

## Assessing heavy metal pollution in mangrove ecosystems of the Kribi-Campo sub-basin, Cameroon

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### Abstract

Mangrove ecosystems provide crucial ecological services, yet they are increasingly threatened by anthropogenic pollution, particularly from heavy metals. This study investigated heavy metal contamination (Pb, Fe, Ni, Cu) in four mangrove sites within the Kribi-Campo sub-basin, Cameroon, during the dry and rainy seasons of 2023. Physicochemical parameters (temperature, pH, conductivity, dissolved oxygen, salinity) were measured *in situ*, and heavy metal concentrations in water samples were determined using X-ray fluorescence spectrometry. Results revealed spatial variations in physicochemical parameters, with the Mpolongwé site showing excessive mineralization (conductivity > 1000  $\mu\text{S}/\text{cm}$ ) likely attributed to industrial and domestic effluents. Lead contamination was restricted to Londji (0.05 - 0.21 mg/L), potentially linked to fishing activities. Iron concentrations were highest at Londji (0.67 mg/L) and Nziou (0.61- 0.68 mg/L), while nickel was absent only at Eboundja. Notably, copper was ubiquitous across all sites (2.68 - 3.31 mg/L), highlighting its widespread distribution. Londji emerged as the most contaminated site, harboring detectable levels of all analyzed metals. These findings underscore the vulnerability of Kribi's mangroves to heavy metal pollution, emphasizing the need for continuous monitoring and implementation of mitigation measures to ensure the sustainable management of this valuable ecosystem.

**Keywords:** Physico-chemical parameters; Contamination; Heavy metal contents; Mangroves; Kribi

### 1. Introduction

Mangroves are a characteristic forest formation of muddy tropical coastal environments, mainly composed of mangrove trees (Ajonina *et al.*, 2015). Nakouzi *et al.* (2018) define mangroves as a complex ecosystem composed primarily of woody vegetation, found in the intertidal zone along the low-lying coasts of tropical regions. These authors only considered the vegetation and geographical location when defining mangroves. However, Taureau *et al.* (2015) define mangroves as "any ecological system characterized by a salty and hypoxic substrate supporting halophytic vegetation,

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mainly woody, located in the intertidal zones of regions where the average seawater temperature of the coldest month is higher than 20 °C."

In Cameroon, numerous authors have highlighted the goods and services provided by mangrove ecosystems (Ajonina and Eyango, 2014; Ajonina *et al.*, 2015; MINEPDEP-RCM, 2017).

**Table 1** Goods and Ecosystem Services (MINEPDEP-RCM, 2017)

<b>Provisioning (Goods &amp; Products)</b>	<b>Regulating (Natural Processes)</b>	<b>Supporting (Natural Processes that Maintain Other Ecosystem Services)</b>	<b>Cultural (Non-material Benefits)</b>
<ul style="list-style-type: none"> <li>* Forest resources (food products, fuelwood, tannins &amp; resins, ornamentals, fodder, construction material)</li> <li>* Fisheries (crustaceans, fish, shrimp and other marine species)</li> <li>* Genetic resources (wild species and genes used for animals, plants, breeding, biotechnology derived from mangrove species)</li> <li>* Biochemical/medicine (traditional and commercial medicine from leaves, fruits, bark and other material)</li> </ul>	<ul style="list-style-type: none"> <li>* Blue carbon storage and sequestration (provide a high rate of stored and sequestered carbon)</li> <li>* Erosion control (contribute to wave attenuation and soil stabilization)</li> <li>* Flood regulation (protect coasts from storms, floods, etc.)</li> <li>* Biofiltration (removal of excess nutrients)</li> <li>* Water regulation (water capture and aquifer recharge)</li> </ul>	<ul style="list-style-type: none"> <li>* Nutrient cycling (maintaining nutrient flows from soils and surrounding vegetation)</li> <li>* Soil stabilization (roots impede water movement and trap sediments)</li> <li>* Primary production (production of organic matter through photosynthesis)</li> <li>* Oxygen production (oxygen released during photosynthesis)</li> <li>* Provision of essential habitat (nursery areas) for a wide range of flora and fauna</li> </ul>	<ul style="list-style-type: none"> <li>* Aesthetics (beautiful landscapes and views)</li> <li>* Educational (research, education and training opportunities)</li> <li>* Recreational, ecotourism (canoeing, sport fishing, walking, bird watching, kayaking)</li> <li>* Heritage and spiritual (local communities place cultural and spiritual value on mangroves)</li> </ul>

Despite all these advantages, pollutants of various natures reach this sensitive ecosystem. These include physical, biological, and chemical agents, and it is the pollution from these latter agents, especially certain heavy metals, that will be the focus of this work.

Chemical pollution results from the release into water of various toxic metals, inorganic substances, mineral salts used in agriculture as fertilizers, and various chemical compounds discharged by industries (Degbey *et al.*, 2010). These chemical pollutants are harmful to fauna, flora, and humans who exploit mangroves. This is because what is diluted in the water is sometimes invisible, and some toxic elements that have infiltrated the water and soil often only produce their effects after a long delay (Ebonji Seth, 2019).

The problems associated with heavy metal contamination were first highlighted in industrialized countries, due to their greater industrial, agricultural, and urban development, inevitably accompanied by problems of aquatic environmental pollution (Nakhlé, 2003).

Cameroon is among the few countries in the world home to mangroves naturally found in intertidal zones in tropical and subtropical areas (MINEPDEP-RCM, 2017). Along the Cameroonian coast, mangroves like those of Kribi are subjected to heavy metal pollution from various sources, which negatively impacts fishery resources in this ecosystem. Although the presence of heavy metals in the environment has gained increasing importance in terms of control in recent years, the lack of studies in Kribi on water contamination by heavy metals, particularly lead, nickel, copper, and iron, in mangrove areas raises questions about their concentrations and their effects on not only the environment but also on health. The degradation of mangrove ecosystems is a reality and should therefore be at the center of socioeconomic, political, and scientific concerns.

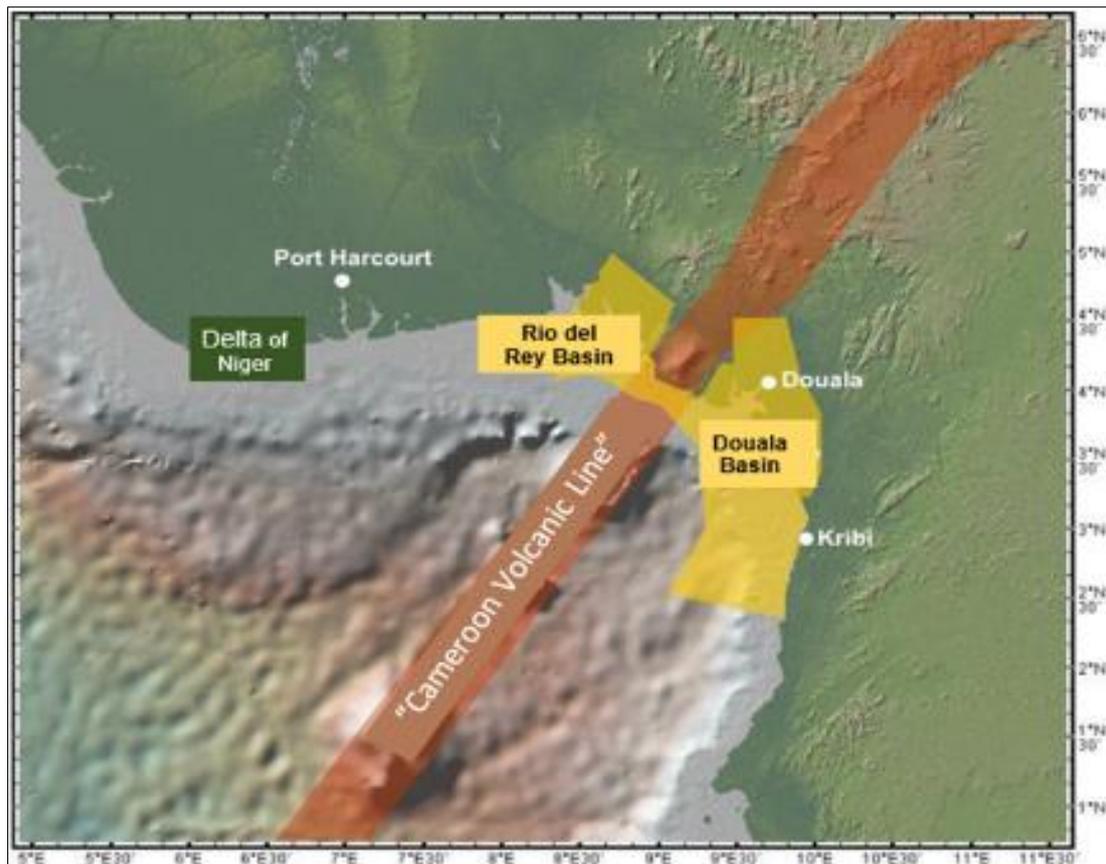
The general objective of this study is to contribute to the sustainable management of mangroves in Kribi (South Cameroon) by assessing the contamination of their waters by heavy metals. More precisely, it aims to characterize the physicochemical environment of the sites and determine the levels of heavy metals present.

## 2. Materials and methods

### 2.1. Geological Context of the Kribi Sub-Basin

#### 2.1.1. Genesis of Cameroon's Coastal Basins

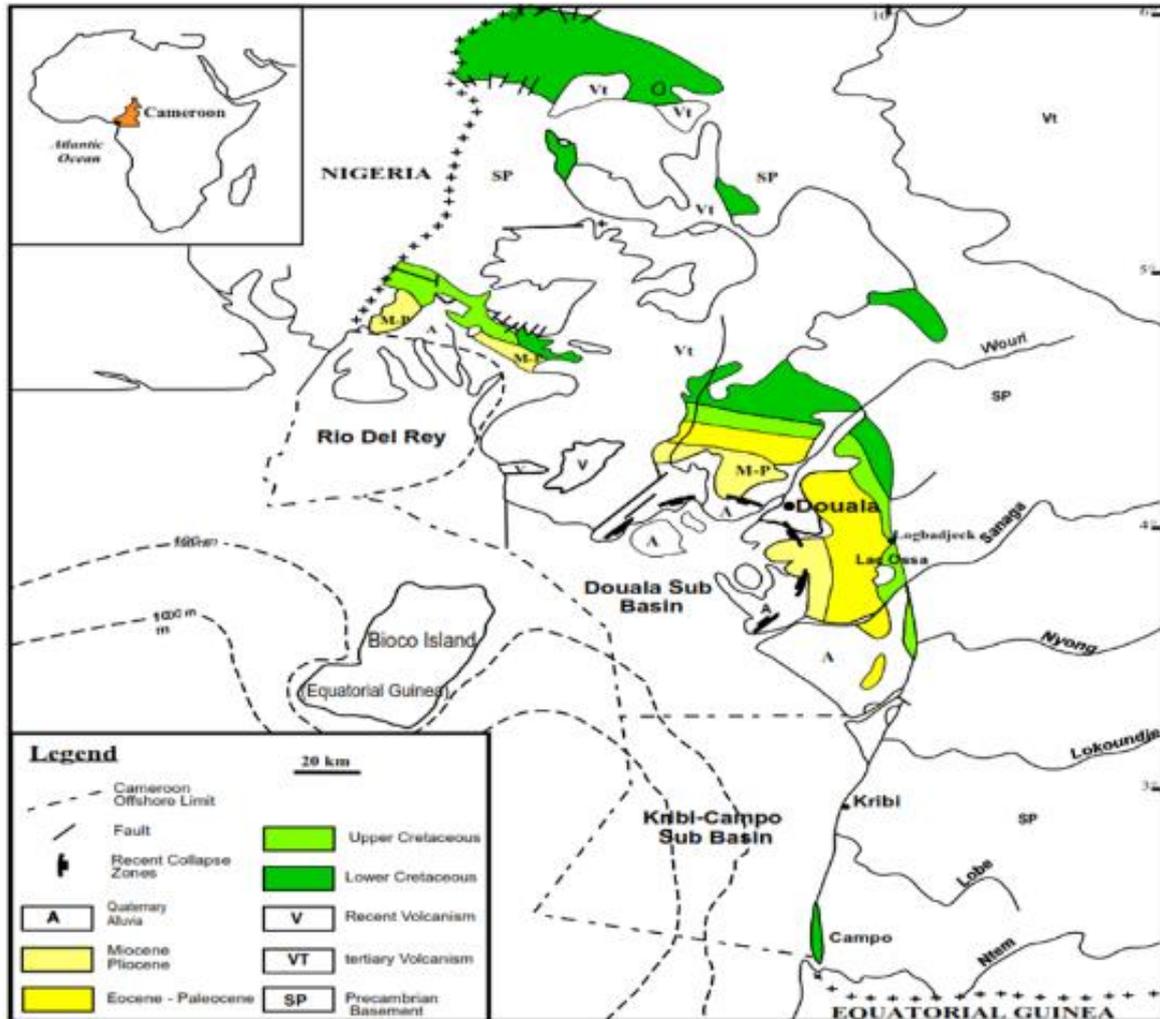
The separation of the South American and African tectonic plates that began in the Early Cretaceous period led to the opening of the South Atlantic Ocean. This gave rise to a series of salt basins in Equatorial West Africa, created by the first marine incursions into the space opened up by the first phase of rifting during which the first oceanic crust was formed (Brownfield and Charpentier, 2006). In Cameroon, along the Atlantic margin, two sedimentary basins are established (Figure 1): the Rio del Rey Basin, representing the southeast extension of the Niger Delta, and the Douala/Kribi-Campo Basin, resulting from the opening of the South Atlantic. The Douala Basin is separated from the Rio del Rey Basin by the horst of the volcanic axis of the Cameroon Volcanic Line (Logar, 1983; Njiké Ngaha, 1984; Rosendahl, 1987; Seguret, 1988; Dupont, 1996; Duarte and Morain, 1996; Vernet *et al.*, 1996; Mbina, 1998; Ndong Ondo, 2002).



**Figure 1** Douala and Rio del Rey Basins (Blin, 2010)

#### 2.1.2. Geographical Setting of the Douala Basin

The Douala Basin covers a total area of 19,000 km<sup>2</sup>. This basin, which extends under the waters of the Gulf of Guinea via a continental shelf of 25 km wide (Nguéné *et al.*, 1992), comprises two sub-basins: the Douala sub-basin (12,000 km<sup>2</sup>, of which 7,000 km<sup>2</sup> are onshore), bordered to the north by the Cameroon Volcanic Line and to the south by the Nyong River, and the Kribi-Campo sub-basin (7,000 km<sup>2</sup>) located between the latter to the north and the Ntem River to the south (Figure 2).



**Figure 2** Simplified geological map of the Cameroonian coastal basins (NHC/UD, 2005)

## 2.2. Geographical Location of the Study Area

Kribi is a seaside town in southern Cameroon, located between 2°56' and 3°02' North latitude and 9°54' and 9°57' East longitude. It is located in the coastal lowlands of the Cameroon Littoral Region with an average altitude of 20 m (Assako *et al.*, 2006). As the capital of the Ocean Division, the town covers an area of approximately 30,000 km<sup>2</sup> and is a strategic point for maritime traffic in the Gulf of Guinea.

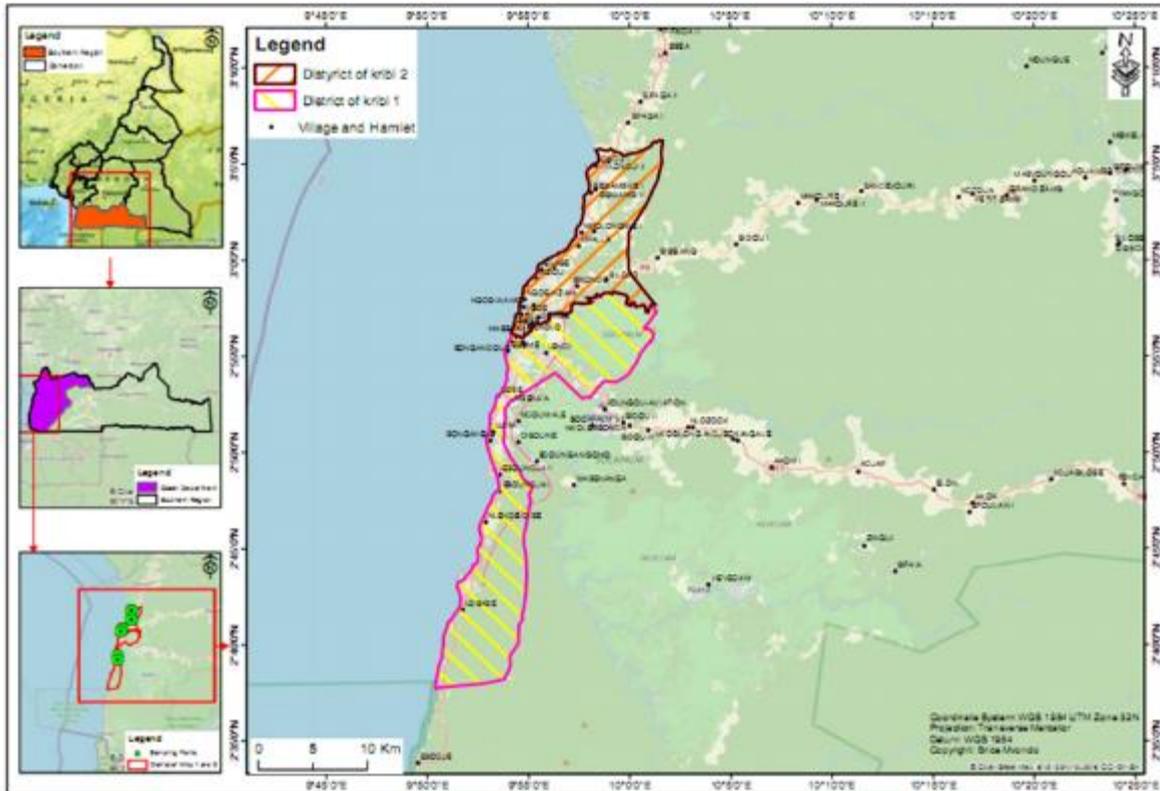


Figure 3 Location map of the study area (NIC, 2023; modified)

### 2.3. Topography, Pedology, Hydrography, and Climate

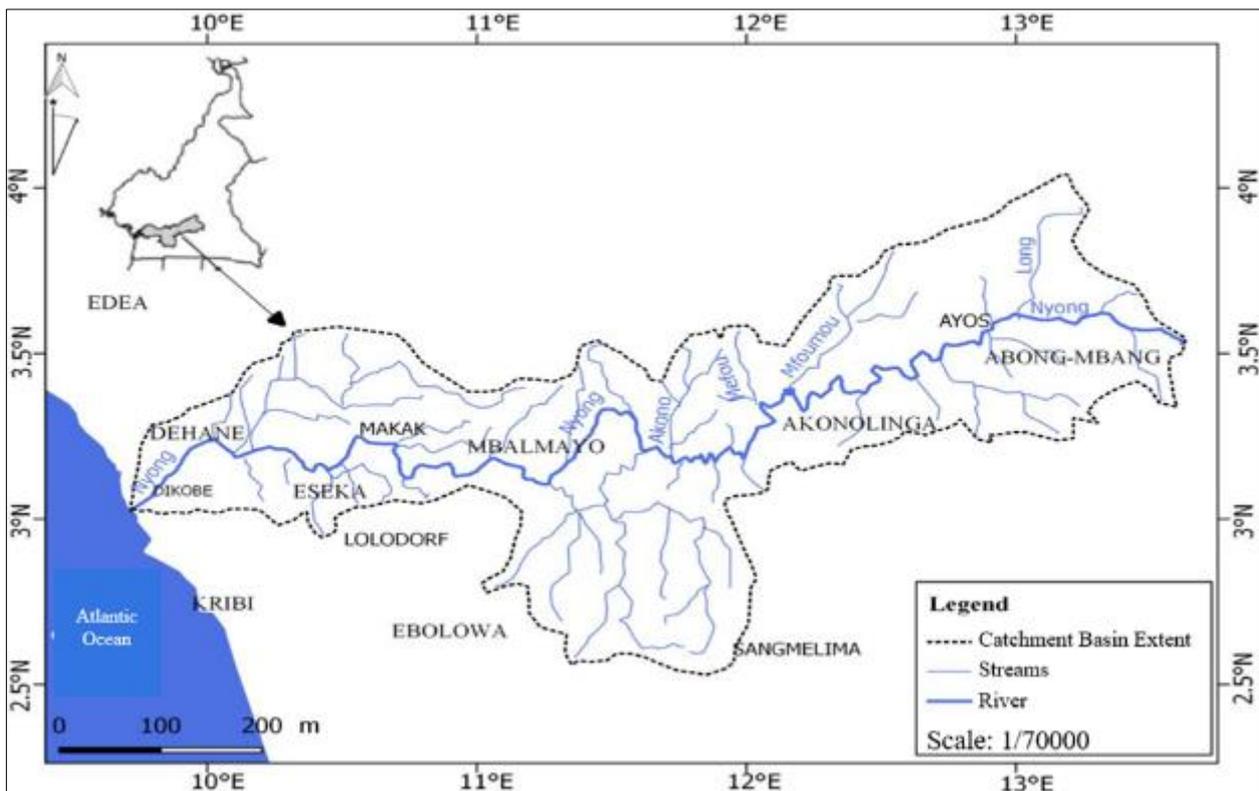


Figure 4 Nyong River Basin (Olivry, 1986)

Kribi is situated on the Cameroonian coastal plain at an altitude of less than 350 m. It consists of a few hills separated by streams with regular flows (Boye *et al.*, 1974; Zogning and Kuété, 1985; Morin and Kueté, 1988; Giresse and Cachet, 1996). Two types of soils are identified there: ferralitic soils and hydromorphic soils (Martin, 1967; Bitom, 1988; Vallerie, 1995; Nkoué-Ndondo, 2008; Nlend, 2014). These soils are also characterized by an acidic pH, and there is an abundance of iron and aluminum hydroxides (Muller, 1987).

The hydrographic network is dense, consisting of numerous rivers and tributaries. The geographic area of the Lokoundjé Subdivision is home to the Nyong River (Figure 4), which, after the Sanaga, is the second largest river in Cameroon (surface area 27,800 km<sup>2</sup>, length 690 km). It joins the coastal plain at the Batanga creek, where it flows peacefully in a navigable channel to the Atlantic Ocean (Olivry, 1986). Kribi enjoys a Guinean-type equatorial climate with a maritime influence, characterized by four seasons: two rainy seasons and two dry seasons. During the year, the highest temperatures are observed during three months (March, April, and May). The lowest temperatures are observed in June and July (SOGREAH-GWP-CMR, 2012).

## 2.4. Vegetation, Flora, and Fauna

Kribi is dominated by secondary forests due to human intervention. However, primary forests are found in areas that are difficult to access (Oslisly, 2001). In addition to the naturally growing species, vast areas are occupied by industrial oil palm plantations belonging to the Cameroon Palm Company (SOCAPALM). There are also many non-timber forest products, as well as herbaceous flora. The terrestrial fauna consists of various wild and domestic species, while the aquatic fauna is diverse and abundant (Vivien, 1991). Elephants, manatees, crocodiles, sea turtles, and chimpanzees are on the list of threatened species.

## 2.5. Human Environment and Socioeconomic Activities

The town of Kribi is made up of several tribes and ethnicities that share a common belonging to the South Region. Its population is divided into six main ethnic groups: Batanga, Ntoumou, Mabea, Bagyeli, Mvae, and Bulu, and is estimated at over 72,454 inhabitants (BUCREP, 2010). This population has slightly increased in recent times. The most important activities in the region are fishing, agriculture, tourism, hunting, sand extraction, oil exploitation, etc. In addition, several industries are established there, such as SOCAPALM, HEVECAM, SNH, COTCO, and the Kribi Autonomous Port.

## 2.6. Data Collection

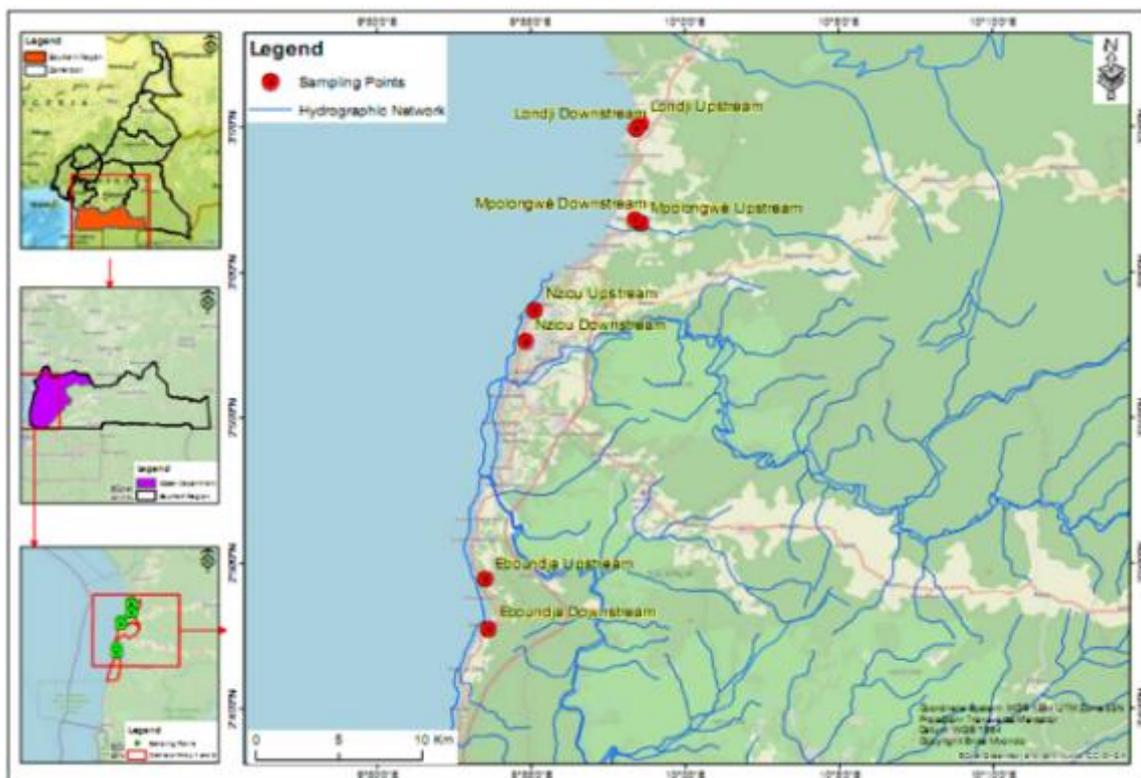


Figure 5 Sampling points in Kribi (NIC, 2023; modified)

This study was conducted from January to July 2023. Data collection was carried out during two one-week campaigns. These field trips consisted of taking in situ measurements of physicochemical parameters and sampling mangrove waters, which were then analyzed in the laboratory. Four sites were chosen, each with two sampling points, one upstream and the other downstream (Figure 5). Samples were collected on board a boat in March, corresponding to the dry season, and in June, corresponding to the rainy season. These sampling points were chosen based on their proximity to pollutant discharges.

### 2.6.1. Measurement of Physicochemical Parameters

The physicochemical parameters were measured in situ using a HANNA multi-parameter (Figure 6). Once the electrodes were immersed in the water, the device automatically recorded several parameters, some of which were chosen for the study: temperature, pH, electrical conductivity, dissolved oxygen, and salinity.



**Figure 6** Measurement of physicochemical parameters

### 2.6.2. Sampling and Analysis of Heavy Metal Contaminants

Water was collected against the current using half-liter polyethylene bottles, stored in a cooler with ice packs at 4 °C, and transported to a cold room before being transferred to Douala to the National Veterinary Laboratory (LaNaVet). The determination of trace metal concentrations in the water samples was carried out by X-ray fluorescence spectrometry using a SHIMADZU EDX-7000 spectrometer (Figure 7). To do this, the water samples taken out of the cold room were introduced into a small polyethylene beaker covered with a plastic film called "Mylar paper" and then placed in the spectrometer. The emitted X-rays pass through the "Mylar paper" to excite the atoms contained in the sample. After excitation, X-ray fluorescence is emitted, which is characteristic of the atoms being sought. Each concentration corresponds to an absorbance, the curve of which is plotted. From this curve, the spectrometer gives readings of the element concentrations after measuring the absorbance of each sample.



**Figure 7** SHIMADZU EDX-7000 fluorescence spectrometer

2.6.3. Data Processing and Statistical Analysis

The figures, graphs, and maps required for this study were produced using the following software: Microsoft Office Excel 2016 for data digitization; SPSS for descriptive statistics; and ArcGIS for map creation.

3. Results

3.1. Characteristics of the Physicochemical Environment

3.1.1. Water Temperature

The water temperature values measured at the different sites are shown in Figure 8. They range from 25.7 °C to 30.9 °C, with an average of 29.39 °C in March (dry season) and 26.08 °C in June (rainy season). These temperature variations follow those of the climate, as the surface layer of water is directly influenced by the climate, which is characterized by a cold season and a hot season.

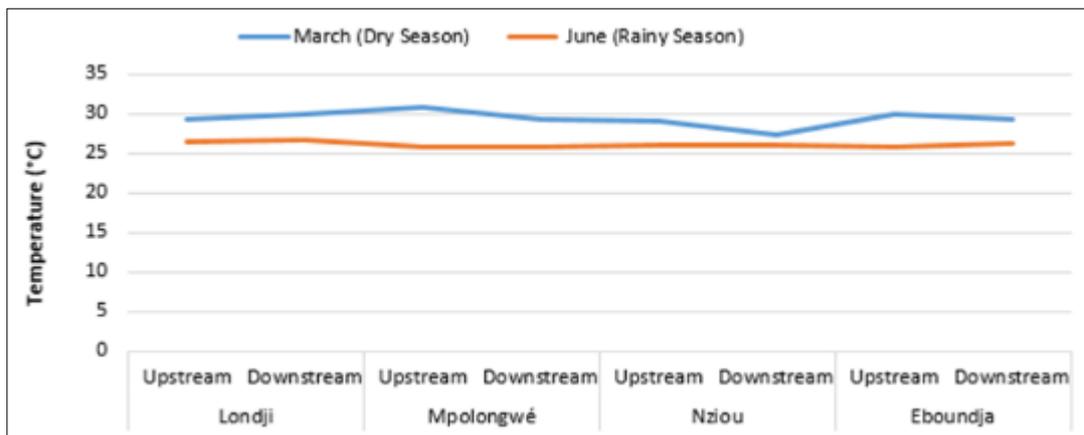


Figure 8 Spatial variation of temperature at the different sites during the seasons

3.1.2. Hydrogen Potential (pH)

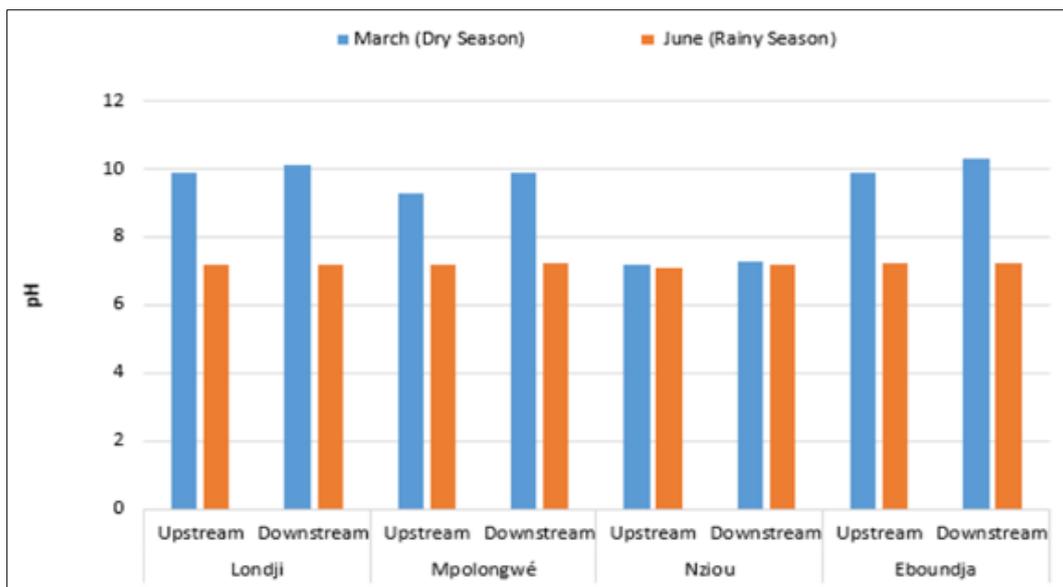


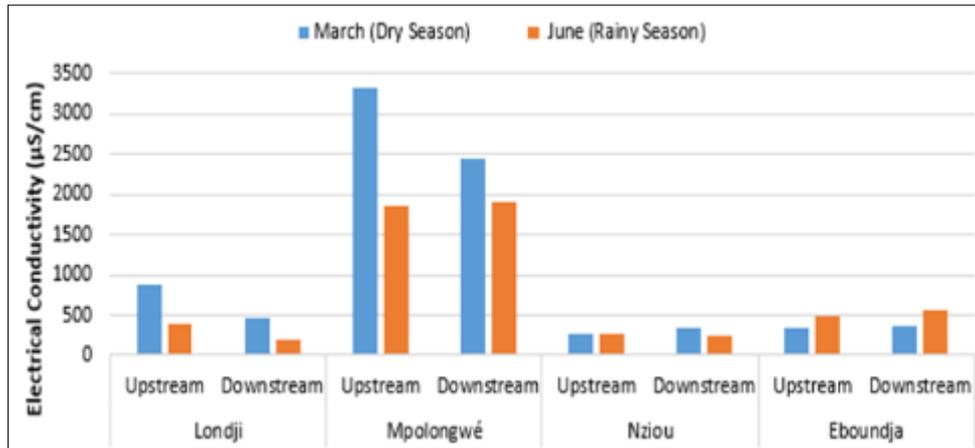
Figure 9 Spatial variation of pH at the different sites during the seasons

pH is a complex factor that influences most chemical and biochemical equilibria. The pH values in the study area range from 7.18 to 11.9 in the dry season and between 7.18 and 7.25 during the rainy season. It can be seen that in the rainy

season the pH values are almost identical across all sites, whereas in the dry season, Londji, Mpolongwé, and Eboundja have high pH values (Figure 9).

### 3.1.3. Electrical Conductivity

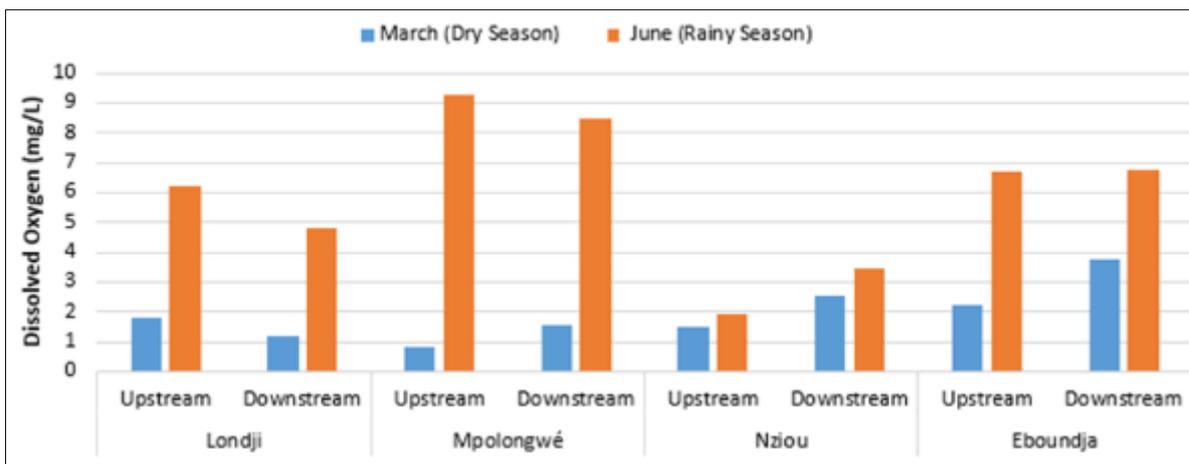
Most substances dissolved in water are in the form of electrically charged ions. Measuring conductivity makes it possible to assess the degree of mineralization of water. In the study area, only the Mpolongwé site has excessively mineralized water, with conductivities greater than 1000  $\mu\text{S}/\text{cm}$ , ranging from 1860 to 3330  $\mu\text{S}/\text{cm}$ . The water in the Nziou mangroves has low mineralization, as all the values at this site are between 200 and 400  $\mu\text{S}/\text{cm}$ . At Eboundja, the waters have low to medium mineralization, ranging from 346.1 to 554  $\mu\text{S}/\text{cm}$ . Finally, at Londji, the electrical conductivity values range from 201 to 870  $\mu\text{S}/\text{cm}$ , which corresponds to low to significant mineralization.



**Figure 10** Spatial variation of conductivity at the different sites during the seasons

### 3.1.4. Dissolved Oxygen

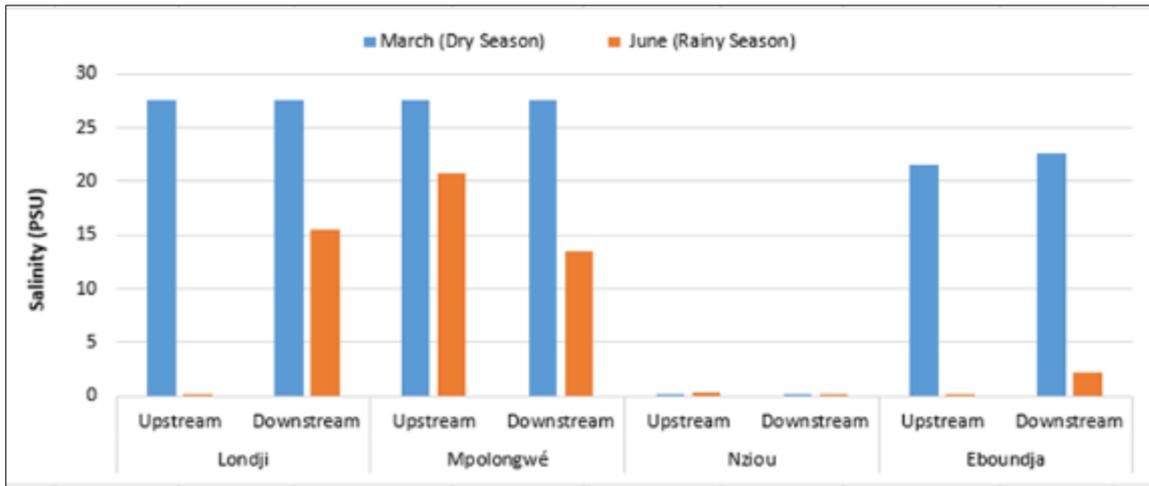
Dissolved oxygen values range from 0.84 to 3.75 mg/l in the dry season and from 1.12 to 9.3 mg/l in the rainy season. It can be seen that dissolved oxygen values are higher in the rainy season at the Londji, Mpolongwé, and Eboundja sites (Figure 11).



**Figure 11** Spatial variation of dissolved oxygen at the different sites during the seasons

### 3.1.5. Salinity

The presence of salt in water determines some of its properties such as density and electrical conductivity. This parameter is more present in coastal waters and is often influenced inland by salt water from the sea. Salinity values are higher at Londji, Mpolongwé, and Eboundja, with higher concentrations in March (dry season), 27.5 PSU at Londji and Mpolongwé; and 21.55 and 22.63 PSU at Eboundja (Figure 12).

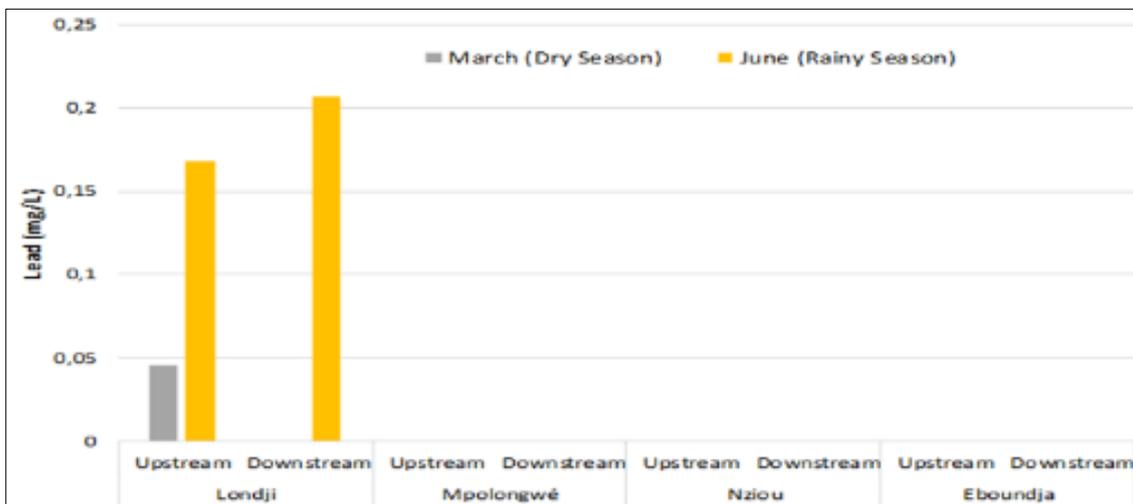


**Figure 12** Spatial variation of salinity at the different sites during the seasons

### 3.2. Metal Concentrations at the Different Sites

#### 3.2.1. Lead

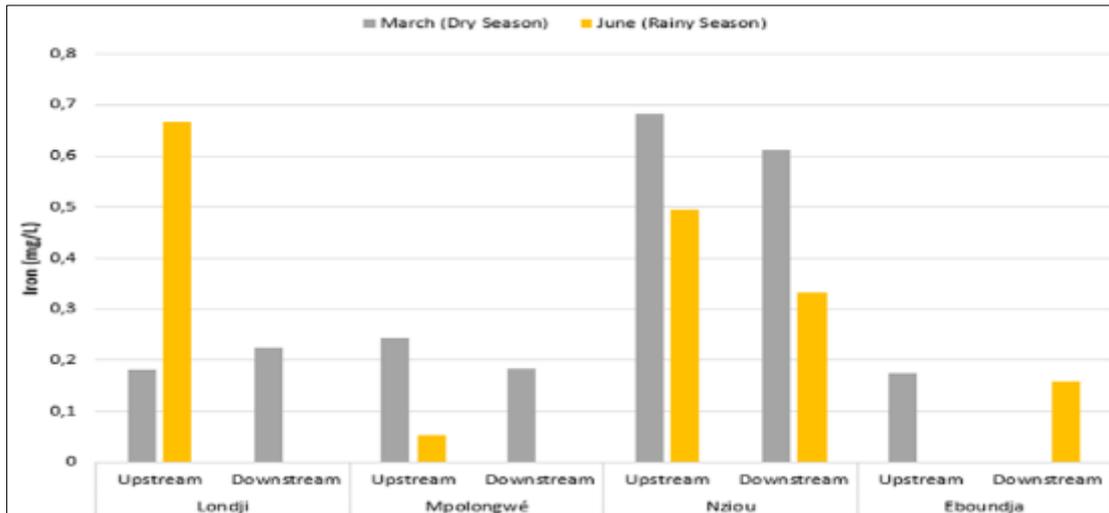
Lead is a very dangerous mineral micropollutant. In the study area, it is only present at the Londji site, with values between 0.05 mg/l and 0.21 mg/l. This mineral was mainly present during the June campaign in the rainy season (Figure 13).



**Figure 13** Lead content at the different sites

#### 3.2.2. Iron

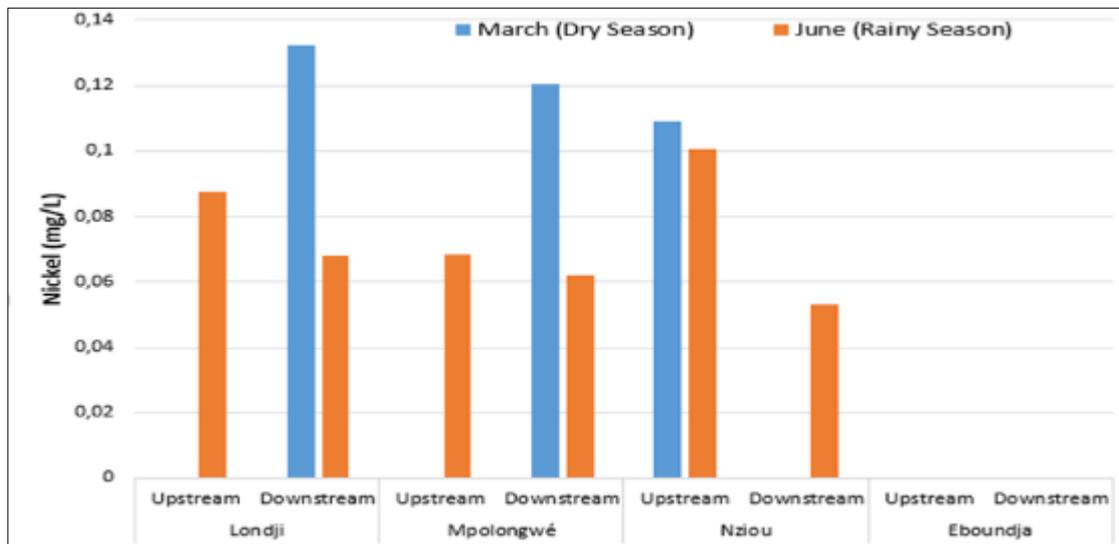
In the study area, iron values are higher at Londji (0.67 mg/l) and Nziou (0.61 and 0.68 mg/l), and lower at Mpolongwé and Eboundja. Overall, iron values in mangrove waters are higher in the dry season (0.29 mg/l on average) than in the rainy season (0.21 mg/l on average).



**Figure 14** Iron content at the different sites

### 3.2.3. Nickel

Nickel is totally absent at the Eboundja site but present at the other three sites in the study area (Figure 15), with values ranging from 0.05 mg/l at Nziou in June to 0.13 mg/l at Londji in March. It can be seen that nickel values are higher at these three sites during the dry season campaign.



**Figure 15** Nickel content at the different sites

### 3.2.4. Copper

Copper is present at all sampling points, with values ranging from 2.68 mg/l at Nziou to 3.31 mg/l at Mpolongwé (Figure 16).

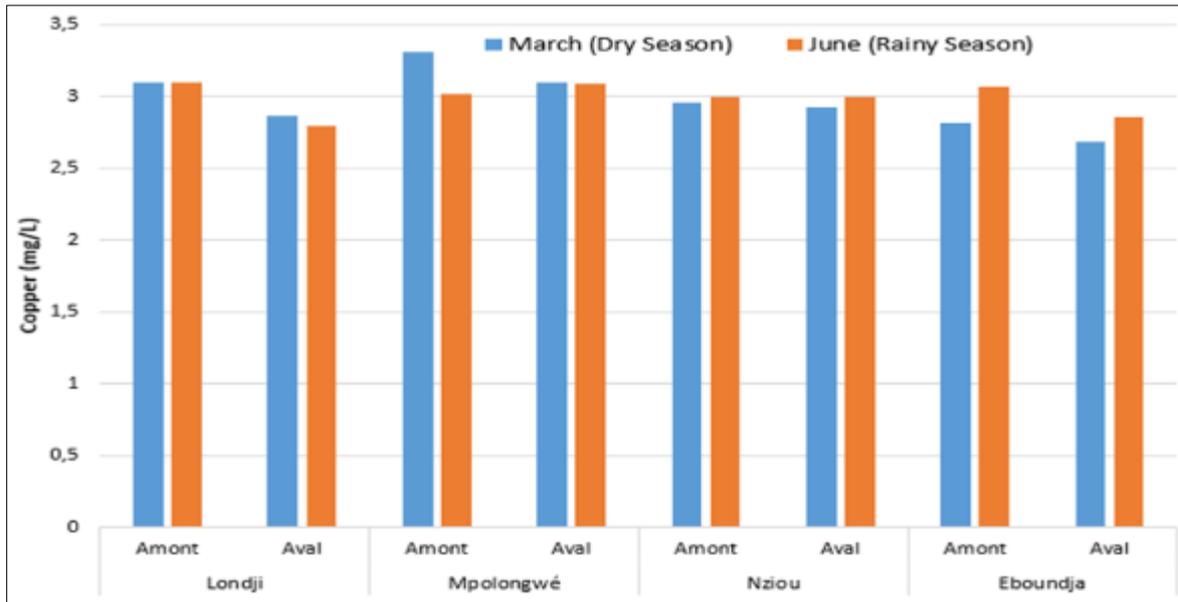


Figure 16 Copper content at the different sites

### 3.3. Principal Component Analysis (PCA)

Concerning the principal component analysis, the observation of Figure 17 shows that Lead (Le) is only present on the Londji site, especially in the rainy season. Iron (Ir) is more abundant in Nziou, but it is found a little in Londji. Nickel (Ni) is a metal present on all sites, except Eboudja. Finally, Copper (Co), which is the metal studied present on all sites, but with a higher value in Mpolongwé, in the dry season. Observation of physicochemical parameters shows that dissolved oxygen (DO) is more abundant in mangrove waters in the rainy season, which is the opposite of parameters such as Salinity (Sal) or Electrical Conductivity (Elc), which are higher in the dry season.

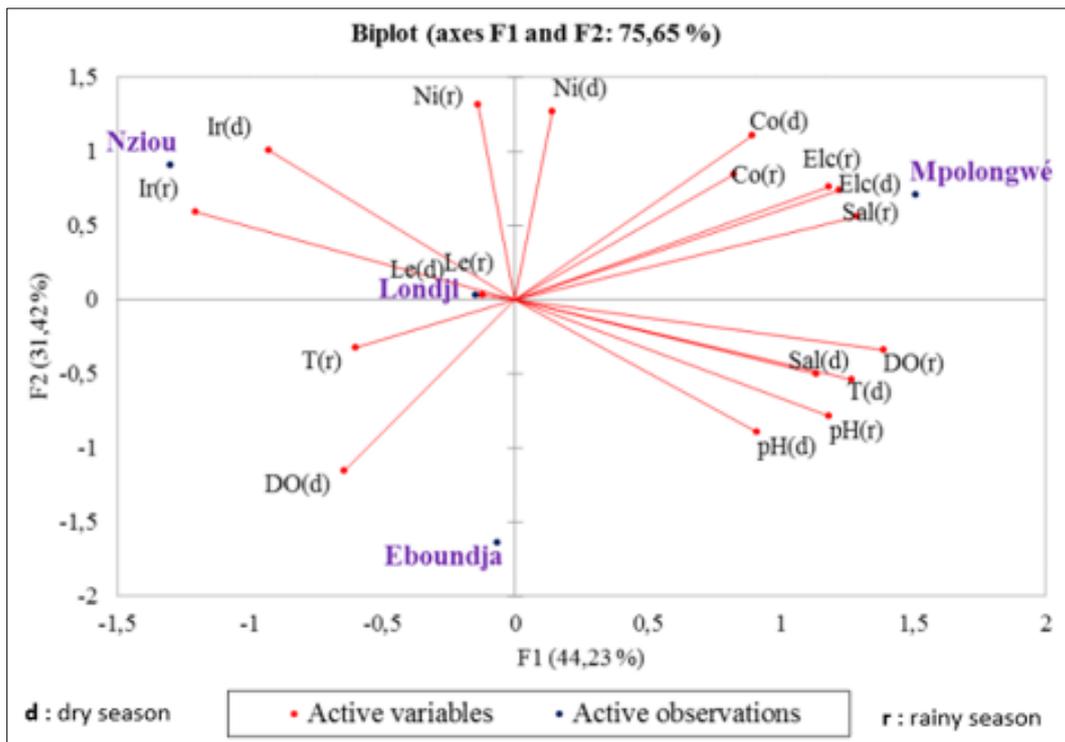


Figure 17 Principal Component Analysis

#### 4. Discussion

The water temperature values measured at the different sites range from 25.7 °C to 30.9 °C, with an average of 29.39 °C in March (dry season) and 26.08 °C in June (rainy season). These values are lower than the average temperature of 31.45 °C obtained by Keumean (2014) on the Comoé River in Côte d'Ivoire. This difference can be explained by the presence of a semi-open canopy in our study area.

Regarding pH, the results obtained in the dry season show an average value of 7.19 at Nziou, which corresponds to a neutral pH, and a basic pH at Londji, Mpolongwé, and Eboundja with 11, 9.6, and 11.6 respectively. These values differ from 6.64, which is the average value obtained by Soro *et al.* in 2021 on the Bandama River in Côte d'Ivoire, also in the dry season. On the other hand, the average pH values of the same sites in the rainy season are 7.18, 7.22, 7.19, and 7.22 respectively. They are slightly higher than 6.53, which is the average pH value obtained by Soro *et al.* (2021). But all these latter values correspond to a neutral pH.

In the study area, only the Mpolongwé site has excessively mineralized waters, with conductivities higher than 1000  $\mu\text{S}/\text{cm}$ , ranging from 1860 to 3330  $\mu\text{S}/\text{cm}$ . This is due to the site's proximity not only to the Kribi gas-fired power plant but also to the inflow of effluents from surrounding hotels. At other sites, electrical conductivity varies between 200 and 400  $\mu\text{S}/\text{cm}$  at Nziou, between 346.1 and 554  $\mu\text{S}/\text{cm}$  at Eboundja, and between 201 and 870  $\mu\text{S}/\text{cm}$  at Londji, where numerous plantations enriched with chemical fertilizers are observed along the watershed. All our values are higher than the average obtained by Soro *et al.* (2021) on the Bandama River in Côte d'Ivoire, with 74.25  $\mu\text{S}/\text{cm}$  in the rainy season and 77.01  $\mu\text{S}/\text{cm}$  in the dry season. Apart from Mpolongwé, the other values are lower than those found by Anselme *et al.* in 2018 on the lower reaches of the Nyong River, with 21337  $\mu\text{S}/\text{cm}$  in the dry season and 12242.9  $\mu\text{S}/\text{cm}$  in the rainy season. This high conductivity in the Nyong River estuary is due to the fact that measurements were taken during high tide, as at Mpolongwé, thus favoring the upwelling of marine salt water into the fresh water of the river.

Salinity values are higher at Londji, Mpolongwé, and Eboundja, with higher concentrations in March (dry season): 27.5 PSU at Londji and Mpolongwé; and 21.55 and 22.63 PSU at Eboundja. This is explained by the strong dilution by fresh water from rivers in the rainy season, which counteracts the evaporation of ocean water in the dry season, thus increasing salinity. As for dissolved oxygen, it can be seen that values are higher in the rainy season because oxygen dissolves more easily in cold water.

Regarding heavy metals, it is noted that lead is only present at the Londji site with values between 0.05 mg/l and 0.21 mg/l. This metal is mainly observed during the June campaign in the rainy season and could come from the materials used in the intense fishing activity. These low lead values at Londji are similar to the results of Daobin Tang *et al.* in 2022 in Zhanjiang Bay, where lead values were slightly to moderately enriched, although the latter worked on sediment instead. Nickel is totally absent at Eboundja but weakly present at the other three sites, with values ranging from 0.05 mg/l at Nziou in June to 0.13 mg/l at Londji.

Copper is present at all sampling points, with values ranging from 2.68 mg/l at Nziou to 3.31 mg/l. These values are higher than the average values, ranging from 17.4 to 21.5  $\mu\text{g}\cdot\text{g}^{-1}$ , found in the city of El Jadida, on the seaweed 'Ulva lactuca', collected in the coastal zone in Morocco (Aziz Kaimoussi *et al.*, 2004).

The average iron values in the mangrove waters of Kribi are 0.29 mg/l in the dry season and 0.21 mg/l in the rainy season. This mineral certainly has a natural origin in the soil and subsoil of the locality.

Although some heavy metals are essential to living organisms, others are dangerous because they are toxic, even at very low concentrations (Crine, 1993; Maynaud, 2012; Messai K, 2014). The risks to humans from heavy metals are due to exposure to the main hazards which are: they replace or substitute essential minerals; they change our genetic code; they produce free radicals; they neutralize amino acids used for detoxification; they cause allergies; and they damage nerve cells (Bekaert, 2004).

Lead can cause neurological, hematological, gastrointestinal, reproductive, immunological, and apoptotic disorders (Miquel, 2001; Xu *et al.*, 2008). The fetus and child are particularly sensitive to the neurobehavioral toxic effect of lead, characterized by a slight or irreversible decline in cognitive abilities (Tremel-Shaub and Fiex, 2005). Chronic exposure can lead to risks of infertility and fetal malformations (Savary, 2003). Nickel can cause skin diseases called dermatitis (Campo *et al.*, 2021). Copper affects the liver, kidneys, and stomach. The effects of copper on the human body are of several origins. It causes poisonings that can be acute or chronic, such as Wilson's disease (Gady, 2000). Ingesting large amounts of iron produces hemochromatosis, tissue damage occurs as a result of iron accumulation (Clark, 1987). Fish nursery grounds also suffer the harmful effects of the presence of these heavy metals.

## 5. Conclusion

This study, which focused on the threats to some Kribi mangroves from heavy metal contamination, characterized the physicochemical parameters of the sites. The results show that the water temperature follows the ambient temperature, and the pH is neutral to basic. The Mpolongwé site exhibits excessive mineralization, probably due to effluents from the Kribi gas-fired power plant, while the water in the Nziou mangroves shows low mineralization. Eboundja waters have low to medium mineralization, while Londji waters have low to significant mineralization. Dissolved oxygen values are low. Salinity is higher at Londji, Mpolongwé, and Eboundja than at Nziou. Regarding heavy metals, lead is only present at the Londji site and may originate mainly from fishing gear. Iron is more present at Londji and Nziou. Nickel is totally absent at the Eboundja site but present at the other three sites. Copper is the only metal present at all sampling points. Londji appears to be the most contaminated site as it contains all the metals analyzed.

## Compliance with ethical standards

### *Acknowledgments*

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### *Disclosure of conflict of interest*

The authors declare that they have no conflict of interest.

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