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Comparative study of physicochemical parameters and dissolved heavy metal dynamics in tropical waters (Bété, Mé, Djibi Rivers and Aghien lagoon) in south of Ivory Coast, West Africa

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ABSTRACT: The study investigates the spatial and temporal variation in water quality parameters at nine different locations in Mé, Bété and Djibi Rivers as well as Aghien Lagoon near Abidjan city for twelve consecutive months. Physicochemical parameters concerned are pH, temperature, electrical conductivity, dissolved oxygen, chlorophyll-*a*, total phosphorus and total nitrogen. Dissolved heavy metals analyzed are Ni, Cu, Zn, Pb, Cd and As. The assessment of physicochemical parameters shown the deteriorate of water quality with significant changes particularly in the Djibi River with high mean concentrations of total phosphorus (0.51 mgP.L⁻¹) and total nitrogen (7.60 mgN.L⁻¹). Nevertheless, the overall mean concentrations of heavy metals in water Cu (1.43 µg.L⁻¹), Cd (0.06 µg.L⁻¹), Pb (0.2 µg.L⁻¹), Zn (9.16 µg.L⁻¹), As (0.3 µg.L⁻¹), Ni (2.77 µg.L⁻¹) were lower than WHO Standard for Drinking Water Quality. Dissolved heavy metal percentage indicates that the order of concentrations was Zn>Ni>Cu>Pb>As>Cd. Multivariate analysis of variance (ANOVA) was used to group the different sampling sites on the basis of spatial similarities and classification, based on contamination sources and origin of pollutants in rivers and lagoon. In conclusion, this study clearly infers the fact that the cause of pollution in this region is mainly due to domestic and industrial effluents, agriculture and finally natural source

KEYWORDS: water quality, physicochemical parameters, nutrients, dissolved heavy metal, Aghien lagoon and its tributaries, Water quality guidelines.

1 INTRODUCTION

Surface waters such as rivers and lakes constitute important sources of water for treatment works, as well as serve for industrial, agricultural and recreational purposes. However, the vulnerability of such water resources to pollution presents serious public health, economic and ecological issues of global concerns [1],[2],[3]. Therefore, monitoring of physico-chemical parameters to evaluate water quality and identify impairments of water resources is important for protection of both the environment and public health [4].

Côte d'Ivoire, a West African state, possesses a vast hydrographic network, mainly in the southern part. This network is threatened by serious pollutions mainly due to the waste generated by the various human activities and rejected into environment. In 1994, a national monitoring network for water quality was established in order to characterise physico-chemical and ecological quality of waterbodies. The monitoring program has covered 55 fixed stations of waterbody withdrawal, sediments and living organisms. 28 stations were counted in inland hydrographic system, 18 stations in Ebrié Lagoon of Abidjan Central Basin and nine stations along the coast from East to West. Actually, this network was focused on three major rivers (Comoé, Bandama, Sassandra) and did not take into account other rivers and water resources which play a key role in economic, social and cultural activities of population's life [5]. This situation explains the lack of long data series and scientific investigations.

In shallow coastal lagoons with deficient connection to the sea, waters contain often various types of pollutants whose nature and amount vary with environmental conditions. Vulnerability of coastal and estuarine systems to natural and anthropic forcing is increasing as a consequence of direct and indirect human interventions in these environments. The anarchic occupation of areas in hydrographic basins has resulted in eutrophication of several waterbodies. The lack of resources to the implementation of domestic and industrial sewage treatment results in the release of the effluents in receptor water bodies (rivers and lakes) [6]. Such discharges are known to contribute to nutrient and heavy metal loading of waterbodies and may introduce pathogenic agents that constitute serious public health risks [7]. After entering the water, many heavy metals are taken up by fauna and flora and eventually, accumulated in marine organisms that are used by human consumption [8]. In addition, agricultural activity has been implicated in several environmental impacts [1]. The rapid and uncontrolled development of agriculture has caused discharge of high levels of nutrient into coastal waters [9]. For lakes, excess of nutrients often generates a biological response with the increase of algae biomass. The Aghien Lagoon and its tributaries (Mé, Bété and Djibi Rivers) are waterbodies of strategic importance for domestic, industrial and agricultural purposes. These aquatic resources of multiple uses are impacted by several pollution sources due to a large number of anthropogenic activities directly link with the population increase. It is worth noting that domestic and industrial effluents are generally rejected in the environment without any treatment. With its varying degree of urbanization as well as industrial and commercial development in the catchments [10], [11], the region provides an excellent laboratory to examine the spatial variations of water quality as a function of surface land use. However, no study has examined physicochemical dynamics by comparing the main lagoon and its tributaries. The present work reports the spatial and seasonal variation of nutrient and heavy metal concentrations in the Aghien Lagoon and its tributaries.

2 MATERIEL AND METHODS

2.1 STUDY AREA AND SAMPLING SITES STUDY AREA

The sites were selected based on a number of factors including geographical location, anthropogenic activities/major water uses and access. A detailed description of the sites is shown in Fig.1.

2.2 STUDY AREA

The study area is located in the Southeast of Côte d'Ivoire between latitudes 5° 21'N and 5° 28'N and longitudes 3° 49'W and 3° 58'W (Fig. 1). Aghien Lagoon is located between the latitudes 5° 22'N and 5° 26'N and the Longitudes 3° 49'W and 3° 55'W. Aghien Lagoon is located at the North of the Ebrié Lagoon from which it is separated by the Potou lagoon. The total area of the lagoon is about 20 km² and its depth varies from 1 to 14 m. The lagoons Aghien and Potou communicate via a natural channel. The climate is typically equatorial, characterized by four seasons including a large dry season from December to March, a major rainy season from April to July, a small dry season from August to September and a small rainy season From October to November. Fresh water enters from the Northern end of the lagoon through the Bété and Djibi Rivers and in the south by the channel connecting Aghien and Potou Lagoons. The catchment of the Aghien Lagoon is located in a covered area by dense evergreen and rain forest. Mé catchment (3958 km²) is essentially rural, the Bété and the Djibi catchments are partially urbanized (10 and 38 % of the catchments, respectively). According to [12], the main crops grown by these farmers are those of market gardeners, Oil palms, coffee, cocoa, hevea, and banana trees (plantain). Activities related to the lagoon environment are mainly fisheries, fish farming, transportation and exploitation of sand quarries.

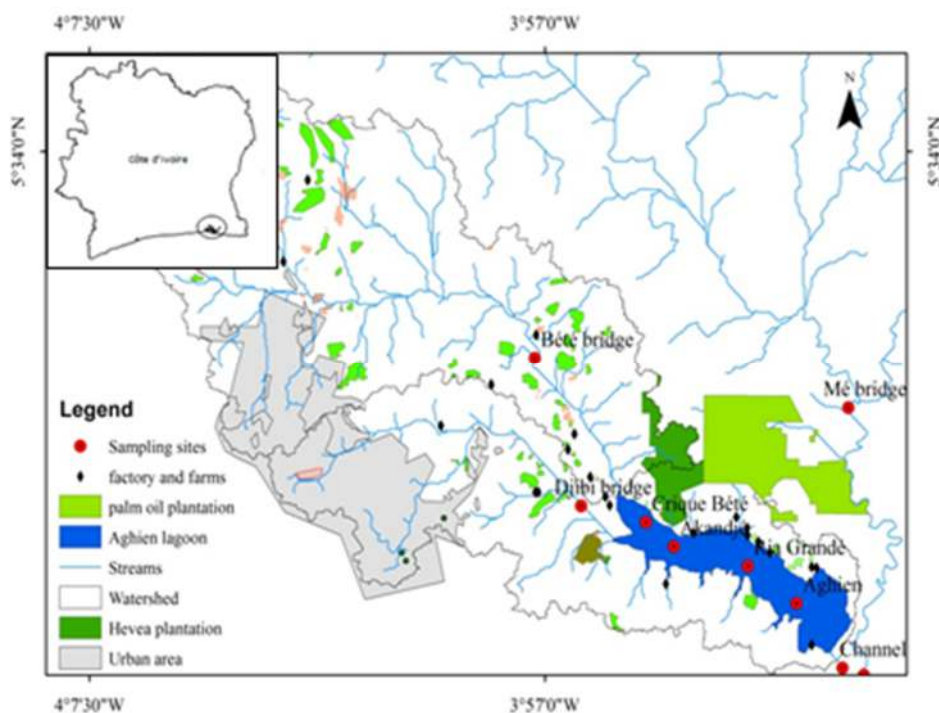


Fig. 1. Aghien lagoon catchment: hydrographic system, land uses and sampling network.

A sampling network of 9 sites was designed for the project: 4 sites located at the 4 gauging stations (Bété bridge (site 1), Djibi bridge (site 2), Mé bridge (site 3) and Aghien/Potou channel (site 9)). 4 sites are also located at the center of the Aghien Lagoon (site 5, 6, 7 and 8) from its upstream zone to its downstream zone. Finally, the last station is located at the Mé River just upstream from its confluence with the Aghien/Potou channel (site 4).

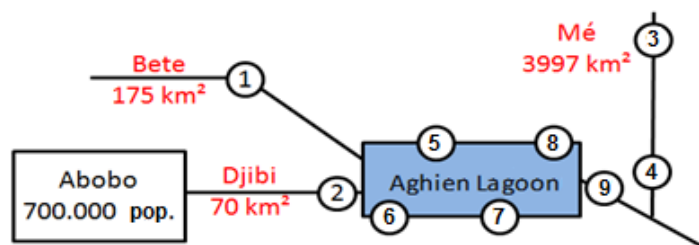


Fig. 2. Situation scheme of the 9 sampling sites

2.3 METHODS

2.3.1 SAMPLE COLLECTION AND ANALYTICAL PROCEDURES

From June 2015 to December 2016, during ten sampling campaigns, water samples were collected at the nine sites. According to the climatology of this area, sampling period has been divided into two seasons: wet season (June, November 2015 and October 2016) and dry season (September 2015 and January, March, May, August, December 2016). Samples were collected to 0.5 meter of depth and put in precleaned polyethylene bottles and preserved in cold box. A total of 6 physicochemical parameters were measured to evaluate water. Dissolved oxygen, electrical conductivity (EC), temperature and pH were determined *in situ* using HACH LANGE specific probes and HQ 40d multimeter. Total nitrogen (TN) and total phosphorus (TP) were analysed using HACH LANGE LCK338 LATON and LCK348 cuvette tests respectively and a double beam UV Visible Spectrophotometer (HACH LANGE, DR 6000). To determine Metallic Trace Elements (MTE), water samples were filtered and preserved by adding very few drops of concentrated HNCO_3 (10% v/v). Concentrations of MTE such as Zn, Cu, Cr,

As, Ni and Pb were estimated by using inductively coupled mass spectroscopy method. Water samples were also filtered with Whatman GF/F membranes for chlorophyll *a* determination.

2.3.2 DATA PROCESSING TOOLS AND STATISTICAL ANALYSIS

Statistical analyses such as correlation matrix, principal component analysis (PCA) were carried out by using XLStat 2014 and STATISTICA (Version 7.1) softwares. The Kruskal–Wallis test in ANOVA analysis was used to determine the significant differences at different sampling sites and on seasonal campaigns. Differences between means were considered significant when $p < 0.05$. Correlation coefficient amongst the physicochemical parameters were calculated by the Pearson correlations test.

3 RESULTS

Mean values, standard deviations, minimum and maximum values of the measured physical and chemical parameters are given for each sites of the sampling network in Table 2 and Table 3. The greatest contrast in variables was observed between wet and dry seasons as well as between rivers sites and lagoon ones. ANOVA test was conducted to determine whether the differences among concentrations could be significant between sites on the one hand and season. Seasonal values were grouped for analysis. The same analysis was performed to determine possible differences in metal concentrations in water

3.1 PHYSICOCHEMICAL PARAMETERS AND NUTRIENT CONCENTRATIONS

Mean temperature values, in the different Aghien Lagoon sites (5, 6, 7 and 8) ranged from $28.7 \pm 2.2^\circ\text{C}$ to $30.2 \pm 1.5^\circ\text{C}$ and did not present important variations from one season to the others ($28.5 \pm 1.5^\circ\text{C}$ to $29.4 \pm 2.3^\circ\text{C}$) (Table. 2). In the rivers sites (1, 2 and 3), temperature are significantly colder ($p < 0.05$) with mean values ranging from $25.7 \pm 2.6^\circ\text{C}$ to $28.2 \pm 2.5^\circ\text{C}$ and are no significantly different from one season to the other.

Mé (sites 3 and 4) and Bété (site 1) presented low mean electrical conductivity (EC) values ranging from 83 ± 14 to $74 \pm 35 \mu\text{S}\cdot\text{cm}^{-1}$ respectively, with the exception of Djibi bridge (site 2) which showed significant difference (Kruskal-Wallis, $p < 0.05$), with mean EC exceeding $200 \mu\text{S}\cdot\text{cm}^{-1}$. Low EC were also found in Aghien Lagoon and channel with mean values from $109 \pm 54 \mu\text{S}\cdot\text{cm}^{-1}$ and $117 \pm 88 \mu\text{S}\cdot\text{cm}^{-1}$ respectively. Although, no clear seasonal trend was observed for EC in rivers, EC values recorded in wet season in the Aghien Lagoon were significantly lower than the mean values of dry season. It is important to note that exceptionally high values of conductivity were recorded on Aghien Lagoon and channel during March 2016 (lagoon: $221 \mu\text{S}\cdot\text{cm}^{-1}$; channel: $339 \mu\text{S}\cdot\text{cm}^{-1}$) and May 2016 (lagoon: $209 \mu\text{S}\cdot\text{cm}^{-1}$; $197 \mu\text{S}\cdot\text{cm}^{-1}$). What induces great standard deviation observed in table 1. With the exception of these peaks, the values of EC observed at the other sampling month in lagoon and channel were relatively low (mean values lagoon: $83 \pm 11 \mu\text{S}\cdot\text{cm}^{-1}$; channel: $79 \pm 19 \mu\text{S}\cdot\text{cm}^{-1}$).

pH measurements at sites 5 to 8 in Aghien Lagoon were alkaline with mean values of 8.1 ± 1.1 while it was slightly acidic in the different river sites (1, 2, 3, 4) and in the channel (site 9) with mean values from 6.7 ± 0.2 to 6.8 ± 0.3 respectively. ANOVA analysis showed that there was significant difference (Kruskal-Wallis, $p < 0.05$) between rivers sites and between lagoon sites. The same analyses showed no significant difference between seasons.

Dissolved oxygen (DO) recorded in rivers are significantly lesser than in the Aghien Lagoon. In the Djibi River (site 2) mean DO saturation was about 10%. At the others sites, in Mé River (sites 3 and 4), in Bété River (site 1) and in the channel (site 9), the mean DO saturation were 71, 78 and 71 % respectively. At the lagoon sites (sites 5 to 8), the mean values of dissolved oxygen saturation do not exceed 100% and not significantly variable from one season to the other (Table 3).

The mean values of total nitrogen (TN) and total phosphorus (TP) concentrations recorded in the Aghien Lagoon (sites 5 to 8) were $2.3 \pm 1.0 \text{ mgN}\cdot\text{L}^{-1}$ for total nitrogen and $0.23 \pm 0.27 \text{ mgP}\cdot\text{L}^{-1}$ for total phosphorus (TP). The mean concentrations of TP and TN were slightly higher in the Mé (sites 3 and 4: $0.25 \text{ mgP}\cdot\text{L}^{-1}$; $2.5 \text{ mgN}\cdot\text{L}^{-1}$) and the Bété Rivers (sites 1: $0.30 \text{ mgP}\cdot\text{L}^{-1}$; $3.7 \text{ mgN}\cdot\text{L}^{-1}$) and were significantly higher (Kruskal-Wallis, $p < 0.05$) in the Djibi Rivers (site 2: $0.59 \text{ mgP}\cdot\text{L}^{-1}$; $7.3 \text{ mgN}\cdot\text{L}^{-1}$). Furthermore, the mean values of dry and wet seasons were not significantly different ($p > 0.05$) for TN but significant differences were observed between dry and wet seasons for TP values ($p < 0.05$) (Table 2), at all sampling sites.

Table 1. Spatial variation of physicochemical parameters (For each parameter and site mean values with different lowercase letters a, b and c (superscripts) indicate significant differences between the mean values (P<0.05))

Rivers

Parameters	Unity		Site 1	Site 2	Site 3	Site 4
Temperature	C°	mean ±SD	25.86 ^a ± 2.63	26.51 ^a ± 1.25	28.2 ^{ab} ± 2.45	27.79 ^{ab} ± 1.91
		range	25.2 – 32.2	25 - 28.9	26.4 - 31.7	26 - 30.7
pH		mean ±SD	6.83 ^{ab} ± 0.27	6.68 ^a ± 0.22	6.79 ^{ab} ± 0.07	6.79 ^{ab} ± 0.24
		range	6.51 – 7.24	6.29 – 6.98	6.71 – 6.89	6.48 – 7.1
%DO		mean ±SD	78.31 ^a ± 8.50	10.30 ^b ± 6.61	70.63 ^{bc} ± 10.64	56.46 ^c ± 16.68
		range	64.80 - 86.30	3.60 – 22.10	52.20 – 78.30	33.30 - 77.7
EC	µS.cm ⁻¹	mean ±SD	83 ^a ± 13.73	215 ^b ± 50.51	62 ^a ± 10.51	85 ^a ± 47.64
		range	58 – 104	117 – 285	47 – 98	45.3-203
TP	mg-P.L ⁻¹	mean ±SD	0.32 ^{ab} ± 0.33	0.52 ^b ± 0.12	0.14 ^a ± 0.08	0.24 ^{ab} ± 0.27
		range	0.039 - 0.82	0.32 - 0.67	0.066 - 0.23	0.049 - 0.71
NT	mg-N.L ⁻¹	mean ±SD	3.54 ^a ± 1.4	7.91 ^b ± 0.68	3.96 ^{cd} ± 0.68	1.87 ^a ± 0.37
		range	1.99 - 5.79	6.16 - 10.80	3.37 - 4.91	1.5 – 2.4
Chl- <i>a</i>	µg.L ⁻¹	mean ±SD	4.25 ^{ab} ± 2.24	3.47 ^a ± 0.97	5.3 ^{ab} ± 1.72	6.55 ^{ab} ± 3.96
		range	1.22 – 7.47	1.78 - 4.78	3.05 – 7.07	3.01 - 13.46

Aghien Lagoon

Parameters	Unity		Site 5	Site 6	Site 7	Site 8	Site 9
Temperature	C°	mean ± SD	29.45 ^b ± 2.03	29.86 ^b ± 1.97	29.89 ^b ± 1.98	29.62 ^b ± 1.88	28.86 ^{ab} ± 1.49
		range	26.4 - 31.5	26.5 - 31.4	26.7-31.9	26.7 - 31.8	26.7 - 30.7
pH		mean ± SD	7.92 ^{bc} ± 1.25	7.98 ^{bc} ± 1.21	8.21 ^c ± 0.83	8.26 ^c ± 1.03	6.62 ^a ± 0.34
		range	6.7 – 9.8	6.7 – 9.6	7.2 – 8.9	7.0 – 9.7	6.02 – 6.9
%DO		mean ± SD	135.52 ^b ± 35.82	135.53 ^b ± 38.03	136.54 ^b ± 26.76	128.97 ^b ± 21.01	71.13 ^a ± 21.01
		range	85.40-197.20	92.8 - 195.70	108 – 189.8	101.5 – 168.9	43.90 – 112.2
EC	µS.cm ⁻¹	mean ±SD	108 ^a ± 49.48	106 ^a ± 50.76	113 ^a ± 59.01	113 ^a ± 73.56	117 ^a ± 88.23
		range	70 – 205	68 – 283	69 – 230	65-277	51-339
TP	mg-P.L ⁻¹	mean ± SD	0.219 ^a ± 0.26	0.2 ^a ± 0.25	0.21 ^a ± 0.21	0.27 ^a ± 0.32	0.24 ^a ± 0.22
		range	0.028 - 0.89	0.021 - 0.84	0.02 - 0.65	0.025-0.87	0.051-0.80
TN	mg-N.L ⁻¹	mean ± SD	2.30 ^{abc} ± 0.40	2.89 ^{abc} ± 2.34	1.92 ^{ab} ± 0.52	1.79 ^a ± 0.52	2.2 ^{abc} ± 1.12
		range	1.82 - 2.95	1.42 - 7.07	1.07 - 2.31	1.12 - 2.53	1.02 - 4.01
Chl- <i>a</i>	µg.L ⁻¹	mean ± SD	47.23 ^c ± 15.92	47.00 ^c ± 21.24	49.57 ^c ± 17.5	38.67 ^c ± 14.42	20.41 ^{bc} ± 9.8
		range	29.68-70.08	19.42 - 78.43	26.31 - 75.86	10.15 - 48.20	6.17 - 30.7

Values of chlorophyll-*a* for the Aghien Lagoon (sites 5 to 8) were relatively high (42.46 ± 17 µg/L) compared to those of the channel (site 9) 21.08 ± 10 µg/L and those of the rivers (sites 1 to 4) 5 ± 2 µg/L (Tables 2 and 3). In addition, for all sampling sites, relatively high values were observed in dry season (53 ± 13µg/L in lagoon and 5 ± 3 µg/L in rivers) compared to those of wet season (31±12 µg/L in lagoon and 4±1 µg/L in rivers). The observed values clearly indicated that there were significant differences between the sampling sites and seasons (Kruskal-Wallis, p<0,05).

Table 2. Temporal variation in physicochemical parameters. (For each parameter and site mean values with different lowercase letters a, b and c (superscripts) indicate significant differences between the mean values according to ANOVA test ($P < 0.05$)).

Rivers

Parameters	Unity	Season	Site 1	Site 2	Site 3	Site 4
Temperature	(C°)	Wet season	25.95 ^a ± 0.36	26.1 ^a ± 0.25	26.6 ^a ± 1.22	26.8 ^a ± 1.32
		Dry season	25.77 ^b ± 1.63	26.8 ^a ± 1.68	28.73 ^a ± 2.7	28.2 ^a ± 1.64
pH		Wet season	6.89 ^a ± 0.4	6.59 ^a ± 0.12	6.78 ^a ± 0.1	6.7 ^a ± 0.21
		Dry season	6.77 ^a ± 0.12	6.72 ^a ± 0.3	6.79 ^a ± 0.09	6.81 ^a ± 0.27
%DO		Dry season	84 ^a ± 1.45	13 ^a ± 7.20	68 ^a ± 14.10	51 ^a ± 18.88
		Wet season	74 ^b ± 8.56	9 ^a ± 6.38	72 ^a ± 8.36	62 ^a ± 14.25
EC	μS.cm ⁻¹	Dry season	77 ^a ± 20.52	214 ^a ± 50.74	54 ^a ± 11.79	55 ^a ± 9.96
		Wet season	85 ^a ± 10.96	216 ^a ± 54.48	66 ^a ± 8.54	101 ^b ± 52.26
TP	mg-P.L ⁻¹	Dry season	0.07 ^a ± 0.058	0.42 ^a ± 0.08	0.118 ^a ± 0.06	0.25 ^a ± 0.31
		Wet season	0.56 ^b ± 0.29	0.64 ^b ± 0.031	0.23 ^a ± 0.2	0.21 ^a ± 0.26
TN	mg-N.L ⁻¹	Wet season	4.16 ^a ± 1.71	9.15 ^a ± 1.43	4.09 ^a ± 0.77	2.0 ^a ± 1.18
		Dry season	2.92 ^a ± 0.92	7.06 ^b ± 0.63	3.52 ^a ± 1.31	1.84 ^a ± 0.38
Chl- <i>a</i>	μg.L ⁻¹	Wet season	1.42 ^a ± 0.69	3.08 ^a ± 1.23	4.04 ^a ± 0.46	3.49 ^a ± 0.45
		Dry season	4.57 ^a ± 2.08	4.30 ^a ± 0.96	6.31 ^a ± 1.78	6.96 ^a ± 3.77

Aghien Lagoon

Parameters	Unity	Season	Site 5	Site 6	Site 7	Site 8	Site 9
Temperature	(C°)	Wet season	29.44 ^a ± 2.35	29.80 ^a ± 1.37	31.1 ^a ± 1.5	29.2 ^a ± 1.31	29.7 ^a ± 2.22
		Dry season	29.44 ^a ± 1.18	29.88 ^a ± 2.26	29.59 ^a ± 2.15	29.7 ^a ± 2.16	28.65 ^a ± 1.47
pH		Wet season	7.67 ^a ± 2.01	7.93 ^a ± 0.2	8.56 ^a ± 1.75	7.95 ^a ± 0.24	6.9 ^a ± 1.22
		Dry season	7.98 ^a ± 1.44	8.00 ^a ± 1.4	8.13 ^a ± 0.94	8.34 ^a ± 1.17	6.5 ^a ± 0.35
%DO		Wet season	140.97 ^a ± 37.7	140.43 ^a ± 41.38	123.83 ^a ± 13.75	118.93 ^a ± 6.65	74.90 ^a ± 34.58
		Dry season	126.43 ^a ± 38.1	132.59 ^a ± 40.57	144.16 ^a ± 31.07	134.99 ^a ± 25.21	68.88 ^a ± 12.57
EC	μS.cm ⁻¹	Dry season	81 ^a ± 15.61	80 ^a ± 17.56	80 ^a ± 11.39	76 ^a ± 16.58	68 ^a ± 17.71
		Wet season	120 ^b ± 10.96	117 ^b ± 57.44	127 ^b ± 66.19	130 ^b ± 83.68	138 ^b ± 99.19
TP	mg-P.L ⁻¹	Wet season	0.12 ^a ± 0.06	0.12 ^a ± 0.34	0.11 ^a ± 0.24	0.13 ^b ± 0.31	0.15 ^a ± 0.28
		Dry season	0.09 ^a ± 0.075	0.11 ^a ± 0.1	0.17 ^a ± 0.20	0.27 ^a ± 0.36	0.14 ^a ± 0.062
TN	mg-N.L ⁻¹	Wet season	2.95 ^a ± 0.47	2.04 ^a ± 0.42	2.21 ^a ± 0.56	1.12 ^a ± 0.64	4.01 ^a ± 1.04
		Dry season	2.14 ^a ± 0.21	3.11 ^a ± 2.65	1.85 ^a ± 0.58	1.96 ^a ± 0.40	1.74 ^b ± 0.56
Chl- <i>a</i>	μg.L ⁻¹	Wet season	39.33 ^a ± 5.44	35.52 ^a ± 6.04	37.48 ^a ± 15.79	37.34 ^a ± 22.55	20.46 ^a ± 5.07
		Dry season	46.28 ^b ± 15.51	47.6 ^b ± 20.77	46.57 ^a ± 17.24	56.12 ^b ± 13.41	21.35 ^a ± 10.86

3.2 DISSOLVED HEAVY METALS

The results of spatial variations of the 6 heavy metals in surface waters were illustrated by box-plots (Fig. 2). Higher value of Zn was recorded in Bété River (site 1: 36.73 ± 68.27 μg.L⁻¹) (Fig. 2a). Furthermore, Aghien Lagoon (site 5 to 8) presented low mean values of Zn (5.40 ± 3.12 μg.L⁻¹). Ni values were relatively homogeny at all sampling sites and the statistical tests do not reveal any significant difference between the sampling sites (Fig. 2b). The mean concentration of Cu in Mé (site 3: 1,90 ± 0,43 μg.L⁻¹) was almost double than in the Aghien Lagoon (site 5: 1,0 ± 0,39 μg.L⁻¹) and site 6 (1,06 ± 0,95 μg.L⁻¹) (Fig. 2c) indicating significant spatial variation ($p < 0,05$) in Cu. The highest mean concentration of Pb was found in the lagoon (site 8: 0,28 ± 0,1 μg.L⁻¹) and the lowest concentration in site 5 (0,11 ± 0,29 μg.L⁻¹) (Fig. 2d). From ANOVA analysis, the results indicate no significant difference ($p > 0,05$) amongst the sampling locations.

Between the rivers, Djibi (site 2) exhibited highest values of As with mean values of 0.75 ± 0,4 μg.L⁻¹. Bété and Mé Rivers (sites 1 and 3 respectively) presented mean values from 0.24 ± 0.05 and 0.22 ± 0.02 μg.L⁻¹ respectively (Fig. 2e). Furthermore, As values were uniform in the Aghien lagoon (sites 5 to 8) with mean concentration about 0.28 ± 0.03 μg.L⁻¹. The results also indicate that significant differences ($p < 0.05$) appeared between Djibi and Mé Rivers (sites 2 and site 3) for this element. As

regards to Cd, there exists a uniform distribution prevailing over Aghien lagoon site ($0.044 \pm 0.07 \mu\text{g.L}^{-1}$) (Fig. 2f). Mé River (site 3) recorded high mean value for Cd ($0.13 \pm 0.28 \mu\text{g.L}^{-1}$).

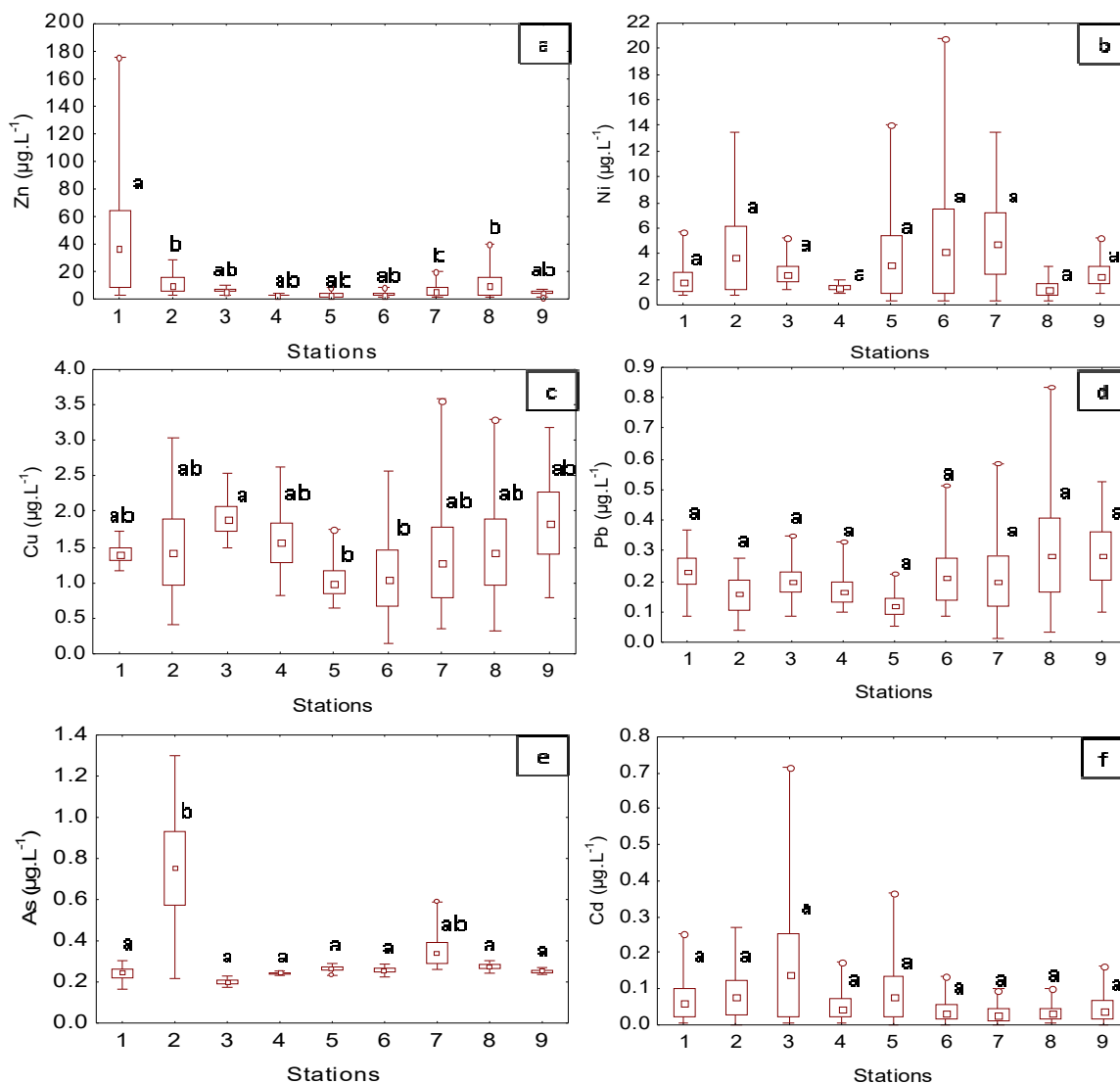


Fig. 3. Cr, Zn, Pb, As, Ni and Cd content in sampling sites of Bété, Mé, Djibi Rivers and Aghien lagoon. Means with different lowercase letters a, b and c are significantly different from one to another according to ANOVA test (P<0.05).

□ Mean □ Mean±SD I Min-Max

A well-defined spatial heterogeneity in distribution of different dissolved metal was observed between the lagoon and the rivers (Fig.3). The relative dominance of the heavy metals in water was observed in the following sequence: Zn>Ni>Cu>Pb>As>Cd.

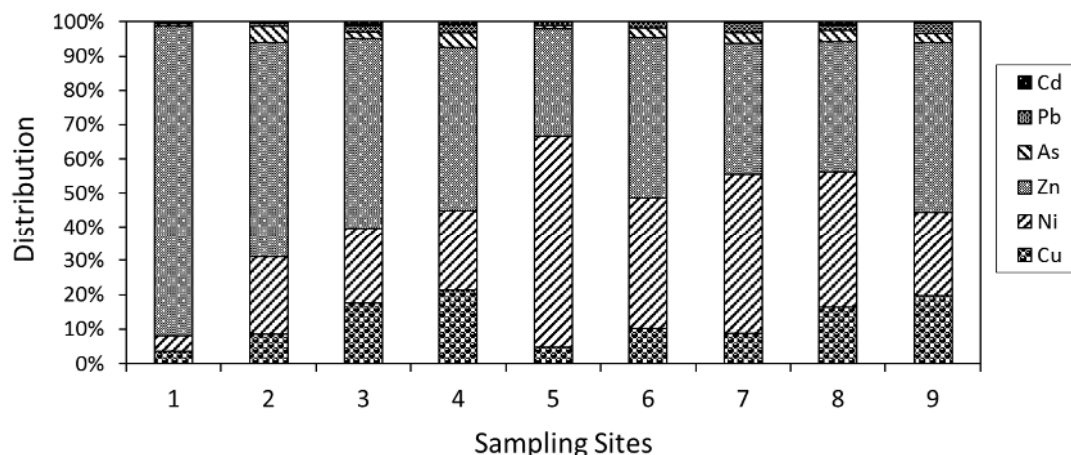


Fig. 4. Distribution of heavy metals in water samples from 9 sampling stations at Bété, Mé, Djibi Rivers and Aghien Lagoon.

Compared with other dissolved heavy metals, Zn possessed high distributions in tributaries (Sites 1, 2, 3 and 4) and channel (Site 9) than those of lagoon (Sites 5, 6, 7, 8). Zn percentage ranged from 52% to 91% in tributaries and 56% in channel. In lagoon the percentage ranged from 38% to 47%. Ni exhibited the highest distribution in lagoon (> 35%) from sampling sites. The percentages of Ni accounted 16%, and 25% for the tributaries and channel, respectively. Cu exposed highest similar distribution in Mé creek (21%) (Site 4) and channel (20%). Pb, As, Cd presented lower distribution (<5%) in the all sampling sites.

3.3 RELATIONSHIP BETWEEN PARAMETERS

The study of different water quality parameters necessitates the correlation analysis of the parameters to discern possible relationships. Table 3 shows the correlation coefficients of physicochemical and chemical parameters in waters.

In lagoon and rivers (Table 3), significant positive correlations were observed TP and TN ($r=0,734$, $p<0.01$; $r=0.876$, $p<0.01$ respectively). There was low inverse relationship ($r=-0.718$) between DO and TP in lagoon, DO and TP ($r=-0.709$), DO and TN ($r=-0.690$) in rivers. Parameters relation reveals also high ($r=0.835$, $p<0.05$) positive correlations between Chl-*a* and DO saturation in lagoon. However, there was high ($p>0.01$) relationships existed between Chl-*a* and with TP ($r=0,801$) and with TN ($r=0,538$, $p>0.05$) in lagoon. There was low ($p>0.05$) inverse relationships existed between temperature and TP ($r=-0.224$ in lagoon), $r=-0.245$ in rivers) and with TN ($r=-0.359$) in rivers.

We can also observe that certain heavy metals show correlations between them. There was a significant positive correlation ($p<0.05$) between Zn and Ni ($r=0,714$) in lagoon. Low correlation ($p>0.05$) correlation existed between As and Ni ($r=0,826$) in rivers.

The inter-relationship of different parameters is useful in revealing some association of heavy metals with the physicochemical conditions in the rivers and in the lagoon.

Table 3 reveal low relationship ($p>0.05$) between DO and Pb ($r=0.814$) in lagoon. However, significant ($p<0.05$) correlation existed between TP and Cd ($r=0.866$) in lagoon and TP and As ($r=0.860$) in rivers. pH also low correlated negatively ($p>0,05$) with Cu ($r=-0.420$), Pb ($r=-0.064$) in lagoon and As ($r=-0.218$), Pb ($r=-0.264$) in rivers. The correlation between temperature and heavy metal is relatively low and negative in rivers and lagoon excepted with Zn ($r=0.657$) in rivers.

Table 3. Correlation half-matrix of physicochemical parameters and dissolved heavy metal

Rivers													
Variables	DO	pH	TN	TP	T°C	Chl- <i>a</i>	EC	Cu	Zn	As	Pb	Cd	Ni
DO	1												
pH	0.012	1											
TN	-0.690	0.369	1										
TP	-0.709	0.261	0.876**	1									
T°C	0.009	-0.751	-0.359	-0.245	1								
Chl- <i>a</i>	-0.250	-0.005	0.269	0.078	0.004	1							
EC	0.858	0.227	0.434	0.278	0.214	0.175	1						
Cu	0.081	-0.030	-0.015	0.198	-0.023	0.473	-0.098	1					
Zn	0.218	0.649*	0.062	0.001	0.657	-0.264	-0.012	-0.032	1				
As	-0.862	-0.218	0.648*	0.860*	0.206	0.218	0.697	-0.068	-0.016	1			
Pb	0.586	-0.264	-0.077	-0.221	0.282	-0.070	-0.231	0.121	0.690	-0.227	1		
Cd	0.021	-0.037	-0.012	-0.114	0.030	0.615	-0.039	0.479	-0.078	-0.021	0.051	1	
Ni	-0.591	0.211	0.459	0.605	0.209	0.605	0.734	0.047	-0.018	0.779	-0.060	0.105	1

Aghien Lagoon													
Variables	DO	pH	TN	TP	T°C	Chl- <i>a</i>	EC	Cu	Zn	As	Pb	Cd	Ni
DO	1												
pH	0.396	1											
TN	0.194	-0.007	1										
TP	-0.718	-0.257	0.734**	1									
T°C	0.152	0.538	0.001	-0.224	1								
Chl- <i>a</i>	0.835*	0.159	0.587	0.821**	0.073	1							
EC	-0.051	0.050	-0.948*	-0.435	0.002	-0.361	1						
Cu	-0.270	-0.420	0.139	0.065	-0.631	-0.037	-0.265	1					
Zn	0.121	-0.246	0.517	-0.178	-0.357	0.345	-0.445	0.372	1				
As	0.013	0.009*	0.642	-0.389	0.154	0.188	-0.738	0.046	0.038	1			
Pb	0.814	-0.064*	0.219	-0.488	-0.002	0.748	-0.071	-0.036	0.433	-0.003	1		
Cd	-0.864	-0.149	-0.686	0.866*	-0.097	-0.782	0.467	0.022	-0.326	-0.304	-0.628	1	
Ni	0.107	-0.269	0.202	-0.049	-0.530	0.206	-0.139	0.277	0.714*	-0.023	0.483	-0.157	1

Legend: (Pearson rank correlations, the asterisk indicates significant correlations at $p < 0.05$).

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

4 DISCUSSION

4.1 PHYSICAL CHEMICAL PARAMETERS IN RIVERS AND LAGOON

The mean values of water temperature obtained are within the limit established by World Health Organization for drinking water, which was between 25 and 30°C [13] and Water quality evaluation system on biological aptitude [14]. Temperature conditions in coastal zones depending upon their insolation, local atmospheric variation, [15]. Lagoon water temperature was comparatively higher than river water temperature. Differences in temperature could be due to low hydraulicity in lagoon which promotes their greater heat storage capacity. Vegetation along the river bank could also play a significant role in influencing the temperature of aquatic ecosystem. Also, similar report was obtained by [11] when they observed that the lagoon temperature ranged between 27,57 and 31,59 °C while rivers Me temperature was between 26.08 and 28,98°C.

Seasonal variations showed higher value of EC in dry season and lower value in wet season due to dilution of the water by the contribution of the waters storm. Among all three rivers, an EC value of Djibi River (200 $\mu\text{S cm}^{-1}$) is much higher and would be explained by the permanent wastewater contributions coming from the commune of Abobo. These values of conductivity remain however in the same range of variation as those obtained by [16] on the rivers of the south-east of Ivory Coast.

The pH of an aquatic system is an indicator of water quality and the extent of pollution in the watershed area. Water normally shows a pH ranging from 6.5 to 8.5 [13] and (pH 9) for Water quality evaluation system [14]. Rivers Me, Djibi and Bete presented low acid mean pH of 6.8. These values compared well with those generally measured in Ivorian coastal rivers (between 6.4 and 7.5). This slight acidity of the waters was coherent with the regional geological basement. Higher pH in lagoon was directly linked to photosynthetic assimilation of dissolved inorganic carbon by plankton [17].

The high dissolved oxygen concentration in lagoon can be attributed to the abundance of phytoplankton that increased photosynthetic activity leading to production of large amount of dissolved oxygen [18]. Compared to previous records from the Aghien lagoon, oxygen concentrations of the present study (7.5-10.18 mg.L⁻¹) were in good agreement with concentrations (7.34-8.52 mg.L⁻¹) reported by [11]. DO saturation was significantly lowest in Djibi River compared to Bété and Mé Rivers. DO reduction observed in the Djibi River (more anthropised) was indicative of poor water quality caused by sewage effluent discharges. Similar results (0.7–3.21 mg.L⁻¹) were also reported by [19] in Banco River Basin in Ivory Coast.

Relatively high Chl-*a* values were observed in Aghien lagoon during dry season due to high phytoplankton productivity during this period as also shown by [20] controlled by bacterial action in the process of denitrification-nitrification. The primary productivity that is a photo-chemical reaction that cannot proceed unless suitable substrate (light), nutrients and bacterial community activity are available [20].

High concentration of TN and TP, in conjunction with other factors, is often associated with discharge of effluents from human activities [21]. This can lead to a considerable alternation in the water quality and will have an impact on the aquatic life ultimately. TN and TP concentrations in Djibi River were very high compared to concentrations recorded at the other sites. This is attributed to effluent discharge from of urban zones. [22] suggested that TN and TP concentrations in eutrophic rivers and streams are higher than 1,5 mgN.L⁻¹ and 0,075 mgP.L⁻¹, respectively. In the present study, TN and TP concentrations at all sites, were higher than the suggested values. Overall, the rivers showed a marked increase of TP during the long wet season. Land use around riverine areas in Abidjan is predominantly for farmland and could be a possible explanation for the high levels of TP due to runoff and leaching during rainy season as observed in this study. This corroborated with the results of [23]. The highest concentration of Cu was found in Me River, but all of the sampling locations were below the WHO standard (2000 µg.L⁻¹). This suggests that these metals may come from natural input [24], [25].

4.2 METAL CONCENTRATION IN WATER

During the study period, the average values of As in the Djibi was significantly high. In the lagoon, As concentrations are relatively homogeny. [26] indicated that As could have divers origins: crustal materials and natural processes, as well as they suggested that the sources were more likely anthropogenic. The highest As concentrations measured in Djibi River could be associated with human activities such as wastewater effluents from the Abobo, discharged without any treatment in the river. As is widely distributed in the environment because of its natural and anthropogenic sources [27]. The lower concentration of As in water could be interpreted as a consequence by various processes like adsorption and desorption of organic matter. This heavy metal show strong interaction with humic acids in forming metal-dissolved organic matter complexes, leading to formation of covalent bonds with the radicals of humic acids [28]. Comparing the average concentrations of studied metals with the limit for drinking [3] (Table 5), it was found that all metals have an average concentration lower than the standard (10 µg/L).

Pb was found to be low in all locations. The recommended safe levels of dissolved Pb should be less than 10 µg.L⁻¹ [3]. Pb normally exists in undissolved forms and its concentration in aquatic systems is normally low except when pollution is indicated [29]. Pb in sampling station demonstrated the influence of untreated domestic sewage discharge from Abobo and/or agricultural runoff.

Ni, Cd and Zn concentrations were below the WHO standard (70, 3 and 5000 µg/L respectively) and Water quality evaluation system (20, 5 and 3000 µg/L respectively) [14] (Table 5) indicating that the source of these dissolved heavy metal is not necessarily as a result of the anthropic activities but may result from natural geological sources [30].

In this study, the elevated content of Cu at certain station is more likely to originate from anthropogenic sources. The difference in the metal levels in the water of the Aghien Lagoon with other lagoon may be due to differences in urban contamination sources or the number of parameters such as clay content, nutrient, Chl-*a* and environmental factors, which control the solubility and, therefore, the availability of metals [31]. Concentrations of the six metals (As, Zn, Cu, Pb, Ni and Cd) in surface waters of the Aghien Lagoon, Mé, Bété and Djibi Rivers were much lower or comparable to the results obtained in others lagoons and rivers references (Table 5). Globally, concentrations are largely under the WHO level recommendations [3] and Water quality evaluation system on biological aptitude [14]. Under environmental conditions, metals are relatively insoluble in water and remain predominantly associated with suspended solids and sediment. When compared with the

previous study conducted in the same area by [11], concentrations carried out on the sediments give us higher mean values for the heavy metal studied (314 $\mu\text{g.g}^{-1}$ for Zn, 100.35 $\mu\text{g.g}^{-1}$ for Cu, 66.43 $\mu\text{g.g}^{-1}$ for Pb, 46.37 $\mu\text{g.g}^{-1}$ for the As, 0.70 $\mu\text{g.g}^{-1}$ for Cd and 226.89 $\mu\text{g.g}^{-1}$ for Cr).

Table 4. Comparison of heavy metal concentrations in Aghien Lagoon and tributaries with those of other water in the world.

Study areas or standard for drinking water and biology	Maximum concentrations ($\mu\text{g.L}^{-1}$)						References
	Cu	Cd	Pb	Ni	Zn	As	
Aghien lagoon	3.57	0.36	0.83	20.81	39.44	0.58	Present study
Tributaries	3.03	0.717	0.368	13.48	175.3	1.3	Present study
Cocody Bay	85	42	27	-	94	-	[32]
WHO (2011)	2000	3	10	70	-	10	[3]
WQES	10	18	52	62	43	100	[14]
Shanomi Creek in the Niger Delta (Nigeria)	811	366	278	-	1383	606	[17]
Tigris River (Turkey)	165	1.368	0.342	72.0	37.0	2.354	[33]

4.3 CORRELATION BETWEEN PARAMETERS

The correlation analysis applied to assess the relationship between physicochemical and chemical parameters showed positive correlations between Chl-*a* and DO saturation in lagoon and rivers. The positive correlation between chl-*a* concentration and dissolved oxygen is due to necessity of the latter for phytoplankton biogeochemical processes. Dissolved oxygen is one of the most important water quality parameters for phytoplankton health because of its influence in a number of biogeochemical processes such as respiration and metabolism that affect their life [34].

Water temperature is most important among various physical factor affecting the distribution and seasonal variation of nutrients [35]. In the present study we have found significant negative correlation with nutrients indicating the influence of the temperature on the biological reactions.

TP was strongly and positively correlated with Chl-*a* in lagoon. The TN and TP are major contributors to eutrophication, which causes an excessive growth of algae that depletes DO through the decomposition process [36]. The showed that DO values usually remain lower when the rates of respiration and organic decomposition are high [37]. When water receives an excessive contribution of nutriments, a lot of dissolved oxygen is rapidly consumed by the biological aerobic processes and may affect the water quality [37]. Positive relationship between chl-*a* and phosphorus suggest thus that TP play a more important role in regulating phytoplankton. Furthermore, in their studies on the Florida Lake, [38],[39] have formerly affirmed that phosphorus is the primary limiting nutrient of the growth of phytoplankton.

The inter-relationship of different parameters is useful in revealing some association of heavy metals with the physico-chemical conditions in the river water and lagoon. The inverse relationship between pH and Cu, Pb and As in lagoon and rivers reveal that pH effect therefore plays a very significant role in metal behavior in water. Among these roles we can note the complexation phenomenon. Indeed, the results of the experiments of adsorption carried out by [40] with various values of pH (pH=5, 6, 7 and 8) showed that in the case of Cu, Cd and Zn, we observed a systematic increase in the rate of adsorption when the pH increases (Cu, 70 to 90 %; Cd, 75 to 90%; Zn, 75 to 95%). For same experiment, the evolution of the adsorption of Pd is not very significant (99 to 97 %).

Zn, As and Cd were negatively correlated to oxygen saturation indicated that heavy metals in water were influenced by DO [18]. Changes in redox conditions that are partly controlled by the oxygen content in the water can strongly affect the mobility of heavy metals in water [41]. Except for DO, some other factors such as temperature can also affect the distributions of heavy metal in water [42]. Significant and non-significant positive correlations were detected between heavy metal content in water and temperature. The adsorption content of heavy metals often decreases gradually with increasing temperature [42].

Based on the correlation matrices obtained for association of heavy metals, Zn strongly correlates with Ni in lagoon suggesting similar sources of input (human or natural) for these two metals in waters. High correlations between heavy metals in water may reflect similar levels of contamination and/or release from the same sources of pollution, mutual dependence and identical behavior during their transport in the river system [43],[44]. These correlations were interpreted as a confirmation of the presence of various anthropogenic or fixed sources of Zn and Cu pollution in the study area. A first source already identified for these dissolved metals is the wastewater discharge from the municipality of Abobo, but earlier studies

[45],[11] suggest that other stationary or diffuse sources such as runoff or leaching of acidic agricultural soils with high pesticide and mineral fertilizer contents. Moreover, in the absence of the industrial activity rejecting heavy metals in Mé basin area, the strong correlation between Zn/Ni and Cu/As raise the assumption of a source (normal) geogenic for these dissolved metals [46].

5 CONCLUSION

This study identifies distinct spatial variations of water quality between the Aghien Lagoon and its tributaries. In the Djibi River, upstream from the Aghien Lagoon, water exhibits poor quality attributed to local pollutant inputs from Abobo. The average concentration of studied dissolved metals (As, Cd, Zn, Cu, Ni, and Pb) for all sites was lower than WHO Standard for Drinking Water Quality and Water quality evaluation system on biological aptitude. Nevertheless, presence of these dissolved metals in water induces a probable contamination of anthropic and in some cases (Mé) of natural origin. Significant relationships between studied variables (PT NT, pH and DO) and heavy metal concentrations were assessed. This suggests that different physicochemical parameters influence the concentrations of some dissolved heavy metals in the water. This research provides a basis for the knowledge of water quality characteristics in the Bété, Djibi and Me Rivers and a reference for pollution control of the Aghien lagoon in the future.

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