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Original Research

Study and assessment of trace metal contamination (As, Cd, Pb, and Hg) in water resources from the headwaters of the Ouémé and Pendjari watersheds in the Copargo Municipality (Northwestern Benin)

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Abstract: Headwaters, considered strategic zones for preserving water resources and crucial for evaluating water quality and streamflow, have been increasingly subjected to anthropogenic pressure in recent years. This pressure, exerted by human activities, has notable negative repercussions on the quality of both water and soil resources. This study aims to assess the contamination of water resources in the headwaters of the Copargo municipality by trace metals (arsenic, cadmium, mercury, and lead). To this end, water samples were collected during two sampling campaigns conducted during the high-water (August 2023) and low-water (November 2023) periods. 42 sampling sites were selected, comprising 9 wells, 7 boreholes, 25 rivers, and 1 dam. These samples were properly preserved and transported to the laboratory for analysis of trace metals, arsenic, cadmium, mercury, and lead using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), according to the EPA 6010B method. The results indicate that the concentrations of arsenic, cadmium, mercury, and lead measured in water resources during the high-water period are significantly higher than those observed during the low-water period ($p<0.05$). Regarding the water quality of Beninese drinking water standards, the concentrations of trace metals in the water from wells, boreholes, and rivers are generally below the established thresholds, except for mercury. Specifically, mercury concentrations of 1.56 µg/L, 1.67 µg/L, and 1.79 µg/L in well, borehole, and river water, respectively, exceed the Beninese standard of 1 µg/L. Furthermore, the results reveal that the average concentrations of arsenic (0.9 µg/L), cadmium (0.71 µg/L), and lead (0.32 µg/L) are slightly higher in groundwater than in surface waters, where they are 0.71 µg/L, 0.2 µg/L, and 0.31 µg/L, respectively. In contrast, surface water's average mercury concentration is higher (0.9 µg/L) than groundwater (0.8 µg/L). The contamination and pollution indices calculated indicate that 88.89% of the wells, 14.3% of the boreholes, and 46.15% of the rivers exhibit a moderate level of contamination ($1 < DC < 3$), while only one borehole (14.3%) shows a high contamination level ($DC = 4.28$). Regarding the pollution load index, all water resources studied show a low level of pollution. Despite the low observed contamination, the mercury concentrations suggest that most of the water resources in the municipality are unsuitable for human consumption. Although water resource contamination is relatively low, the toxicological risk remains concerning due to the cumulative nature of trace metals. This situation underscores the need for a modeling study of pollutant transfer to enable dynamic monitoring and better prediction of the quality of these water resources.

1. INTRODUCTION

The global expansion of development activities has significant implications for the environment, particularly for water resources and human health humaine (Adje et al., 2021; OECD, 2012) Industrial, agricultural, and urban growth inevitably leads to issues related to contamination and degradation of ecosystems, including aquatic systems (D'Adamo et al., 2008; Rao et al., 2007). In the agricultural sector, declining crop yields, driven by soil depletion and the impacts of climate change, compel populations, especially in developing countries to intensify the use of agricultural inputs while expanding into new fertile lands suitable for farming. In this context, wetlands, regarded as fertile areas, are increasingly occupied and exploited (Gnonhoue, 2020; Mathieu and Bernard, 2020). However, most of these wetlands are located in source areas, also known as headwaters (Lhéritier, 2012). Headwaters refer to areas that feed the initial streams of a river network, playing a crucial role in regulating water flow and maintaining downstream water quality. These hydrosystems, characterized by a high density of streams (rivulets), provide essential ecosystem services, often considered vital for local communities (Dourotimy Rachel et al., 2020). Given their fragility and central role in regulating water resources, headwaters require special management attention within water resource planning frameworks (Dourotimy Rachel et al., 2020; Michelet et al., 2015). However, these areas are increasingly being exploited for various purposes, particularly affecting water quality in physical, chemical, and biological aspects (Chaussis and Suaudeau, 2012). This phenomenon presents a major challenge for the sustainable management of water resources, as the integrity of headwaters is essential for properly functioning hydrosystems and downstream rivers (Baudoin, 2007).

Benin, where the agricultural sector employs approximately 70% of the active population and contributes 33.2% to the Gross Domestic Product (GDP) INSAE (2008), is no exception to this issue. Many aquatic ecosystems are degrading due to increasing anthropogenic activities, with a direct impact on water quality (Agbanou, 2018; INSAE, 2008). The municipality of Copargo, located in the northwest of the country, serves as a typical example of this situation. It is strategically located as the source of two major rivers: the Ouémé River (nationally significant) and the Oti/Pendjari River (internationally significant). This area is highly sought after for agricultural production due to the fertility of its land, partly nourished by the presence of wetlands. However, these wetlands, classified as headwaters, are increasingly exploited for agricultural purposes, including the cultivation of cotton, cereals, yams, and beans. To optimize agricultural yields, the use of inputs such as chemical fertilizers and pesticides (including herbicides and insecticides) has become widespread. These practices result in the contamination of water resources with chemicals (Sun et al., 2019). These contaminations have serious effects on aquatic ecosystems' integrity and pose major risks to public health.

In this context, it is imperative to assess the impact of pollution by trace metals, which are widely recognized for their toxicity to both aquatic organisms and human health. Some trace metals, such as copper (Cu), nickel (Ni), and zinc (Zn), are essential at low levels but can become toxic when their concentration exceeds a critical threshold (Chiffoleau et al., 2004). Metals like mercury (Hg), lead (Pb), and arsenic (As) have no known biological role and are especially dangerous due to their persistence in the environment and ability to bioaccumulate in aquatic food chains. (Boucheseiche et al., 2002; Chiffoleau et al., 2004). Pollution by these trace metals poses a direct public health threat to riparian populations that rely on surface water, often easily accessible, for their drinking water supply.

To date, studies have addressed the hydrological, hydrogeological, and hydrochemical aspects of groundwater in the region (Ahlonsou et al., 2024; N'tcha et al., 2020; Sambiénou, 2019; Sambiénou et al., 2018). No in-depth research has been conducted on the issue of trace metal element pollution in the municipality of Copargo. However, this region, characterized by intensive agricultural activities, is marked by the frequent use of pesticides and chemical fertilizers. These practices are likely to introduce metallic pollutants such as arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb) into the water resources of Copargo's headwater basins. As upstream zones of river systems, water contamination in this locality, if left unaddressed, could propagate downstream, impacting the entire hydrographic network. This situation poses a major risk to riparian populations who rely on these waters for consumption and may face health issues associated with trace metal element pollution.

The development of effective policies for the protection of water resources fundamentally depends on a rigorous assessment of their quality and the quantification of the various pollutants they contain. In this context, the present study aims to determine the contamination levels of water resources of the headwaters of the Ouémé and Pendjari rivers within the municipality of Copargo by trace metal elements (As, Cd, Hg, and Pb) during periods of high and low water flow. The findings will provide essential scientific data to support decision-makers in implementing informed measures and ensuring the sustainable management of water resources of Copargo's headwaters.

2. MATERIALS AND METHODS

Study area

The present study was conducted in the municipality of Copargo, located between 9°40'50" and 10°4'31" North latitude and between 1°20' and 1°45' East longitude. The municipality covers an area of 876 km² and has a population of approximately 71,000 inhabitants. It is bordered to the northwest by Boukombé, to the north and northeast by Kouandé, to the southwest by Ouaké, to the southeast and east by Djougou, and the west by the Republic of Togo (Fig. 1).

Copargo is influenced by a Sudano-Guinean climate, moderated by the Atacora mountain range. During the dry season, the Harmattan wind, dry and cool, blows across the region. The climate in the municipality is characterized by two distinct seasons: a dry season from mid-October to mid-April, and a rainy season from mid-April to mid-October. Annual precipitation ranges from 800 mm to 1300 mm, with an uneven distribution, particularly in the months of high rainfall, notably in August and September (Mathieu and Bernard, 2020). March has an average monthly maximum temperature of 36 C, while August has an average monthly minimum temperature of 32 C.

The vegetation of the municipality is dominated by wooded and grassy savannas, which characterize the region's landscape. Common plant species include shea trees, locust beans, and mango trees, which are found ubiquitously. The municipality also hosts a classified forest spanning 1,091 hectares and a gallery (République du Bénin, 2019).

The topography of the municipality is marked by significant diversity, with a mountainous area dominated by the Atacora mountain range, whose highest peak, located at Tanéka-Koko, reaches an altitude of 654 m, in the western part of the municipality. The rest of the area consists of vast forested plains interspersed with valleys and depressions, often wet and suitable for agriculture. Wetlands are primarily concentrated in the northwestern part of the municipality, where altitudes range between 329 m and 396 m (Mathieu and Bernard, 2020).

Copargo benefits from a dense hydrographic network, crossed by several rivers, the most significant being the Ouémé and Pendjari rivers, which form two distinct watersheds. The Pendjari River has a seasonal flow regime, while the Ouémé River exhibits permanent flow towards the Atlantic Ocean (République du Bénin, 2019). The soils in the municipality are predominantly ferrallitic tropical soils, leached, unconsolidated, and sometimes hardened, which cover the summits and slopes. Lighter soils, with low water retention capacity, are found mainly in the municipalities of Anandana and Singré (Mathieu and Bernard, 2020).

Geologically, the rock formations of the municipality extend from outcrops of the Atacora series (which continues into Togo and Ghana) to the first outcrops of the Dahomey or Benino-Togolese basement, composed of very ancient volcanic rocks, followed by geological series including quartzites, shales, mica-schists, and deposits from the Buem series (UNEP/GEF/Volta/NR Benin, 2010).

The water resources exploited in the municipality are primarily groundwater and surface water. The local economy is predominantly based on agriculture but includes fishing, hunting, trade, and manufacturing industries. Agriculture is the primary economic activity in the municipality, employing more than 90% of the active population. The three main agricultural sectors contributing to the formation of the local GDP are yam (80.12%), maize (14.95%), and cashew (7.43%), while additional sectors such as chili, rice, and cotton also exhibit growing dynamics. Water-intensive crops, such as rice and market gardening, are primarily developed in the municipality's wetland areas (INSAE, 2008).

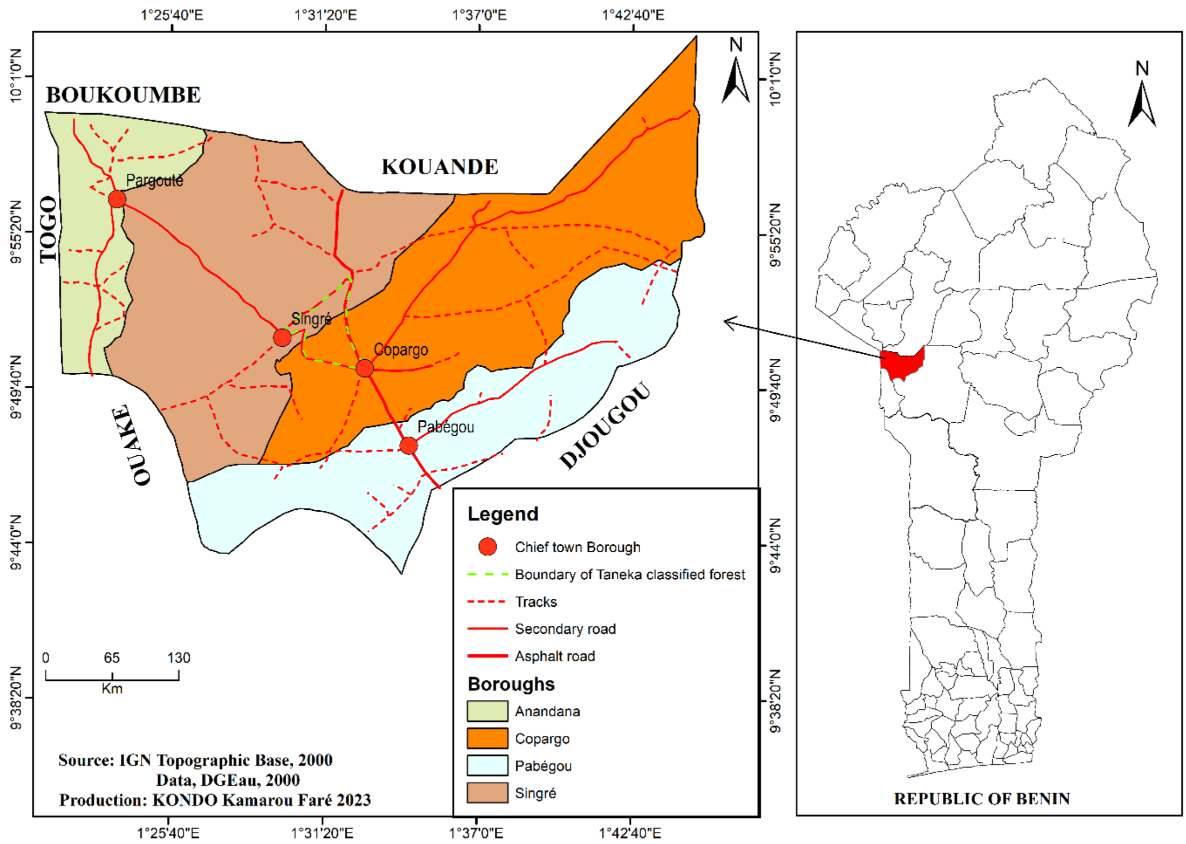

Fig. 1: Geographical location of the study area: Copargo municipality

Sampling and Analytical Methodology

Sampling

Water samples were collected during two periods in 2023: during the high-water period (August 2023) and the low-water period (November 2023). This study samples two types of water resources: surface water resources (reservoir and river) and groundwater resources (boreholes and wells).

Selection of sampling sites

The specific study area is the headwaters of the Copargo watersheds. In the context of our study, a headwater is an area (small watershed) drained and delineated by first-order and second-order streams or rivers, according to Strahler's classification, and discharges into a second-order stream or the confluence of two second-order streams, according to Strahler's classification. Thus, in order to obtain representative samples of the Copargo watershed headwaters, the selection of sampling sites was based on the definition and delineation of a headwater. Based on this definition and delineation of headwater, surface water samples (rivers) were collected from the outflows of each headwater. The municipality of Copargo has 25 headwaters, which corresponds to 25 river sampling sites. Unfortunately, one river site was inaccessible, and we were only able to sample 24 sites (river waters) out of the 25 sites. For dam waters, well waters, and borehole waters, their sampling sites were chosen based on their existence in a reasoned manner to ensure their representativeness within each of the headwater.

In total, 16 groundwater sites (7 boreholes and 9 wells) and 25 surface water sites (1 reservoir and 24 rivers) were identified and sampled. 84 water samples were collected, with 42 samples taken during each period. All water samples were collected in 0.5-liter polyethylene bottles previously cleaned with 10% nitric acid and rinsed with distilled water. Before each sampling, the bottles were rinsed several times with the water to be collected. Surface water samples were collected at a depth of 30 cm below the surface. Well water samples were collected using a bailer and transferred into the polyethylene bottles. Borehole water samples were collected directly from the pump, after flushing out any standing water in the pipes. Each water sample was acidified with 1 mL of concentrated nitric acid (HNO3) to preserve trace elements in their ionic form (Rodier, 2009). The water samples were then properly stored in coolers with ice packs (4°C) and transported to the laboratory for analysis. All sampling procedures followed the guidelines of the French Association for Standardization (AFNOR) (Rodier, 2009). The trace metals analyzed in the laboratory were arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb).

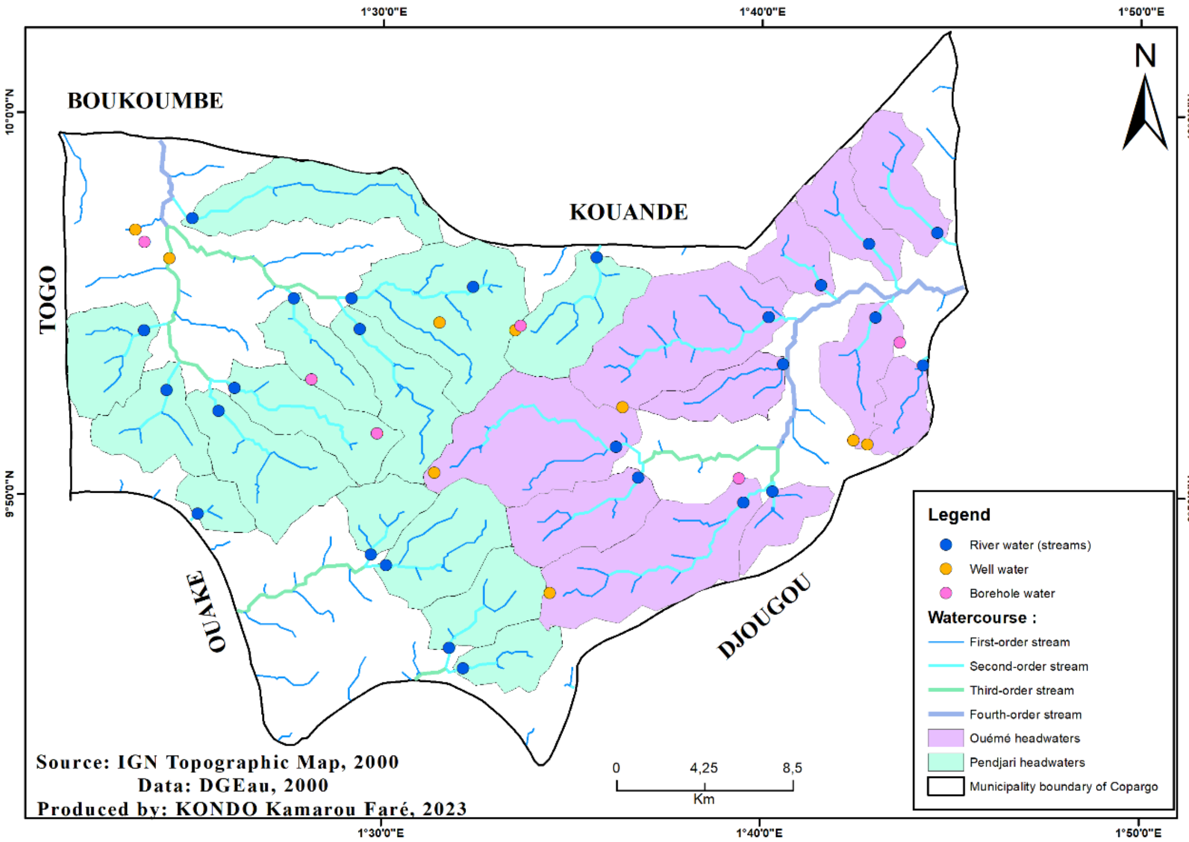

Fig. 2: Map of the distribution of water sampling sites

Sample Analysis

***In-situ* measurements**

In-situ measurements focused on pH (hydrogen potential), electrical conductivity, and temperature of the water samples. These measurements were performed using the multiparameter LAQUA HORIDA WQ-330 device.

Laboratory analyses

In the laboratory, the analyses targeted As, Cd, Hg, and Pb. These trace metals were analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) according to the EPA 6010B method.

Table 1: Equipment and methods for analyzing study parameters

Physicochemical Parameter	**Method**	**Equipment**
pH	Electrometry (AFNOR NF T90-008)	LAQUA HORIDA Multiparameter
Conductivity, Temperature	Conductimetry (AFNOR NFEN 27888)	
Trace metals		
Arsenic, Cadmium, Mercury, Lead	Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) – EPA Method 6010B	Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)

The detection limits and precision of the ICP-OES equipment used for the analyses

A detection limit is the lowest concentration of an element or substance that the equipment can reliably detect. The detection limits of the ICP-OES equipment used for determining the analyzed trace elements are summarized in the following table:

Table 2: Detection limits of the ICP-OES equipment used for determining the analyzed trace elements

Parameters	Detection Limit (µg/l)
Arsenic (As)	0,02
Cadmium (Cd)	0,01
Mercury (Hg)	0,08
Lead (Pb)	0,05

The precision of the ICP-OES equipment used for the analyses is 1%.

Data Processing and Statistical Analysis

Data processing and statistical analysis were carried out using Excel 2013 spreadsheet software and the R statistical software. Excel 2013 was used for various calculations, as well as for generating tables and graphs. Multivariate statistical analysis was performed using R software. In R, Pearson's correlation was calculated to determine the correlation coefficients between the different parameters studied, thereby identifying the relationships between these parameters in pairs. Principal Component Analysis (PCA) was performed using the FactoMineR and factoextra packages in R, as described by (Lê et al., 2008). PCA was employed to emphasize the associations among the different trace metals analyzed and to explore patterns in water resources concerning these elements. The applicability of this exploratory technique relies on selecting the number of factor axes that represent the maximum amount of inertia while retaining the fewest possible factors. Generally, PCA for a region is considered valid when the factor planes retain at least 70% of the information (Abdou Babaye, 2012; Faillat and Drogue, 1993; N'tcha et al., 2020; Sambiénou, 2019). Below this threshold, it is considered that the study of the region has not accounted for a substantial amount of information. Since periodic variability in trace element concentrations in water resources was observed both over time and across different sampling sites, the Student's t-test at a 5% significance level was used to compare the variability of trace element concentrations in the water samples.

Evaluation of Contamination Levels

The drinking water standards of Benin were used to evaluate both the quality of water resources and the level of contamination through indices. Three indices assessing drinking water quality were calculated. The Contamination Factor (CF), Degree of Contamination (DC), and Pollution Load Index (PLI) (AR, 2016; Belkhiri et al., 2018; El-Hamid and Hegazy, 2017; Hakanson, 1980; Li et al., 2013; Sahli et al., 2014; Tomlinson et al., 1980).

- **Contamination Factor (CF)**

The Contamination Factor (CF) was calculated using the following equation (Hakanson, 1980):

$$\text{CF} = \frac{\text{Concentration of the trace metal in water}}{\text{Beninese standard for the element in drinking water}} \quad \ldots(1)$$

According to Hakanson (1980), this index is classified into four categories, providing four types of information:

– **CF < 1** Indicates low contamination;
– **1 < CF < 3** Indicates moderate contamination;
– **3 < CF < 6** Indicates considerable contamination;
– **CF > 6** Indicates very high contamination.

- **Degree of Contamination (DC)**

The level of contamination of water by trace elements can also be evaluated by calculating the Degree of Contamination (DC)(Belkhiri et al., 2018). The Degree of Contamination is calculated using the following equation:

$$\text{DC} = \sum_{i=n}^{n} \text{CFi} \quad \ldots(2)$$

Where CFi is the contamination factor of the i-th parameter, and n represents the normative value for the trace metal.

The DC provides three types of information:

– Low contamination if **DC < 1;**
– Moderate contamination if **1 < DC < 3**;
– High contamination if **DC > 3**.

- **Pollution Load Index (PLI)**

The Pollution Load Index (PLI) is an index originally proposed by Tomlinson et al. (1980), and later widely used by Li et al. (2013) and Sahli et al. (2014). This index provides valuable information and guidance to decision-makers regarding the level of pollution in an aquatic ecosystem. The PLI for a single site is calculated using the following equation:

$$\text{PLI} = \sqrt[n]{\text{CF1}\times\text{CF2}\times\cdots\times\text{CFn}} \quad \ldots(3)$$

In this context, n represents the count of trace metals identified at each location. The PLI offers important insights regarding the habitat:

– **PLI = 0** indicates perfection;
– **PLI < 1** indicates the presence of pollutants at low levels;
– **PLI = 1** indicates the presence of pollutants at threshold levels;
– **PLI > 1** indicates a progressive deterioration of the site and the quality of the habitat.

3. RESULTS

3.1. *In-situ* Measurements (temperature, electrical conductivity, and pH)

3.1.1. Groundwater

✓ **Wells Water**

Table 3 below presents the descriptive statistics of the in-situ parameters for well water from the headwaters of the Copargo Municipality. According to this table, the temperature of the well water ranges from 25.4°C to 29.38°C, with an average of 27.72°C ± 1.23°C and a median of 28.22°C. These waters exhibit a relatively narrow temperature range, which is reflected in a low variation amplitude, as indicated by the coefficient of variation (CV = 4.45%).

Regarding electrical conductivity, it ranges from 26.42 µS/cm to 270.5 µS/cm, with an average of 169.75 µS/cm ± 99.75 µS/cm and a median of 174.3 µS/cm. The amplitude of variation in electrical conductivity is high, as confirmed by a relatively significant coefficient of variation, equal to 58.76%.

For pH, the values measured in the well water during the study campaigns range from 5.58 to 7.44, with an average of 6.02 ± 0.6 and a median of 7. The variation in pH is relatively narrow, as confirmed by the coefficient of variation (9.52%).

Tableau 3: *In-situ* parameters for well water

	NEPB/WHO	Min	Max	Average	Median	SD	CV (%)
T °C	25/-	25,4	29,38	27,72	28,22	1,23	4,45
Cond (µs/cm)	1000/400	26,42	270,5	169,75	174,3	99,75	58,76
pH	6,5-8,5/6,5-8,5	5,58	7,44	6,02	6,14	0,6	9,62

T = Temperature, **Cond** = Electrical Conductivity, **CV** = Coefficient of Variation, **SD** = Standard Deviation

✓ **Borehole Water**

According to Table 4, which presents the descriptive statistics of the in-situ parameters for borehole water in the study area, the temperatures of the borehole water range from 29.3°C to 30.08°C, with an average of 29.68°C ± 0.37°C and a median of 29.83°C. The temperature variation amplitude is 1.26%.

Regarding electrical conductivity, the measured values range from 147.93 µS/cm to 551.5 µS/cm, with an average of 311.53 µS/cm ± 150.7 µS/cm and a median of 264 µS/cm. The coefficient of variation is relatively high, at 48.37%.

For pH, the average of the recorded values is 6.68, with a standard deviation of 0.31, and extreme values ranging from 6.13 to 7.17. The median is 6.7, and the coefficient of variation is 4.6%.

Tableau 4: *In-situ* parameters for borehole water.

	NEPB/WHO	Min	Max	Average	Median	SD	CV (%)
T °C	25/-	29,03	30,08	29,68	29,83	0,37	1,26
Cond (µs/cm)	1000/400	147,93	551,5	311,53	264	150,7	48,37
pH	6,5-8,5/6,5-8,5	6,13	7,17	6,68	6,7	0,31	4,6

T = Temperature, **Cond** = Electrical Conductivity, **CV** = Coefficient of Variation, **SD** = Standard Deviation

3.1.2. Surface Water (Rivers and one dam waters)

According to Table 5, which presents the descriptive statistics of the in-situ measurements conducted on river and dam waters in the study area, the average temperature during the study period is 26.72°C ± 1.61°C, with extreme values ranging from 23.75°C to 30.92°C. The associated coefficient of variation is 6.03%.

Regarding conductivity, the recorded values range from 13.55 µs/cm to 85 µS/cm, with an average of 46.73 µs/cm ± 18.3 µS/cm, and a coefficient of variation of 23.23%.

For pH, the measured values fluctuate between 5.69 and 7.35, with an average of 6.61 ± 0.42 and a coefficient of variation of 6.35%.

Table 5: *In-situ* parameters for surface water

	NEPB/WHO	Min	Max	Average	Median	SD	CV (%)
T°C	25/-	23,75	30,92	26,72	27,075	1,61	6,03
Cond (µs/cm)	1000/400	13,55	85,15	46,73	44,43	18,3	23,23
pH	6,5-8,5/6,5-8,5	5,69	7,35	6,61	6,61	0,42	6,35

T = Temperature, **Cond** = Electrical Conductivity, **CV** = Coefficient of Variation, **SD** = Standard Deviation

3.2. Descriptive analysis of As, Cd, Hg, and Pb concentrations in groundwater and surface water resources during the study periods in the headwaters of Copargo

3.2.1. Well water

The descriptive statistics of trace metal concentrations in well water for the different study periods are presented in Table 6. The table shows that arsenic concentrations range from 0.27 to 4.28 µg/L, with an average concentration of 1.95 ± 1.18 µg/L during the high-water period. In contrast, during the low-water period, the average concentration is 0.046 ± 0.14 µg/L, with a maximum of 0.42 µg/L. For cadmium, the concentrations recorded during the high-water period range from 0.21 to 0.64 µg/L, with an average of 0.38 ± 0.16 µg/L. During the low-water period, the average value is 0.034 ± 0.07 µg/L, with a maximum concentration of 0.21 µg/L.

Regarding mercury, concentrations observed during the high-water period range from 0.14 to 2.57 µg/L, with an average concentration of 1.56 ± 0.84 µg/L. These values exceed the Beninese standard for drinking water, which is set at 1 µg/L. During the low-water period, mercury concentrations are below the detection limit of the instrument (0.08 µg/L), rendering detection impossible. Finally, for lead (Pb), the average concentration recorded during the high-water period is 0.81 ± 0.65 µg/L, with a maximum of 1.8 µg/L. During the low-water period, the average concentration is 0.046 ± 0.14 µg/L, with a maximum of 0.41 µg/L.

Table 6: Trace metals in well water during high and low water periods

	Trace metals (µg/L)			
	As	**Cd**	**Hg**	**Pb**
High water (n=9)				
Minimum	0,27	0,21	0,14	<DL
Maximum	4,28	0,64	2,57	1,8
Mean	1,95	0,38	1,56	0,81
SD	1,18	0,16	0,84	0,65
CV (%)	60	42,7	53,69	80,53
Low water (n=9)				
Minimum	<DL	0	<DL	<DL
Maximum	0,42	0,21	<DL	0,41
Average	0,046	0,034	<DL	0,046
SD	0,14	0,07	<DL	0,14
CV (%)	300	213,89	<DL	300
T-test (p)	0,0001881	0,00000267	0,0000048	0,0033
Beninese drinking water standard	50	5	1	50

DL = Detection Limits (µg/L): As = 0,02; Cd = 0,01; Hg = 0,08 et Pb = 0,05; SD = Standard Deviation

3.2.2. Borehole Water

The results of the descriptive statistical analysis of trace metal concentrations in borehole water, measured during the high-water and low-water periods, are summarized in Table 7.

According to the table, the average arsenic concentration in borehole water is 1.49 ± 1.39 µg/L during the high-water period, with a maximum value of 3.39 µg/L. In contrast, during the low-water period, the average arsenic concentration is 0.05 ± 0.14 µg/L, with a maximum concentration of 0.36 µg/L.

For cadmium, concentrations observed during the high-water period range from 0.06 to 0.62 µg/L, with an average of 0.31 ± 0.22 µg/L. During the low-water period, the maximum concentration recorded is 0.71 µg/L, with an average value of 0.11 ± 0.27 µg/L.

Regarding mercury, the average and maximum concentrations observed during the high-water period are 1.64 ± 3.02 µg/L and 11.8 µg/L, respectively. These values exceed the Beninese drinking water standard, which is set at 1 µg/L. During the low-water period, no mercury concentrations were detected, as values were below the detection limit of the instrument (0.08 µg/L).

Finally, for lead (Pb), the average and maximum concentrations during the high-water period were 0.25 ± 0.66 µg/L and 1.74 µg/L, respectively. During the low-water period, the average and maximum values were 0.13 ± 0.23 µg/L and 0.57 µg/L, respectively.

Table 7: Trace metals in borehole water During high and low water periods

	Trace metals (µg/L)			
	As	**Cd**	**Hg**	**Pb**
High water (n=7)				
Minimum	<DL	0,06	<DL	<DL
Maximum	3,39	0,62	8,15	1,74
Average	1,49	0,31	1,64	0,25
SD	1,39	0,22	3,02	0,66
CV (%)	93,44	70,81	183,36	264,58
Low water (n=7)	0,05			
Minimum	<DL	<DL	<DL	<DL
Maximum	0,36	0,71	<DL	0,57
Average	0,05	0,11	<DL	0,13
SD	0,14	0,27	<DL	0,23
CV (%)	264,58	248,5	<DL	179,97
T-test (p)	0,01858	0,1418	0,1746	0,65
Beninese drinking water standard	50	5	1	50

DL = Detection Limits (µg/L): As = 0,02; Cd = 0,01; Hg = 0,08 et Pb = 0,05; SD = Standard Deviation

3.2.3. Surface Water (Rivers + dam)

According to Table 8, which summarizes the descriptive statistics of trace metal concentrations in surface water during the study periods, the average arsenic concentration is 1.42 ± 0.93 µg/L during the high-water period. In contrast, during the low-water period, arsenic concentrations fall below the detection limit of the instrument (0.02 µg/L).

Regarding cadmium, the average concentration observed is 0.4 ± 0.18 µg/L during the high-water period. Similar to arsenic, no detectable cadmium concentrations were found during the low-water period, as the levels were below the detection limit of the instrument (0.01 µg/L).

For mercury, the recorded average and maximum concentrations were 1.79 ± 2.34 µg/L and 7.8 µg/L, respectively, during the high-water period. These values exceed the national drinking water standard for Benin, which is set at 1 µg/L. However, during the low-water period, the maximum observed concentration was 0.24 µg/L.

Concerning lead, the average concentration during the high-water period was 0.4 ± 0.57 µg/L, with a maximum value of 1.6 µg/L. During the low-water period, the average lead concentration was 0.23 ± 0.73 µg/L, with a maximum concentration of 3.63 µg/L.

Table 8: Trace Metals in Surface Water During High and Low Water Periods

	Trace metals (µg/L)			
	As	**Cd**	**Hg**	**Pb**
High water (n=26)				
Minimum	<DL	0,09	<DL	<DL
Maximum	3,15	0,78	7,8	1,6
Average	1,42	0,4	1,79	0,4
SD	0,93	0,18	2,34	0,57
CV (%)	65,22	45,82	130,07	142,63
Low water (n=26)				
Minimum	<DL	<DL	<DL	<DL
Maximum	<DL	<DL	0,24	3,63
Average	<DL	<DL	<DL	0,23
SD	<DL	<DL	0,04	0,73
CV (%)	<DL	<DL	509,9	316,87
T-test (p)	$3{,}228^{e-10}$	$1{,}18^{e-14}$	0,0002881	0,36
Beninese drinking water standard	**50**	**5**	**1**	**50**

DL = Detection Limits (µg/L): As = 0,02; Cd = 0,01; Hg = 0,08 et Pb = 0,05; SD = Standard Deviation

3.3. Comparative study of average trace metal concentrations in the water resources of the headwaters of Copargo watersheds

3.3.1. Comparison of average concentrations of as, cd, hg, and pb in well water, borehole water, and river water

Fig. 3 below illustrates a histogram presenting the average concentrations of each trace metal (arsenic, cadmium, mercury, lead) in well water, borehole water, and surface water (river) during both high-water and low-water periods. According to this comparison, well water shows the highest average concentrations of arsenic (0.99 µg/L), followed by borehole water (0.77 µg/L) and surface water (0.71 µg/L). However, these differences are not statistically significant ($p > 0.05$).

For cadmium, the average concentrations in all three types of water are almost identical, with 0.21 µg/L for both well water and surface water and 0.20 µg/L for borehole water, with no statistically significant difference ($p > 0.05$).

Regarding mercury, surface water exhibits the highest average concentration (0.9 µg/L), followed by borehole water (0.82 µg/L) and well water (0.78 µg/L). Again, no statistically significant difference was observed between these values ($p > 0.05$).

For lead, the highest average concentration is recorded in well water (0.43 µg/L), followed by surface water (0.31 µg/L) and borehole water (0.19 µg/L). The differences between these values are also not statistically significant ($p > 0.05$).

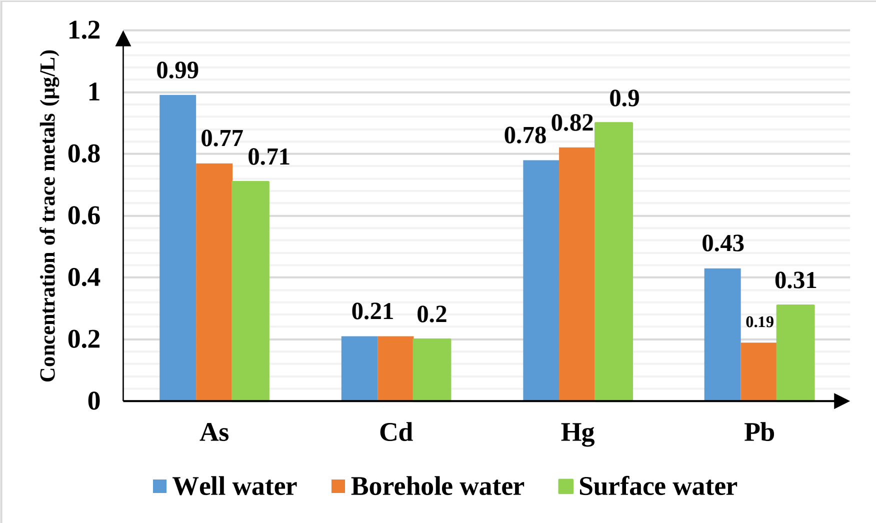

Fig. 3: Average concentrations of As, Cd, Hg, and Pb in well water, borehole water, and surface water for both study periods.

3.3.2. Comparison of average concentrations of as, cd, hg, and pb in groundwater and surface water

The average concentrations of trace metals observed in groundwater and surface water are presented in Figure 4. According to this figure, the concentrations of arsenic (As), cadmium (Cd), and lead (Pb), which are 0.9 µg/L, 0.21 µg/L, and 0.32 µg/L, respectively, are higher in groundwater compared to those observed in surface water. In contrast, for mercury (Hg), the concentrations measured in surface water (0.9 µg/L) slightly exceed those in groundwater (0.8 µg/L). However, it is important to note that the observed differences are not statistically significant.

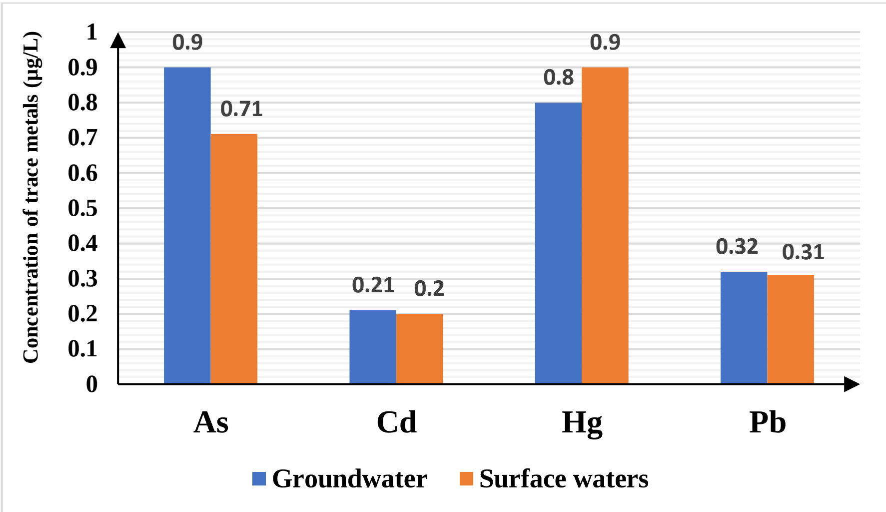

Figure 4: Average concentrations of As, Cd, Hg, and Pb in groundwater and surface water

3.4. Spatio-temporal variations in trace metal concentrations in water resources from the headwaters of the Copargo watersheds

3.4.1. Variation in arsenic (As) concentration

According to the data presented in Fig. 5, arsenic concentrations recorded in both groundwater and surface water during the high-water period are consistently higher than those observed during the low-water period. All arsenic concentrations measured in groundwater and surface water during the low-water period fall below the detection limit of the measurement instrument (0.001 µg/L), except at the following sampling points: well P8, borehole F5, and river R12, where concentrations of 0.42 µg/L, 0.36 µg/L, and 0.2 µg/L, respectively, were recorded.

During the high-water period, arsenic concentrations range from 0.27 µg/L at well P2 to 4.28 µg/L at well P5. For borehole waters, concentrations range from 0.36 µg/L at borehole F6 to 3.39 µg/L at borehole F7, while concentrations at boreholes F4 and F5 remain below the detection limit.

Concerning surface water, only river R15 shows arsenic concentrations that are undetectable by the instrument. For other measurement points, concentrations range from 0.2 µg/L at river R13 to 3.15 µg/L at river R4.

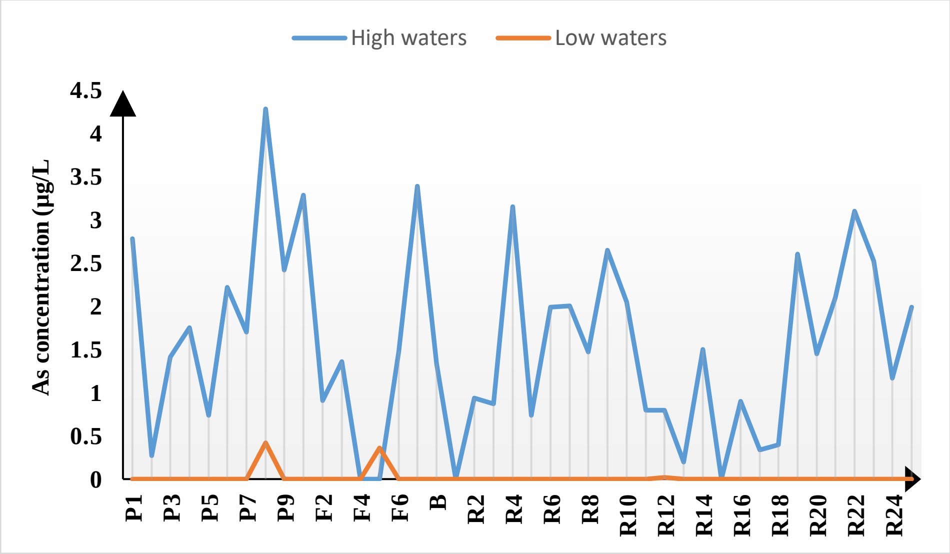

Fig. 5: Spatio-temporal variation in arsenic concentrations in groundwater and surface water

3.4.2. Variation in Cadmium (Cd) Concentrations

Fig. 6, which illustrates the distribution of cadmium (Cd) concentrations, shows that during the low-water period, cadmium was detected only in certain groundwater samples: wells P2 (0.21 µg/L) and P8 (0.1 µg/L), as well as boreholes F3 (0.04 µg/L) and F5 (0.06 µg/L). Regarding surface waters, only rivers R8, R12, and R18 recorded concentrations of 0.06 µg/L, 0.1 µg/L, and 0.02 µg/L, respectively, during the same period. In general, cadmium concentrations measured in both groundwater and surface water during the high-water period are higher than those observed during the low-water period. The concentrations observed during the high-water period range from 0.22 µg/L at well P3 to 0.64 µg/L at well P2, from 0.07 µg/L at borehole F3 to 0.62 µg/L at borehole F7, and from 0.09 µg/L at river R11 to 0.78 µg/L at river R7.

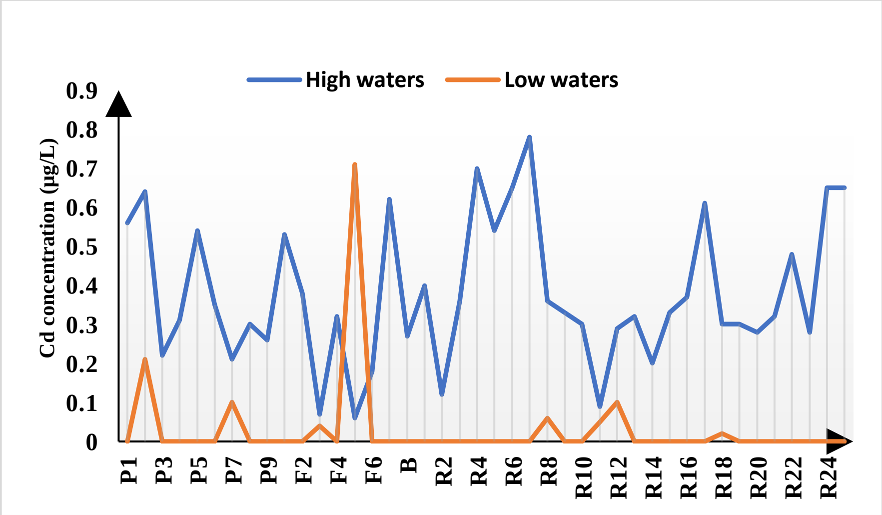

Fig. 6: Spatio-temporal variation in cadmium concentrations in groundwater and surface water

3.4.3. Variation in mercury (Hg) concentrations

The low-water period results depicted in Fig. 7 indicate that all of the water resources examined displayed mercury levels that were beneath the detection limit of the measuring device, except river R23, which recorded a concentration of 0.24 µg/L. During the high-water period, only 16.66% of the water samples analyzed displayed concentrations below the detection limit. For samples with concentrations exceeding the detection limit, mercury levels varied significantly. In groundwater, levels ranged from 0.14 µg/L at well P8 to 8.15 µg/L at borehole F1.

Mercury levels in surface water varied from 0.1 µg/L in river R12 to 7.8 µg/L in river R22. Thus, mercury concentrations observed during the high-water period were consistently higher than those measured during the low-water period.

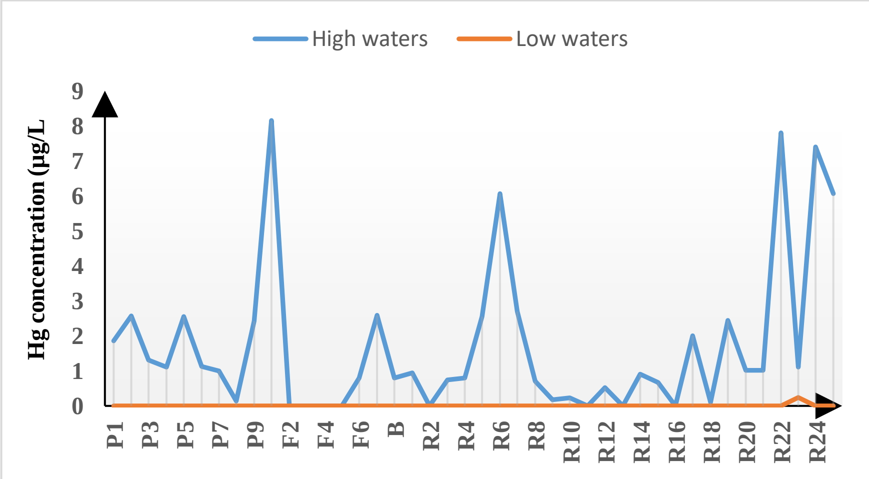

Fig. 7: Spatial and temporal variation in mercury concentrations in groundwater and surface water

3.4.4. Variation in lead (Pb) concentrations

According to Fig. 8, which illustrates the Spatial and temporal variation in lead concentrations in groundwater and surface water, it appears that concentrations measured during the high-water period are higher than those observed during the low-water period, except for river R8, where the lead concentration reaches 3.63 µg/L.

During the high-water period, 59.53% of the sampled sites exhibited lead concentrations below the detection limit of the measurement instrument, compared to 78.57% during the low-water period. The recorded concentrations range from 0.06 µg/L at well P9 to 1.74 µg/L at borehole F1 for groundwater, and from 0.09 µg/L in river R19 to 1.6 µg/L in river R22 for surface water during the high-water period. In the low-water period, concentrations range from 0.32 µg/L at borehole F4 to 0.57 µg/L at borehole F3 for groundwater, and from 0.35 µg/L in river R13 to 3.63 µg/L in river R18 for surface water.

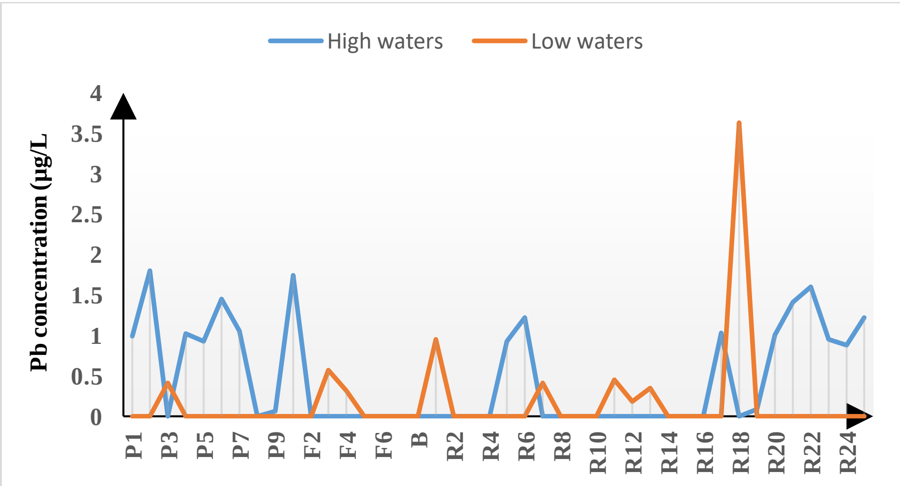

Fig. 8: Spatial and temporal variation in lead concentrations in groundwater and surface water

3.5. Multivariate statistical analysis

3.5.1. Pearson correlation

The relationship between the variables, along with the corresponding correlation coefficients, are presented in the correlation matrices shown in Fig. 8A and 8B for the high-water and low-water periods, respectively. According to the adopted representation model, a stronger correlation between two variables is indicated by a darker blue color.

Analysis of Fig. 8A, which pertains to the high-water period, reveals a significant correlation between lead (Pb) and mercury (Hg) (64%), as well as between cadmium (Cd) and mercury (Hg) (61%). In contrast, analysis of Fig. 8B, corresponding to the low-water period, highlights more pronounced correlations between cadmium (Cd) and arsenic (As) (59%) and between temperature and conductivity (64%).

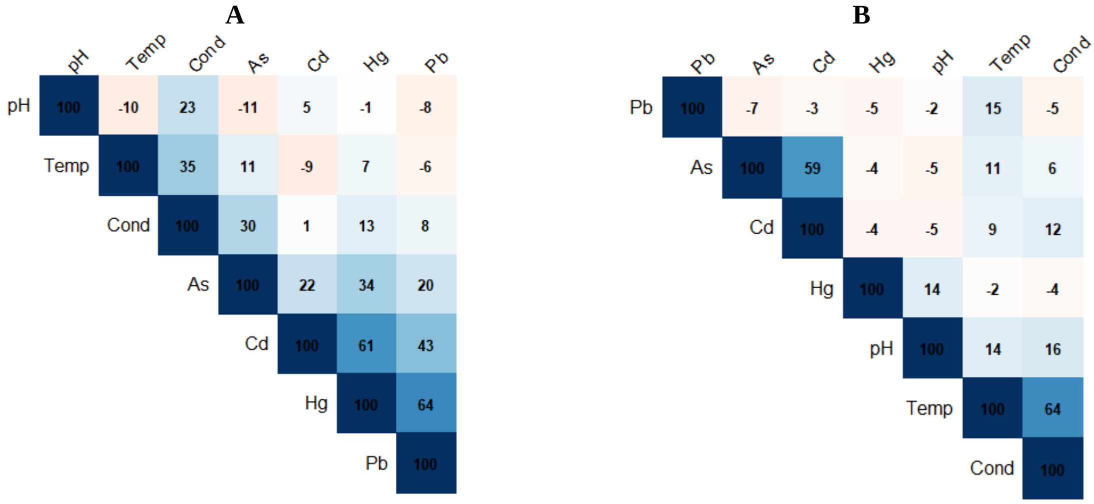

Fig. 8: Pearson correlation between chemical elements during the high-water period (A) and the low-water period (B)

3.5.2. Principal Component Analysis (PCA)

- ✓ **Selection of the number of principal axes**

In this study, the selection of the number of principal axes was determined based on the proportion of variance explained, considering a threshold of 75% and the elbow rule. Fig. 10 and 11 present the percentages of variance explained by each principal component, for the high-water and low-water periods, respectively.

The application of the elbow rule to the variance curves reveals a noticeable inflection point starting from the fourth component in Fig. 10 and 11. This observation led us to retain the first four principal components, which explain the maximum amount of relevant information. As a result, the eigenvalues, along with the explained and cumulative variance percentages for the first four factors, are summarized in Table 7.

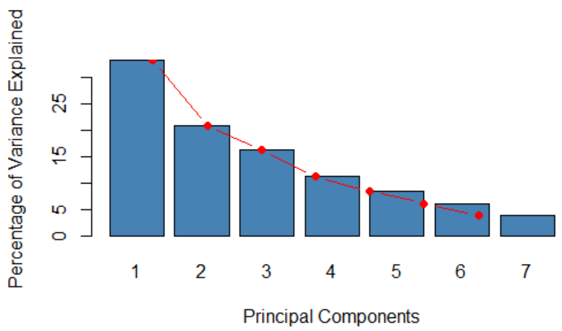

Fig. 10: Percentage of variance explained by each component during the high-water period

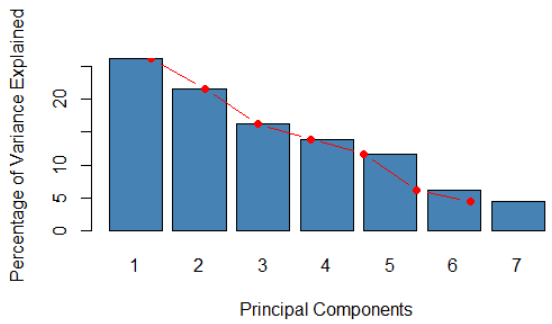

Fig. 11: Percentage of variance explained by each component during the low-water period

According to the results presented in Table 9, the variability explained by the first two principal components of the PCA during both the high-water and low-water periods remains below 75%. The factor plane (F1 × F2) explains 54% of the variance during the high-water period and 47.72% during the low-water period. In contrast, the factor plane (F1 × F3) explains 70.26% of the variance during the high-water period and 63.94% during the low-water period. These levels of variability are therefore not sufficiently significant to allow for a clear interpretation of the overall behavior of the samples. Consequently, the first four principal components were retained, as they together explain a larger proportion of the total variance. Thus, these four components explain 81.49% of the variance during the low-water period (F1 = 33.15%, F2 = 20.85%, F3 = 16.26%, F4 = 11.22%), and 77.82% of the total variance during the high-water period (F1 = 26.11%, F2 = 21.61%, F3 = 16.21%, F4 = 13.88%).

Table 9: Eigenvalues and percentage of variance explained during the high-water and low-water periods

	High water				**Low water**			
	F1	**F2**	**F3**	**F4**	**F1**	**F2**	**F3**	**F4**
Eigenvalues	2,32	1,46	1,14	0,79	1,82	1,51	1,13	0,97
% of Variance Explained	33,15	20,85	16,26	11,22	26,11	21,61	16,21	13,88
Cumulative % of Variance Explained	33,15	54	70,26	81,49	26,11	47,72	63,94	77,82

✓ Projection of variables in the factorial plane f1 × f2

Principal Component Analysis (PCA) in the factorial plane F1 × F2, for the high-water and low-water periods, is illustrated in Fig. 13. This figure highlights the observed groupings along the factorial axes. Thus, the factorial axis F1 (explaining 33.1% of the variance) is primarily associated with mercury (Hg), lead (Pb), and cadmium (Cd) during the high-water period (Fig. 13A), while the factorial axis F2 (explaining 21.6% of the variance) is associated with arsenic (As) and cadmium (Cd) during the low-water period (Fig. 13B). These factorial axes reflect the accumulation of water resources enriched in trace metals; a phenomenon likely linked to anthropogenic activities.

Furthermore, factorial axis F2 (explaining 20.9% of the variance) during the high-water period (Fig. 13A) and axis F1 (explaining 26.21% of the variance) during the low-water period (Fig. 13B) are each positively influenced by physicochemical variables such as electrical conductivity and temperature. These axes thus reflect the physicochemical characteristics of the water resources, which are influenced by the nature of the underlying rocks, the characteristics of the water reservoir, and the ambient temperature.

A **B**

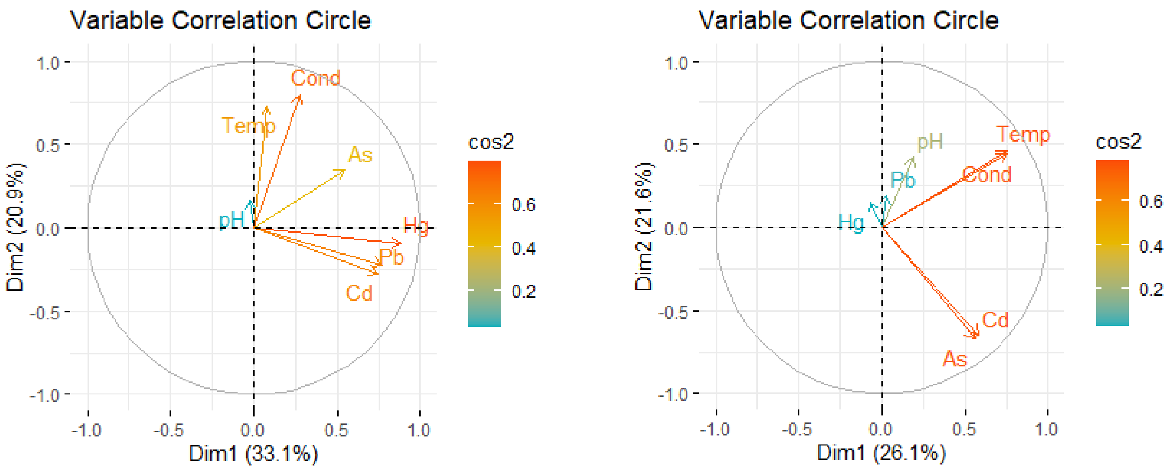

Fig. 13: Factorial variables in the F1 × F2 space during the high-water period (A) and the low-water period (B)

✓ Projection of sampling sites (individuals) and variables in the factorial plane F1 × F2

Fig. 14 presents the overlay plots of sampling sites and studied variables with a squared cosine greater than 50%, for both the high-water and low-water periods. This representation allows the distinction of three groups of sampling sites during the high-water period (Fig. 14A), reflecting three types of water in the study area.

The first group consists exclusively of river waters (R6, R7, R22, R24, and R25), characterized by high concentrations of cadmium (Cd) and mercury (Hg). The second group is made up solely of borehole waters (F1 and F7), which are distinguished by high temperatures and conductivities, as well as significant concentrations of cadmium (Cd) and mercury (Hg). The third group includes well waters (P9) and borehole waters (F2 and F6), characterized by high conductivities and temperatures as well.

During the low-water period (Fig. 14B), two distinct groups of sampling sites are observed. The first group includes well waters (P6 and P9) and borehole waters (F1, F2, F3, F5, and F6), which exhibit high temperatures and conductivities during this period. The second group consists solely of the water from borehole F5, which is distinguished by relatively high concentrations of arsenic (As) and cadmium (Cd).

A B

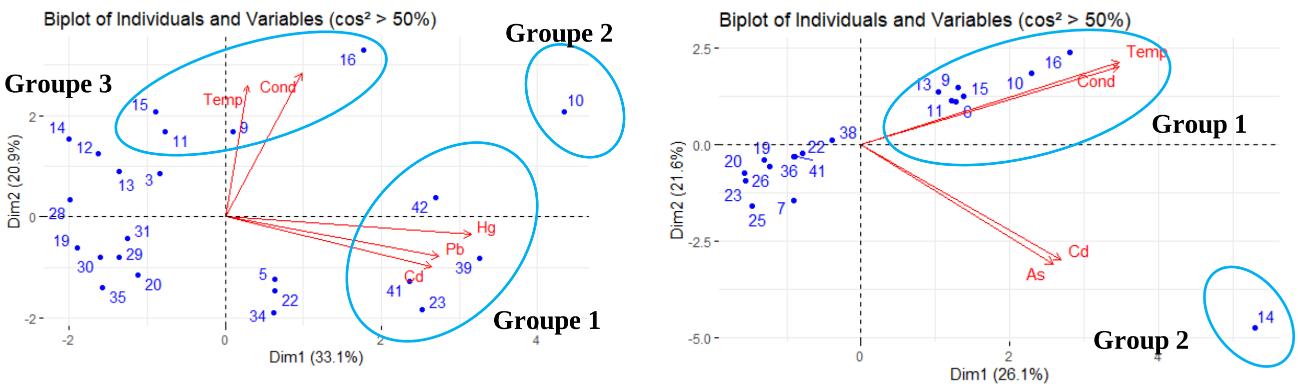

Fig. 14: Overlay plots of individuals (sampling sites) and variables in the factorial plane F1 × F2 during the high-water period (A) and the low-water period (B)

✓ **Projection of variables in the factorial plane F3 × F4**

Fig. 15 presents the projection of variables in the space defined by the factorial axes F3 × F4, for both the high-water and low-water periods.

During the high-water period (Fig. 15A), the factor F3 (explaining 16.3% of the variance) is primarily determined by pH. This axis therefore reflects the alkalinity of the water resources. Factor F4 (explaining 11.2% of the variance) is defined, in its negative part, by arsenic (As). These axes highlight the chemical properties of the water resources, particularly alkalinity and the presence of arsenic.

During the low-water period (Fig. 15B), factor F3 (explaining 16.2% of the variance) is positively influenced by mercury (Hg), while factor F4 (explaining 13.9% of the variance) is defined, in its positive part, by lead (Pb). These findings indicate that the existence of these trace metals in water resources could be associated with human activities, like industrial or agricultural practices.

A B

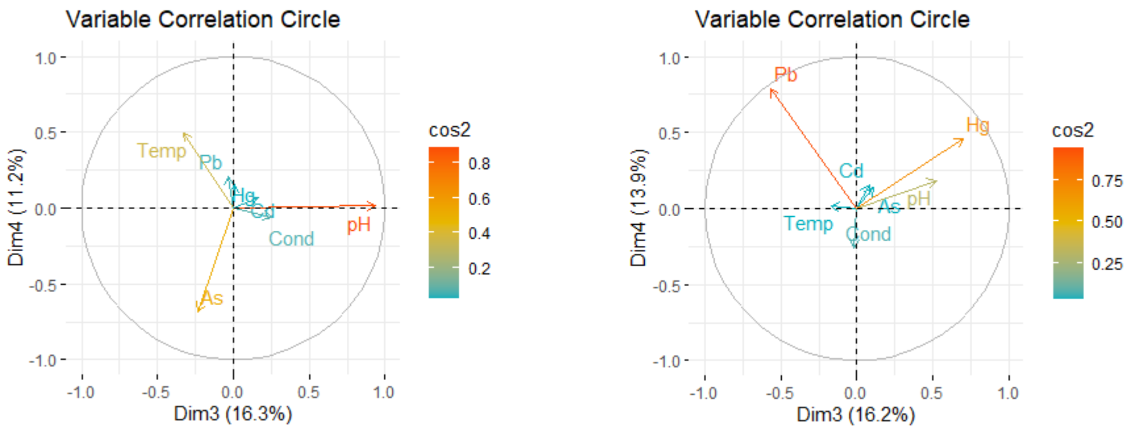

Figure 15: Factorial variables in the F3 × F4 space during the high-water period (A) and the low-water period (B)

✓ **Projection of sampling sites (individuals) and variables in the f3 × f4 factorial plane**

Fig. 16 presents the biplots of the sampling sites and variables with a squared cosine greater than 50% for both high-water and low-water periods (Fig. 16A and 16B). These projections allow for the identification of two distinct groups of sampling sites for each period, corresponding to two specific types of water.

During the high-water period (Fig. 16A), the first group consists exclusively of well P4, which stands out from the others due to its slightly alkaline pH, higher than neutral. The second group includes water from well P8, as well as from rivers R4 and R11. Waters in this group are characterized by relatively high concentrations of arsenic (As).

In the low-water period (Fig. 16B), two groups are observed, both consisting solely of river waters. The first group is formed by river R23, whose waters exhibit high concentrations of mercury (Hg). The second group comprises rivers R1 and R18, which are characterized by elevated levels of lead (Pb) compared to other water resources in the study area.

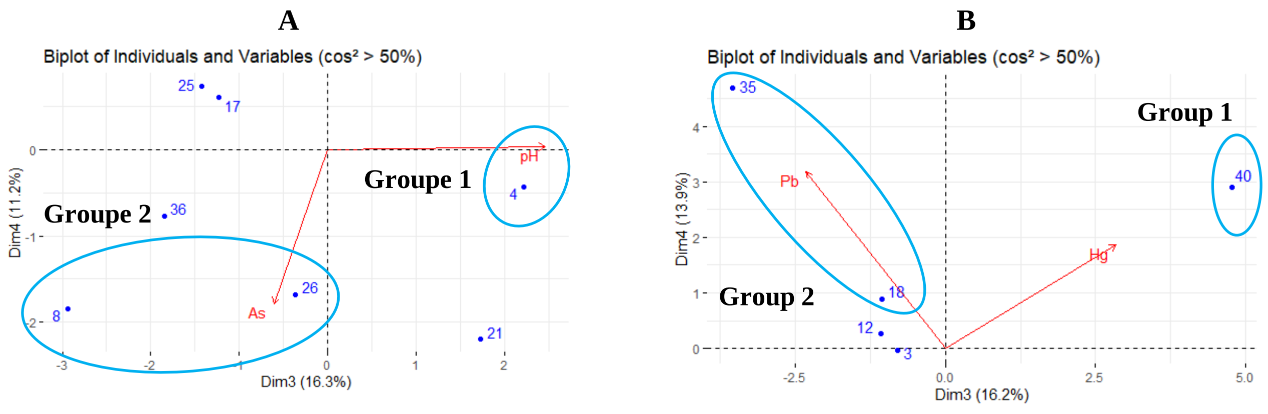

Fig. 16: Biplots of sampling sites (individuals) and variables in the F3 × F4 factorial plane during the high-water (A) and low-water (B) periods.

3.6. Contamination and pollution indices for water resources by trace elements

3.6.1. Contamination factor (CF), degree of contamination (DC), and pollution load index (PLI)

The average values of the contamination factor (CF), degree of contamination (DC), and pollution load index (PLI) are presented in Table 10. Analysis of this table reveals that wells, boreholes, and river waters exhibit low contamination by arsenic (As), cadmium (Cd), and lead (Pb) ($CF < 1$) during both high-water and low-water periods. However, well and river waters show moderate contamination by mercury (Hg) ($1 < CF < 3$) during the high-water period, while borehole waters demonstrate considerable contamination by mercury ($CF = 3.979$) during the same period.

Regarding the degree of contamination (DC), which estimates the intensity of water contamination, it indicates a high level of contamination for borehole waters during the high-water period (DC > 3). Well and river waters, on the other hand, show a moderate degree of contamination (1 < DC < 3) during this period.

Finally, the pollution load index (PLI), which assesses the overall level of pollution in water resources, indicates the presence of pollutants in all resources (wells, boreholes, and rivers), but at relatively low levels (PLI < 1).

Table 10: Contamination (CF and DC) and pollution indices (PLI) for water resources in Copargo

		CF				DC	PLI
		As	**Cd**	**Hg**	**Pb**		
Wells water	High water	0,039	0,075	**1,564**	0,021	**1,699**	0,099
	Low water	0,008	0,031	< DL	0,008	0,119	0,013
Boreholes water	High water	0,042	0,062	**3,84**	0,035	**3,979**	0,137
	Low water	0,007	0,075	< DL	0,009	0,091	0,018
Rivers	High water	0,031	0,079	**2,126**	0,021	**2,257**	0,145
	Low water	0,0004	0,011	0,24	0,02	0,271	0,007

3.6.2. Classification of water quality in the headwaters of the Ouémé and Pendjari river basins in the Copargo municipality based on contamination degree and pollution load index

The results of the classification of sites based on their degree of contamination and pollution level are presented in Table 11. Analyzing this table, it is observed that 11.11% of the wells exhibit a low degree of contamination, while 88.89% of the wells are characterized by a moderate degree of contamination. Regarding the pollution load index (PLI), 100% of the wells display a low level of pollution. For boreholes, 71.4% show a low degree of contamination, while 14.3% are categorized as having moderate to high contamination levels. However, concerning the PLI, 100% of the boreholes have a low pollution level. Regarding surface waters, the analysis of contamination degrees reveals that 53.85% of the sites, including one reservoir and 13 rivers, are weakly contaminated, while 46.15%, representing 12 rivers, exhibit a moderate degree of contamination. Similar to groundwater, the pollution load index for surface waters shows that 100% of the rivers and the reservoir have a low pollution level.

Table 11: Classification of water resource quality in the study area based on contamination degree and pollution load index

	Index	Classification	Contamination and pollution degree	Number of samples	% of samples	Sampling site
Wells n = 9	**DC**	< 1	Low	01	11,11	P8
		1 < DC < 3	Medium	08	88,89	P1-P7, P9
		> 3	High	00	0,0	-
	PLI	= 0	Perfection	0	0,0	-
		< 1	Low level	9	100	P1-P9
		= 1	Threshold level	0	0,0	-
		> 1	Deterioration of quality	0	0,0	-
Boreholes n = 7	**DC**	< 1	Low	5	71,4	F2-F6
		1 < DC < 3	Medium	1	14,3	F7
		> 3	High	1	14,3	F1
	PLI	= 0	Perfection	0	0,0	-
		< 1	Low level	7	100	F1-F7
		= 1	Threshold level	0	0,0	-

		> 1	Deterioration of quality	0	0,0	-
Rivers + dam n = 26	**DC**	< 1	Low	14	53,85	B, R2, R3, R8-R16, R18, R23
		1 < DC < 3	Medium	12	46,15	R1, R4-R7, R17, R19-R22, R24-R25
		> 3	High	0	0,0	-
	PLI	= 0	Perfection	0	0,0	-
		< 1	Low level	26	100	B, R1-R25
		= 1	Threshold level	0	0,0	-
		> 1	Deterioration of quality	0	0,0	-

4. DISCUSSION

***In-situ* measurements (temperature, pH, and electrical conductivity)**

The groundwater and surface water in the headwaters of the Copargo catchments exhibit average temperatures of 27.72°C for wells, 29.68°C for boreholes, and 26.72°C for rivers and reservoirs. These values exceed both the Beninese standard (25°C) and the World Health Organization (WHO) guideline value (25°C) (République du Bénin, 2001; World Health Organization, 2017). Water temperature is a critical ecological factor with the potential to significantly influence aquatic ecosystems (Leynaud, 1968). However, although the observed temperatures surpass the 25°C threshold, they do not pose an immediate health risk to consumers. These temperature variations are largely influenced by environmental conditions, local geography, the geology of the aquifers, the hydrology of the area, and, most notably, the climate (Rodier, 1984).

The average pH values of groundwater and surface water in the study area are slightly below 7, indicating a moderate acidity of the water resources. Generally, water exhibits a more acidic pH during low-flow periods compared to high-flow periods. This trend is characteristic of humid tropical zones, where acidification primarily results from the biodegradation of plant matter, a process intensified by low rainfall during dry seasons. This biodegradation produces CO_2 in the upper soil layers, contributing to water acidity (Ahoussi et al., 2010). Our study's findings align with these observations during low-flow periods. Regarding surface waters, our results are consistent with those of Veneros et al. (2024), whose study highlighted higher pH values during the rainy season compared to the dry season. These authors reported average pH levels of 8.38 during the wet season, in contrast to 7.7 during the dry season. However, our results differ slightly from those of Orou et al. (2016), who recorded pH values of 6.10 and 6.30 during the rainy and dry seasons, respectively, in the groundwater of the Agboville basement zone. Similarly, Traore et al. (2022) reported pH values of 6.22 and 6.67 during the rainy and dry seasons, respectively, in the groundwater of the Man basement zone. These studies demonstrated slightly higher acidity in groundwater during the rainy season. Regarding surface water, our results also contrast with those of Zinsou et al. (2016), who measured average pH values of 6.22 and 6.34 during the high-flow and low-flow periods, respectively, in the Ouémé River. The observed discrepancies may be attributed to differences in measurement accuracy and the unique geological and hydrogeological characteristics of each study area.

As for electrical conductivity, the low values observed in both groundwater and surface water suggest that the water resources in the headwaters of the Copargo catchments are weakly mineralized. Indeed, 95.24% of the analyzed samples exhibit conductivities below 400 µS/cm, a threshold beyond which the WHO recommends increased monitoring. Only 4.76% of the samples exceed this limit, remaining well below the Beninese standard of 2000 µS/cm. It is noteworthy that water is more mineralized during low-flow periods, with an average conductivity of 196.71 µS/cm, compared to 172.92 µS/cm during high-flow periods. This difference is primarily attributable to the dilution effect of surface waters during heavy rainfall, which infiltrates and mixes with groundwater, reducing electrical conductivity and the mineralization of water resources. In comparison with the findings of Veneros et al. (2024), our results also confirm an increase in the electrical conductivity of surface waters during the dry season relative to the rainy season. Indeed, these authors reported average conductivities of 55.5 µS/cm during the rainy season, compared to 89.78 µS/cm in the dry season. These low electrical conductivities and therefore mineralization during the rainy season also reflects the influence of rainfall inputs, which alter the physical and chemical characteristics of the region's water resources, particularly during high-flow periods.

Trace metal elements (TME) in water resources

The trace metal elements (TME) analyzed in this study, namely arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb), were detected at least once in the water resources of the study area, which includes wells, boreholes, rivers, and a reservoir, during the two measurement periods. Descriptive statistical analysis of the concentrations of these TMEs in different water resources revealed that the mean and maximum concentrations of As, Cd, and Pb were all below Benin's drinking water quality standards. In contrast, for mercury (Hg), the mean and maximum concentrations observed in both groundwater and surface water exceeded the thresholds set by Beninese regulations, particularly during the high-water period. Indeed, the highest TME concentrations were recorded during this period, while during the low-water period, most concentrations were undetectable due to the detection limit of the measurement equipment used.

During the high-water period, arsenic (As) was present in 100% of well water, 71.43% of borehole water, and 92.31% of surface water. In contrast, cadmium (Cd) was detected in 100% of wells, boreholes, and surface water samples. Mercury (Hg) was found in 100% of well water, 42.86% of borehole water, and 84.62% of surface water. Lead (Pb) was present in 88.88% of well water, 14.89% of borehole water, and 38.46% of surface water. During the low-water period, 88.88% of well water, 85.71% of borehole water, and 96.15% of river water exhibited arsenic concentrations below the detection limit of the equipment (0.01 µg/L). For cadmium, 77.77% of well water, 71.43% of borehole water, and 84.62% of surface water had concentrations below this limit. For mercury, 100% of well and borehole water and 95.15% of surface water displayed concentrations below the detection limit. Lead concentrations were below the detection limit in 88.88% of well water, 71.43% of borehole water, and 76.92% of surface water. The findings indicate that lead levels in water resources tend to be more enduring than those of other trace metal elements (TMEs) during periods of low water, likely because of lead's extensive and longstanding utilization since ancient times (Adje et al., 2021).

The results highlight significant variability in TME concentrations depending on the period and sampling sites. Concentrations observed during the high-water period were higher than those during the low-water period ($p < 0.05$), consistent with Ajdé et al. (2021), who reported temporal variations in TME concentrations in Lake Nangbéto, Togo. Similarly, the study by Sun et al. (2019) revealed that the concentrations of heavy metals analyzed in the surface water of a small plain stream in eastern China are higher during the high water period (August) compared to the low water period (October). This variability appears primarily driven by TME inputs associated with agricultural practices, particularly pesticide use (insecticides and herbicides), which are leached or carried by runoff into surface water or infiltrated into groundwater. The high-water period, favorable for agricultural activities, thus promotes higher contamination levels. Spatial variability in TME concentrations largely depends on anthropogenic activities, notably agricultural and urban practices near water resources, with surface waters, particularly rivers and reservoirs, being more exposed.

The TME concentrations measured generally remain below Benin's drinking water standards, except for mercury. Maximum mercury concentrations in well water (2.53 µg/L), borehole water (8.15 µg/L), and surface water (7.8 µg/L) exceeded the regulatory thresholds for drinking water quality in Benin (1 µg/L). However, these values remain below WHO guidelines.

A comparison of TME concentrations among different water resources (wells, boreholes, rivers) did not reveal statistically significant differences ($p > 0.05$), suggesting these variations may result from random effects. Overall, concentrations of As, Cd, and Pb were slightly higher in groundwater than in surface water. In contrast, mercury concentrations were higher in surface water, likely due to the facilitated transport of mercury by runoff. Generally, well water contains higher concentrations of As, Hg, Pb, and Cd, in that descending order. These findings differ from those of Kpiagou et al. (2022), who reported a different frequency order of As, Cd, Hg, and Pb concentrations in well water from the Didagou watershed in Togo.

Sampling site groups identified by principal component analysis (PCA) are located in anthropized areas characterized by agricultural and urban practices. These activities likely explain the presence of TMEs in water resources in the headwaters of the Copargo watershed. Local agricultural practices, such as pesticide use, represent a significant source of water resource contamination. According to Kondo et al. (2024), insecticides and herbicides are used in 35.71% and 54.29% of cases, respectively, by agricultural producers. The use of these pesticides near water resources, especially surface water, is a major source of pollution. The presence of TMEs in surface water reflects recent pollution by these elements. The effects of TMEs on public health and the environment are extensively documented, showing clear connections between their presence in food chains and illnesses like cancer. Furthermore, heavy metals from public landfills contaminating drinking water resources pose significant environmental risks, particularly in rural areas where environmental conditions are as concerning as in urban areas (Chofqi et al., 2004; Ogoronon, 2007).

The calculated contamination and pollution indices for water resources provide a detailed overview of their quality. The contamination index for arsenic, cadmium, and lead indicates low contamination levels, with contamination factors (CF) below 1, suggesting limited presence of these elements in water resources. In contrast, mercury has a CF greater than 1, indicating significant contamination. Regarding pollution, mercury concentrations in wells, borehole, and river water exceed Benin's standards for drinking water by 1.564, 3.84, and 2.126 times, respectively, indicating non-compliance with drinking water standards for mercury. The pollution load index revealed that all water types studied exhibit low pollution levels. Regarding the degree of contamination, 88.89% of well water, 46.15% of surface water, and 14.3% of borehole water show moderate contamination levels, requiring enhanced monitoring. For 14.3% of boreholes, water exhibits a high degree of contamination, warranting their closure to protect public health.

Most other studies conducted on TME in other developing regions also show a concerning prevalence of metal contamination in various types of water in Africa and elsewhere (Azokpota et al., 2021; Hizir, 2024; Kone et al., 2024; Kpiagou et al., 2022). They identify mining, agricultural activities, and domestic waste discharge as the main sources of pollution. The diversity of geographical contexts and methodologies enriches the overall understanding of the impact of trace metals on water resources.

Specifically, within the framework of our study, public authorities must strengthen regulations and controls on agricultural inputs, establish hydrological monitoring stations in the watershed heads to monitor water quality in real time and identify potential pollution sources, strengthen water quality monitoring, develop an Integrated headwater management plan for the Ouémé and Pendjari rivers, conduct awareness-raising and educational actions for stakeholders.

In light of result, particularly concerning mercury, it is essential to take the action to reduce its contamination in the area. To achieve this, it will be necessary to address the source by limiting the use of pesticides and fertilizers containing mercury and promoting sustainable agricultural alternatives. Improved agricultural practices, such as conservation farming and vegetated buffer zones, can minimize the leaching of pollutants. Treating contaminated water, through suitable technologies such as activated carbon filtration, is crucial for securing water resources. Integrated watershed management, combined with ecosystem restoration, will strengthen natural protection against pollution. Community awareness and farmer training are necessary to encourage responsible practices. Additionally, regular monitoring of mercury levels, research on its sources, and technological advancements will help guide actions. Finally, a strict legal framework, supported by financial incentives and regional collaborations, will ensure the effective implementation of strategies, thus contributing to the protection of public health and the environment.

5. CONCLUSIONS

This study, conducted on the water resources of the headwaters of the Ouémé and Pendjari rivers in the municipality of Copargo, revealed the presence of arsenic, cadmium, mercury, and lead in wells, boreholes, and surface water at varying concentrations, and assessed their contamination levels. All measured trace metal element (TME) concentrations were below Benin's drinking water standards, except for mercury, whose recorded concentrations during the high-water period exceeded the regulatory threshold. However, compared to WHO standards, all measured concentrations of TME (As, Cd, Hg and Pb) are below the WHO guideline values. The assessment indicates low contamination levels for arsenic, cadmium, and lead, whereas mercury contamination ranged from moderate to high, particularly in groundwater resources. The highest contamination levels were observed during the high-water period, coinciding with the intensification of agricultural activities. Based on the pollution load index, groundwater, and surface water resources exhibited low pollution levels for the analyzed trace elements. While naturally occurring, these trace metal elements may also originate from industrial, mining, and agricultural activities. Our findings highlight significant pollution risks from agricultural inputs, particularly pesticides. Although the observed concentrations are generally below drinking water standards, their presence warrants continuous monitoring due to their cumulative toxicological risks. As an outcome of this study, further research will involve conducting complementary studies on the transport and fate of trace metals in the headwaters to better understand their contamination mechanisms. Additionally, the development of modeling tools for the transfer of these pollutants will allow for forecasting the impact of human activities on water resource quality. Finally, solutions for treating water in which mercury concentrations exceed the standards will be sought, or if necessary, banning the consumption of such water by the population.

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