the heavy rains observed in the area favor a very intense and complete alteration of the primary minerals of the bedrock by hydrolysis, resulting in significant quantities of iron oxides which infiltrate the soil to the water table (Eblin et al., 2014).

The average HQ values for these two routes of exposure, obtained for all MTEs in well and borehole water, are less than one, indicating non-carcinogenic toxic risk to the population (children and adults). However, mercury is the metal contributing most to water toxicity, with a higher HQ value than the other elements. Also, some works (wells and boreholes) have recorded Hg HQ values greater than one. This resulted in nine wells and two boreholes in children and adults, respectively. This involvement of mercury in water toxicity may be due to mining activities. According to (Ettien, 2010), mining is an activity that has been taking place in the area since the 1940s and 1950s. The abusive and illegal use of mercury could lead to an accumulation of this substance in the soil and increase its concentration in groundwater (Djadé et al., 2020). The work carried out by these authors on the quality of groundwater in the zone using metal pollution indices revealed that gold panning is the main source of mercury in water. Indeed, mercury is used during extraction processes to dissolve gold and form an amalgam with it. This amalgam is then heated, releasing the mercury into the atmosphere and promoting its deposition in uncovered wells, house roofs, soils, etc. Due to the high rainfall recorded in the area, the infiltration water loaded with mercury will increase its vertical transfer to the groundwater table. Calculation of the hazard quotient shows that certain structures may present risks of causing certain non-cancerous diseases related to this substance at low concentrations of Hg. It has been reported that short and long-term oral exposures to mercury can lead to kidney damage and possibly kidney failure. They can also cause fatigue, insomnia, nausea, vomiting, pain, ulceration, diarrhea, withdrawal, depression, nervousness, irritability, and memory problems (WHO, 2003).

Children remain more sensitive to this contamination than adults, with high HQ. Among them, the hazard indices in wells and boreholes are all higher than one, with values of 1.22 and 1.39, respectively, indicating that the occurrence of non-carcinogenic toxic effects is probable. In children, mercury toxicity may

manifest as edema, pain, redness, scaling of fingers and toes (acrodynia), and hypertension (Böse-O'Reilly et al., 2010). Several authors have made this observation (Xiao et al., 2018; Al-Khatib et al., 2019; Lu et al., 2019). Their still-developing bodies and low body weight explain this vulnerability of children (Olujimi et al., 2015; Tanouayi et al., 2015). These assertions are supported by the work of (Walker et al., 2006), according to which children younger than 15 years of age are more vulnerable to exposure because their central nervous system is still developing. Also, high mercury concentrations in drinking water expose populations to kidney dysfunction, gastrointestinal disorders, and high blood pressure (Bisen-Hersh et al., 2014).

The most toxic form of mercury is methylmercury. Its presence in drinking water as a potential source of illness is negligible, according to (WHO, 2005). However, work carried out by (Yard et al., 2012), among artisanal gold miners in Madre de Dios, Peru, revealed significant concentrations of total mercury in the urine and methylmercury in the blood of participants drinking well water. The latter can cross the placental barrier between mother and fetus, resulting in a decrease in the child's intellectual quotient, brain damage, and mental retardation (Perrera & Viswanathan, 2007; Grandjean & Herz, 2011). The World Health Organization (WHO, 2017) recommends a value of  $6 \mu\text{g}\cdot\text{L}^{-1}$  for drinking water. However, the U.S. Environmental Protection Agency (USEPA, 2004) recommends  $2 \mu\text{g}\cdot\text{L}^{-1}$  as the maximum contaminant value for children. According to them, mercury values above this maximum value can cause kidney damage, particularly in children through long-term exposure. On this basis, several wells sampled in this study are not without risk to the population's health.

In addition, one well (W5F) recorded an arsenic HQ above one. This means that the occurrence of non-carcinogenic arsenic-related toxic effects cannot be excluded the well-recorded high arsenic concentrations. The high arsenic presence in this well is due to contamination of the well by plant protection products and fertilizer (Djadé et al., 2020). Indeed, W5F is well located at the edge of the cultivation area. Also, the water level is equal to the soil level. The use of fertilizers and phytosanitary products can facilitate contamination into the water, especially as the water depth is almost nil.

The consumption of water from this well exposes the populations who use it to diseases of the cardiovascular, dermatological, nervous, hepatobiliary, renal, gastrointestinal, and respiratory systems, such as arterial hypertension, skin lesions, diabetes, hearing loss, hematological disorders, etc. (Tchounwou et al., 2012).

In addition, oral ingestion of water from some wells and boreholes contaminated with mercury and arsenic, listed above, exposes the population, especially children, to several forms of cancer. They are exposed to cancer of the liver, lungs, kidneys, bladder, and skin (Tchounwou et al., 2012; Fashola et al., 2016; Xiao et al., 2018). The consumption of these waters should be done in moderation, especially in children.

## 4. Conclusion

This study aims to assess the health risks linked to the consumption of these waters by the population. The results showed that the average concentrations of mercury, lead, cadmium, and arsenic in groundwater align with the WHO recommended values for water intended for human consumption. However, iron is the only metal whose concentrations obtained in all facilities are above the threshold value. The human health risk assessment shows that children are more vulnerable to pollution by MTEs than adults. The average hazard quotients and cancer risk values of the five MTEs are below the various required threshold values, showing that these elements pose no threat to populations.

On the other hand, the occurrence of non-cancerous and cancerous adverse effects due to water contamination by mercury and arsenic is likely, via consumption of water from 10 wells and 6 boreholes. Mercury is the main contributor to the risk of disease in populations. Oral exposure poses no risk of toxic effects to people.

Since the presence of MTEs in groundwater resources poses a threat to the health of the population, and epidemiological case-control study must be carried out to establish a relationship between the different elements considered and the associated diseases identified in other countries. Furthermore, since only oral and dermal exposure was considered in this study, it is recommended that it be extended to all routes of exposure that could bring chemical elements to the human body (fisheries resources, food crops, and inhalation).

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## The Author's Contributions

All the authors contributed to the research design, analysis, interpretation of the data, and the manuscript's writing.

## Conflicts of Interest

The authors do not declare any conflict of interest.

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