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Assessment of the chemical quality of a water resource in Daloa city, central - western Côte d'Ivoire

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The objective of this study is to assess the chemical quality of Lobo river waters through the

analysis of some water quality parameters. Lobo River is located in Daloa in the center-west of Côte d'Ivoire. It is an important source of water for city population. The work consisted

of taking water samples from five stations located along the river. These samples were analyzed, using standard methods, for pH, dissolved oxygen, major ions $(Ca^{2+}, Mg^{2+}, SO_4^{2-})$

, Cl⁻), nutrient salts (NH₄⁺, NO₂⁻, NO₃⁻, PO₄⁻³⁻) and heavy metals (Fe, Mn). In general,

dissolved oxygen, sulphate ions, ortophosphate and nitrate recorded high levels during the

dry season, while pH, ammonium, nitrite, chloride, calcium, magnesium, iron and

manganese had higher values in the rainy season. However, all parameters analyzed, had

values in line with the World Health Organization (WHO) recommended standards for human drinking water except for dissolved oxygen, iron and manganese. Indeed, Lobo river waters contain low levels of dissolved oxygen and are subject to metal pollution. In addition,

the Bravais-Pearson linear correlation matrix revealed strong correlations between the different parameters. It appears from this study that the enrichment of water in Fe and Mn

is not under the control of pH and dissolved oxygen. High Fe and Mn levels are mainly due to anthropogenic activities such as domestic wastewater, agricultural runoff and fishing.

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1. Introduction

Water is an essential product for human life [1]. It is an important element in keeping the health of individuals and the socio-economic development of human communities. Access to drinking water has always been at the center of development projects because man cannot live without this resource [2]. It meets basic human needs in various fields such as: agriculture, electricity production, industries as well as domestic uses. However, access to drinking water is one of the problems facing the governments of all states [3]. Indeed, millions of people in the world suffer from a lack of fresh and clean water [4].

Côte d'Ivoire has so well understood the tasks of access to safe water that it has initiated actions to help access to the public drinking water service for a large number of populations. This political will resulted in the application of the National Human Hydraulics Program (NHHP) as early as 1973. Despite this impetus, the need for drinking water has continued to grow due to climatic risks, pollution and rapid population growth [5].

Abstract

Previous studies conducted in Côte d'Ivoire on water resources by Coulibaly et *al.* [6] and Soro *et al.* [7] described on the one hand the being of many sources of pollution both in groundwater and surface water, and on the other hand a risk of water pollution due to anthropogenic activities.

Surface water (rivers, streams, lakes, ponds) is opposed with an enduring degradation of its quality due to anthropogenic activities. Thus, Lobo river (surface water) whose waters are exploited for multiple uses such as the drinking water supply in one of the major cities of Côte d'Ivoire, particularly Daloa, is not on the fringe of this reality. Indeed, in this region with an agricultural ability, Lobo river is opposed with unprecedented pressure linked to agricultural activities, in this case coffee and cocoa production [8]. These anthropogenic activities, due to the waste discharged, could affect the quality of the water in the river. What affects human and aquatic life [9]. The studies carried out by Yao *et al.* [8] on this river only concern the quantitative aspect of the resource. The chemical quality of the waters of Lobo river which constitute the basis of the drinking water supply of the populations of the commune of Daloa has not yet been studied.

The evaluation of the water quality of rivers using various physicochemical parameters has been reported in the literature. Knowing these parameters in fact gives an estimate of the water quality [10]. The present work therefore aims to assess on the one hand the chemical quality of the Lobo river waters through the study of certain chemical parameters, major ions, nutrient salts and heavy metals. On the other hand, it proposes to establish a correlation between the different parameters.

2. Material and Methods

Water sampling of the Lobo River was conducted during the months of February and July 2019 corresponding to dry and rainy seasons periods respectively.

2.1. Presentation of the study area

The relief of the basin is composed of plains and low uplands of altitudes varying between 160 m and 480 m occupied by dense humid forest. This forest heritage has been degraded in recent years by agricultural exploitation with a landscape alternating between crops and fallow land.

Lobo river is a tributary of Sassandra river. Its watershed is located in West Africa, in centralwestern Côte d'Ivoire, 25 km from Daloa between 6°05 and 6°55 north latitude and between 6°20 and 7°55 west longitude (Figure 1). It has its source in the region of Séguéla, draining an area of 12 722 km² and covers 355 km with a perimeter of 530 km. Sampling points were chosen taking into account the sources of water pollution in the Lobo River and according to their accessibility. Five sampling stations were selected along the Lobo river and located using a GARMIN 76 GPS navigator. These are sites S1 (KP 11), S2 (Gnah), S3 (Cr Babo), S4 (Mignoré) and S5 (Nibehibe) located in Figure 2.

2.2. Collecting and storing water samples

The water was taken from a bottle of Niskin. The samples were immediately placed in new 100 mL polyethylene bottles that were rinsed with water from the site to be sampled. Once filled, they were stored in a cooler at 4°C for transport to the laboratory for further analysis.

2.3. Analysis of water chemical quality parameters

These analyses concerned the determination of hydrogen potential (pH), dissolved oxygen (O₂), major ions (Ca²⁺, Mg²⁺, SO₄²⁻, Cl⁻), nutrient salts (NH₄⁺, NO₂⁻, NO₃⁻, PO₄³⁻) and heavy metals (Fe, Mn).

pH and dissolved oxygen were measured with a previously calibrated multiparameter field meter model HANNA 9828.



Figure 1: Location of the Lobo watershed.



The spectrophotometer (HACH DR 5000) was used for the determination of all important chemical elements in water, namely: nitrate, nitrite, ammonium, chloride, sulphate and orthophosphate ions. The determination of the contents of major cations (calcium, magnesium) and heavy metals (Fe, Mg) was carried out by atomic absorption with air-acetylene flame AAS 20 type VARIAN.

2.4. Statistical analysis

The STATISTICA software (Version 7.1) allowed us to perform the Bravais-Pearson correlation test to establish a relationship between chemical parameters, major ions, nutrient salts and heavy metals. The Bravais-Pearson linear correlation coefficient r varies from -1 to +1. Where the values -1 and +1 indicate a perfect negative correlation and a perfect positive correlation respectively. The value 0 shows an absence of correlation between the parameters. Furthermore, the closer the r value is to -1 or +1, the stronger the linear relationship. However, the closer the r-value is to 0, the weaker the linear relationship [11].

3. Results and Discussion

3.1 Spatial and temporal variation of chemical parameters and major ions

Seasonal variations in chemical parameters and major ions are presented in Table 1. Hydrogen potential (pH) is an important parameter in water quality assessment [12]. It characterizes a large number of physico-chemical equilibria and depends on several factors including the origin of water [13]. pH values vary between 6.51 and 7.50 in the dry season and between 6.97 and 7.52 in the rainy season. Over the two seasons, the lowest values are observed at PK 11 (S1) and the highest values at Gnah (S2). The pH remains basic throughout the study period at the stations Gnah (S2), Cr Babo (S3) and Mignoré (S4); acidic at station PK 11 (S1). For the Nibehibe station (S5), it is basic in the dry season and acidic in the rainy season. The acidic character of S1 and S5 would be essentially due to the biological activity of the environment [14]. The majority of the stations studied present an alkaline bicarbonate character. Indeed, they have a pH below 8.3 [15]. However, the pH of Lobo river water is within the range recommended by the World Heath Organization (WHO) for human consumption which is 6.5 - 8.5 [16].

Dissolved oxygen (O_2) is essential for water quality assessment. Indeed, its value provides information on the degree of pollution of the water and consequently on its degree of self-purification [17]. Dissolved oxygen in waters of Lobo river ranges from 1.04 to 8.02 mg/L in the dry season and 0.64 to 7.36 mg/L in the rainy season. Except for station 2 (both seasons) and station 5 (dry season), the other stations have values below the WHO standard (5 - 8) mg/L for drinking water. The low levels of dissolved oxygen recorded would probably be due to the effect of temperature [18], the nitrification process or the decomposition of organic matter and detrital matter that consumes dissolved oxygen [19]. Furthermore, low dissolved oxygen values could favour the development of pathogenic germs in water [20].

Water with a high sulphate content (SO_4^{2-}) can produce laxative effects in humans [21]. In the fact, they cause gastrointestinal disorders and can give an unpleasant taste [22]. The study reveals that sulphate ion levels range from 0 mg/L (S2) to 20.82 mg/L (S4) in the dry season and from 0 mg/L (S1, S3 and S4) to 4 mg/L (S5) in the wet season. The presence of sulphate in the river water would be related to the use of fertilizers for agricultural production along the river. Indeed, according to Abboudi *et al.*, [23], the use of chemical fertilizers leads to sulphide production. However, the values recorded in this study are well below the WHO drinking water guideline of 250 mg/L (Table 1).

Chloride ions (Cl⁻) are inorganic anions often used as a pollution index. They are contained in varying concentrations in natural waters, generally in the form of sodium (NaCl) and potassium (KCl)

salts [24]. High doses of sodium chloride in drinking water cause hypertension [25]. The values obtained for this parameter vary between 18 and 45 mg/L in the dry season and between 4.9 and 71.6 mg/L in the rainy season. Higher levels are found in the rainy season than in the dry season. The high levels in the rainy season could be explained by the leaching of fertilizers used in agriculture on this river. All waters of Lobo river have chloride levels below the WHO guidelines (250 mg/L) for drinking water in both seasons [16]. Calcium (Ca²⁺) is a major component of total water hardness and is generally the dominant element in drinking water. High calcium levels can cause intestinal diseases [26] and concretions in the body such as kidney or bladder stones and urinary irritation [15]. In addition, calcium deficiency could lead to cardiovascular disease [27]. The calcium content of the samples is between 11.8 and 29.1 mg/L in the dry season and between 13.6 and 34.4 mg/L in the rainy season. Over both seasons, the lowest concentrations were recorded at station 2 and the highest at station 3. Whereas, higher concentrations in the wet season than in the dry season were observed at all stations. However, all waters have values below the maximum allowable concentration for human consumption which is 100 mg/L [16]. This characteristic makes the Lobo river suitable for domestic uses such as laundry [28].

Magnesium (Mg^{2^+}) is more abundant after calcium compared to sodium and potassium. It is known for its influence on the scaling phenomenon [29] and represents an essential factor in water hardness [30]. High magnesium concentrations can cause cardiovascular disease [31] and water hardness [26]. Magnesium levels range from 3.37 to 7.45 mg/L in the dry season and 0.23 to 50.30 mg/L in the wet season. Concentrations are generally higher in the wet season than in the dry season except for Stations 2 and 5. These values are well below the WHO standard of 50 mg/L for water intended for human consumption except for station 1 in the rainy season (Table 1).

Chemical parameters and major ions			WHO					
		PK 11GnahCr BaboMignoré(Station 1)(Station 2)(Station 3)(Station 4)			Mignoré (Station 4)	Nibehibe (Station 5)	Standards [16]	
рН	SS	6.51	7.50	7.01	7.31	7.09	(5 9 5	
	SP	6.97	7.52	7.37	7.38	6.98	0.5 - 8.5	
$O_2 (mg/L)$	SS	1.04	8.02	4.01	2.25	7.7	5 0	
	SP	0.64	7.36	4.94	3.38	3.89	5-8	
a^{2-1}	SS	3.24	0	17.54	20.82	10.11	250	
$SO_4 (mg/L)$	SP	0	1	0	0	4	250	
Cl ⁻ (mg/L)	SS	18.6	26.7	41.3	18	45	250	
	SP	26.7	4.9	71.6	40.6	14.5	250	
Ca ²⁺ (mg/L)	SS	14.6	11.8	29.1	18.1	15.7	100	
	SP	20	13.6	34.4	19.1	17.6		
Mg^{2+} (mg/L)	SS	5.19	3.37	6.85	7.45	4.22	50	
	SP	50.30	0.49	17.25	11.2	0.24	50	

Table 1. Chemical parameters and major ions in Lobo River waters.

SS: Dry season (February 2019); SP: Wet season (July 2019)

3.2 Spatial and temporal variation of nutrient salts and heavy metals

The results of the nutrient salt and heavy metal analysis carried out on Lobo river waters are given in Table 2. The nutrients measured in the different waters are nitrates (NO₃⁻), nitrites (NO₂⁻), ammonium (NH₄⁺) and orthophosphate (PO₄³⁻). Phosphates are not toxic to humans, but a very high phosphate content in water can cause digestive problems [32]. Orthophosphate levels range from 0.49

to 1.75 mg/L in the dry season and 0.10 to 0.25 mg/L in the wet season with higher values in the dry season than in the wet season. This presence of phosphates in Lobo river is due to the nature of the land crossed and the decomposition of organic matter [33] on the one hand; and to the discharge of wastewater and agricultural activities [34] on the other hand. The waters sampled all have values below the WHO standard (1.41 mg/L) except at station 1 during the dry season.

Ammonium is the most toxic form of nitrogen. Depending on the dose and duration of exposure, ammonium salt can cause health problems in humans: pulmonary oedema, dysfunction of the nervous and renal systems, increased blood pressure [35]. Ammonium levels vary in the dry season from 0.171 to 0.197 mg/L, while in the rainy season they range from 0 to 3.44 mg/L.

With the exception of station 1 in the rainy season, all the values observed are below the WHO recommended standard of 0.5 mg/L.

The presence of nitrite ions of natural origin is very rare [36]. Water that contains nitrite ions should be considered suspect because this presence is often associated with a deterioration in microbiological quality [37]. An excess of nitrites in drinking water can in some cases cause methemoglobinemia, sometimes even asphyxiation in bottle-fed babies [16]. In this study, nitrite ion levels ranged from 0 to 0.053 mg/L during the dry season. In the rainy season, these values range from 0 to 0.054 mg/L. The highest values are observed in the rainy season except for station 5. However, these values obtained are all below the WHO authorized standard for drinking water which is 0.1 mg/L.

Nitrates are the most common form of nitrogen in natural waters. These nutrients are not directly toxic to humans because they are rarely present in drinking water [30]. However, the risk comes from their transformation into nitrites in the digestive tract. The latter, in fact, cause the oxidation of haemoglobin into methaemoglobin, making it incapable of transporting oxygen to the cells [34]. Nitrate ion concentrations range from 3 to 26.6 mg/L in the dry season and 0 to 13.5 mg/L in the rainy season. In general, concentrations are higher in the dry season than in the rainy season, except for station 3 where the opposite is observed. The high nitrate concentrations in the dry season would probably be due to the lower water level that concentrates the salts [38, 20]. The concentrations in all the waters studied are well below the maximum limit set by the WHO, which is 50 mg/L (Table 2). These waters are therefore not at risk of pollution by this nutrient. In addition, the consumption of water with nitrate concentrations above the standard but below 100 mg/L is temporarily acceptable, except for infants and pregnant or nursing women [39].

This study reveals the presence of metals in all sampled waters. The concentrations of the metals iron (Fe) and manganese (Mn) are shown in Table 2. Iron is an essential element for the human body, including the blood system [40]. However, high concentrations affect the organoleptic properties of water and also stain laundry [15]. Iron concentrations range from 0.202 mg/L (S2) to 1.78 mg/L (S5) during the dry season. In the rainy season, these values range from 0.745 mg/L (S2) to 2.705 mg/L (S3). The values obtained in the wet season are higher than those in the dry season except for station S5.

The high iron content (1.78 mg/L) observed at Station 5 during the dry season is thought to be due to the dissolution of sediments and the release of iron into the overlying water. Finally, the lowest value recorded at station 2 during the rainy season may be due to the oxidation of Fe (II) to Fe (III) and precipitated as hydroxide [41]. The results of this study are above the WHO standard for drinking water potability (0.3 mg/L) with the exception of station S2 during the dry season.

Manganese is a micronutrient that functions as an essential constituent for bone structure, reproduction and normal functioning of the enzyme system [41]. However, the presence of manganese at high concentrations in drinking water can cause consumer discomfort such as discoloration or taste, unpleasant odors and also cirrhosis of the liver in humans [42]. Manganese levels range from 0 to 0.245

mg/L in the dry season and 0.2 to 3.3 mg/L in the wet season. Concentrations are higher in the wet season compared to the dry season. However, in both seasons the values recorded are above the WHO guidelines (0.05 mg/L) with the exception of station S1 (0 mg/L) in the dry season (Table 2).

In general, concentrations of heavy metals (iron and manganese) in water are higher in the rainy season than in the dry season. These high metal levels during the rainy season can be attributed to runoff and leaching of plantations by rainwater, resulting in residues of fertilizers, agrochemicals and pesticides in the water [17]. The low level observed during the dry season may be due to the absorption of metallic elements by phytoplankton, zooplankton, fish and other aquatic organisms in the water [17]. Iron and manganese levels above the WHO standard could lead to adverse effects on human health. Indeed, all metals are toxic when present above the tolerance limit [43].

Nutritional salts and heavy metals			WHO Storedoredo					
		PK 11 (Station 1)	GnahCr Babo(Station 2)(Station 3)		Mignoré (Station 4)	Nibehibe (Station 5)	[14]	
PO ₄ ³⁻ (mg/L)	SS	1.75	0.69	0.49	0.67	0.6	1.41	
	SP	0.10	0.12	0.24	0.22	0.25		
NIT $+$ ($ /$ $)$	SS	0.173	0.195	0.181	0.197	0.171	0.5	
$\mathbf{NH}_4 \ (\mathbf{III}_2/\mathbf{L})$	SP	3.44	0.13	0.17	0.36	0	0.5	
$NO^{-}(ma/I)$	SS	0	0.001	0	0.053	0.014	0.1	
NO_2 (mg/L)	SP	0	0.017	0.004	0.054	0.009		
$NO^{-}(ma/I)$	SS	12.1	3	7.9	26.6	7.1	50	
$NO_3 (IIIg/L)$	SP	0	1.1	13.5	2.9	1.5		
E. (ma/I)	SS	0.874	0.202	0.832	1.33	1.78	0.3	
ге (mg/L)	SP	1.674	0.745	2.705	1.944	1.026		
Mer (ma/L)	SS	0	0.0948	0.245	0.0545	0.128	0.05	
win (mg/L)	SP	2.2	0.2	3.2	3.3	0.2	0.05	

Table 2. Nutrient Salts and Heavy Metals in Lobo River Waters

SS: Dry season (February 2019); SP: Wet season (July 2019)

3.3 Correlation between water chemical quality parameters

The Bravais - Pearson correlation matrix was developed to elucidate the relationships between the chemical water quality parameters measured in the Lobo river. The correlation coefficients are presented in Table 3. Examination of the matrix indicates the existence of a positive and significant correlation between pH and dissolved oxygen: pH-O₂ (r = 0.72). This strong correlation could be explained by the fact that changes in pH and dissolved oxygen are both affected by algal photosynthesis, aquatic respiration, water temperature and oxidative decomposition of organic matter [19]. The study also reveals strong positive correlations between PO₄³⁻ - NH₄⁺ (r = 0.99), PO₄³⁻ - Mg²⁺ (r = 0.88), PO₄³⁻ - Mn (r = 0.57), NH₄⁺ - Mg²⁺ (r = 0.92), NH₄⁺ - Mn (r = 0.63), NO₂⁻ - SO₄²⁻ (r = 0.66), SO₄²⁻ - Cl⁻ (r =0.68), SO₄²⁻ - NO₃⁻ (r = 0.70), SO₄²⁻ - Ca²⁺ (r = 0.66), SO₄²⁻ - Fe (r = 0.82), Cl⁻ - Ca²⁺ (r = 0.98), Cl⁻ - Fe (r = 0.77), NO₃⁻ - Ca²⁺ (r = 0.65), NO₃⁻ - Fe (r = 0.73), NO₃⁻ - Mn (r = 0.92), Cl⁻ - Fe (r = 0.74), Ca²⁺ -Mn (r = 0.50), Mg²⁺ - Mn (r = 0.87), and Fe - Mn (r = 0.59). These correlations show the mutual dependence of the parameters on each other or a similar behaviour of their influence. Indeed, according to Suresh *et al.*, [44], a high correlation coefficient between the variables means their common source, mutual dependence, and identical behavior during transport. Significantly negative correlations were found between O₂ - PO₄³⁻ (r = -0.75), O₂ - NH₄⁺ (r = -0.77) and O₂ - NO₃⁻ (r = -0.87).

	рн	\mathbf{O}_2	PO ₄	NH4	NO ₂	\mathbf{SO}_4	CI	NU ₃	Ca	Mg	re	NIN
pН	1											
O_2	0.72*	1										
PO ₄ ³⁻		-0.75*	1									
$\mathbf{NH_4}^+$			0.99*	1								
NO ₂ ⁻	0.45	-0.14	-0.31	-0.34	1							
SO ₄ ²⁻	0.22	-0.28		-0.38	0.66*	1						
Cl	-0.07	-0.11	-0.37	-0.29	-0.09	0.68	1					
NO ₃	-0.34	-0.87	0.36	0.40	0.46	0.70	0.36	1				
Ca ²⁺	-0.12	-0.21	-0.25	-0.16	-0.14	0.66*	0.98*	0.45	1			
Mg^{2+}	-0.79		0.88	0.92*	-0.27	-0.04	0.06	0.65*	0.21	1		
Fe	-0.35		-0.05	-0.01	0.30	0.82	0.77*	0.73*	0.74*	0.28	1	
Mn	-0.52	-0.91*	0.57*	0.63*	0.09	0.44	0.36	0.92*	0.50*	0.87	0.59	1

* Significant correlation at p < 0.05

This indicates the depletion of dissolved oxygen for nutrient augmentation as well as oxygen consumption during the nitrification process [19]. The negative correlations observed between pH- PO_4^{3-} (r = -0.81) and pH- NH_4^+ (r = -0.82) show that decreasing pH or low pH values lead to an increase in nutrients. In addition, significantly negative correlations are observed between pH - Mg^{2+} (r = -0.79), pH - Mn (r = -0.52), O₂ - Mg^{2+} (r = -0.89), O₂ - Fe (r = -0.55) and O₂ - Mn (r = -0.91). These results suggest that the enrichment of Mg^{2+} , Mn and Fe in the waters of Lobo river is not under the control of pH and dissolved oxygen.

Conclusion

This study permitted to analyze the chemical parameters, major ions, nutrient salts and levels of certain heavy metals in the waters of Lobo river in order to assess their potability. It was found that river waters recorded pH values ranging from 6.51 to 7.52. The concentrations of sulphate ions (0 - 20.82 mg/L), chlorides (4.9 - 41.3 mg/L), calcium (11.8 - 34.4 mg/L), magnesium (0.24 - 50.30 mg/L), orthophosphates (0.10 - 1.75 mg/L), ammonium (0 - 3.44 mg/L), nitrates (0 - 26.6 mg/L), nitrites (0 - 0.054 mg/L) are low. However, at station 1 the concentrations of orthophosphate ions (dry season) and ammonium and magnesium ions (wet season) are high. Comparison of the heavy metal contents with the WHO recommended standards for drinking water shows that Lobo river waters are polluted with very high concentrations in some places. Therefore, the river needs to be protected for the preservation of the water resource and the health of the population.

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