Reference values of the physico-chemical parameters of the water streams of Tai national Park (Côte d'Ivoire)

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ABSTRACT
In the absence of reference conditions, the evaluation of the physico-chemical quality of water in West Africa is based on European standards which are inadequate. This study was carried out in order to determine the threshold values of physico-chemical parameters for the monitoring of water quality in tropical forest rivers in West Africa. Thus, physico-chemical parameters were measured in 324 surface waters collected in three typical rivers of Taï National Park (Côte d’Ivoire) from May 2016 to April 2017. Subsequently, the sampling stations were categorised as natural, transitional and impacted based on a principal component analysis (PCA). The results confirmed the typology of sampling stations reported in the literature. Based on best professional judgment (BPJ) and trisection methods, the reference values for Tai National Park are Temperature: 25.10-25.33°C; pH: 6.86 - 7.04; DO: 6.33 - 6.40 mg/L; EC: 37.13 - 38.20 µS/cm; TSD: 27.50 - 29.03 mg/L; NO₂⁻: 0.005 - 0.009 mg/L; NO₃⁻: 0.450 - 0.625 mg/L; PO₄³⁻: 0.053 - 0.054 mg/L; TP: 0.123 - 0.134 mg/L; FCl: 0.03 - 0.04 mg/L; TCl: 0.04 - 0.05 mg/L. These data could be used as threshold values for monitoring rivers and rainforest wetlands in West Africa.

Keywords: Water quality, watershed, rivers, reference conditions, protected area, West Africa.

INTRODUCTION
Freshwaters constitute an important natural resource for life (Dudgeaon et al., 2005). They constitute the essential support for the socio-economic development of a country. Unfortunately, these natural resources are subject to strong anthropogenic pressures (Silva et al., 2010; Fonsceca et al., 2014). These anthropogenic threats are for the most part related to the demographic explosion, the rapid expansion of urbanization and the conversion of forests into agricultural areas. Several authors have recognized that urbanization represents a source of heavy metals (Tomazelli et al., 2003; Campos et al., 2009) and organochlorine compounds (Baudino et al., 2003; Silva et al., 2008). The land use changes involve physical and
chemical alterations that may alter the structure and how aquatic systems function (Niyogi et al., 2004; Silva et al., 2012). The chemical alteration affect nitrate, ammonium, calcium, potassium and aluminum concentration, as was proven in streams located in temperate (Wang et al., 2006; Kamisako et al., 2008; Rai et al., 2010) and tropical regions (Neill et al., 2006; Andrade et al., 2011; Silva et al., 2011). All these anthropogenic pressures are threatening directly or indirectly the chemical quality of freshwaters (Alexander et al., 2000; Neill et al., 2006). Therefore, sustainable management of freshwaters are needed for both the natural diversity and the ecological balance.

Establishing reference concentrations in rivers and streams is an important tool for environmental management (Cunha et al., 2011). It allows to assess until which level a measured condition differs from a desired, expected or previous situation (Hawkins et al., 2010). Indeed, the analysis of water chemistry provides a measure of the quality and the integrity of the aquatic ecosystem because this river represents the local and regional hydrosphere and provides some basic functions of ecosystems (Thomas et al., 2004; Niyogi et al., 2004).

This water quality assessment approach has been explored in North America (Dodds and Welch, 2000; Dodds and Oakes, 2004; Christ et al., 2007; Weigel and Robertson, 2007), Western Europe (Schneider et al., 2003; Irmer and Rechenberg, 2004; Nijboer et al., 2004; Vighi et al., 2006; Baattrup-Pedersen et al., 2009), Oceania (Newall and Tiller, 2002; Snelder et al., 2004) and recently in tropical areas in Brasilia (Cunha, 2011; Fonséca et al., 2014). This work has significantly contributed to establishing or strengthening baselines for better monitoring of rivers and streams in Europe (DCE) and North America.

In Africa, no such studies have been done. However, this continent is not excepted from the impacts of the use of chemical substances in agriculture and the destruction of forests in favor of agricultural activities (Kouamé et al., 2008; Dovonou et al., 2011; Dianou et al., 2011 and Kamelan et al., 2013). In addition, the population growth of African countries, for the most part, coincides with a decline in the economy. It follows a widespread insalubrity affecting surface water supplies. In the absence of a reference condition, the water quality assessment for developing countries such as Côte d’Ivoire is based on European standards (Dianou et al., 2011). Yet, reference conditions may vary depending hydrographical watersheds relation to the geological and biological configuration of the land from where runoff flows (Cunha et al., 2011). This fact fostered the establishment of reference conditions by ecoregions for the evaluation of rivers and lake as has been the case with the North America, Western Europe, Oceania and Brasilia. On this basis, it is urgent to implement such a study to establish the reference conditions for the objective and effective monitoring of African watercourses.

Because human activity is widespread, establishing standard physico-chemical parameters for forest tropical areas remains an ambitious project. Nevertheless, undisturbed natural habitats still exist and could constitute areas of study to implement such research. Indeed, the Tai National Park (TNP) (Côte d’Ivoire, West Africa) is a typical forest of undisturbed natural habitat. Classified as Biosphere Reserve and World Heritage Site by UNESCO, the TNP is the last unspoiled ecosystem of primary forests under protection in West Africa (Kouakou et al., 2009). This park is the largest and best preserved remnant of the Upper Guinea rainforest of West Africa. Recent studies have revealed an excellent quality of freshwaters in the Tai National Park as evidenced by the abundance of Mormyridae, a family of indicator fish of good water quality (Grell et al., 2012; Kamelan, 2014; Kamelan et al., 2014) (Hugueny et al., 1996; Kamdem-Toham and Teugels, 1998).

Several methods have been proposed to define the limits between trophic status levels in aquatic systems and to determine reference
concentrations for water variables. Among these methods, the best professional judgment (BPJ) is based on the selection of less affected rivers and streams in a given watershed and analysis of nutrients in those waters (Cunha et al., 2011). The trisection method has been used by various bioassessment protocols to estimate baseline conditions in the absence of pristine or reference sites. Other techniques are based on statistical methods that eliminate the influence of human land use (Dodds and Oakes, 2004) and models for predicting expected concentrations in a given ecosystem (Smith et al., 2003; Soranno et al., 2008), but these methods require more data than are available for some countries (Cunha et al., 2011). According to Cunha et al. (2011), the preferred method for determining reference conditions depends upon three main factors: (i) data availability, (ii) reference site availability; (iii) specific objectives of the work. The objective of this study was to examine physico-chemical parameters of rivers in the Taï National Park for using them as potential threshold values by the method BPJ and the trisection method for monitoring physico-chemical parameters of tropical forest rivers in West Africa.

MATERIALS AND METHODS

Study area

The Taï National Park (TNP) is located in south-western Côte d'Ivoire (Figure 1). This park is the largest and best-preserved remnant of the ‘Upper Guinea' rainforest of West Africa. The Taï National Park consists of 5340 km of tropical evergreen forest (OIPR, 2016). The park is situated on a Precambrian granite penplain of migmatites, biotites and gneiss which slopes down from the gently undulating drier north to the more deeply dissected land in the south, where the rainfall is heavy. The annual average temperature, humidity, precipitation and sunstroke in the South-West ranges from 24 to 33°C, 50 to 80%, 1500 to 2300 mm/m², and 100 to 230 h/j, respectively (Ceda, 1997). The rainfall gradient is from north-east to south-west. The TNP is drained by several permanent rivers, of which the mains are the Meno and the San Pedro Rivers that take their source in the park. Except for the Hana River that rises out of the park and flows into the Cavally River. The characteristics of each river are given in Table 1.

Three sampling stations were chosen based on the degree of anthropogenic disturbance: a station in the peripheral zone of the park, a station located in the park away from anthropogenic activities, and an intermediate station (Figure 1). The typology of these sampling sites was defined on the basis of the work done by Grell et al. (2012), Diarrassouba (2014) and Kamelan (2014). Table 2 presents the environmental characteristics of each study station.

Data collection and chemical analysis

The physicochemical parameters of the Taï National Park were measured monthly from May 2016 to April 2017 in 9 stations. Water temperature, pH, dissolved oxygen, conductivity, total dissolved solids and oxidation reduction potential were measured in situ between 7:00 and 8:00 a.m., 12:00 noon and 1:00 p.m., and between 3:00 p.m. and 4:00 p.m. using a Lovibond type multipara meter Senso Direct 150 according to Rodier et al. (2009). Nitrite, nitrate, ammonium, total phosphorus, free and total chlorine were measured directly using Checher digital mini-photometers HANNA mark, by adding their specific reagents (Hi 764: nitrites; Hi 713: Phosphates, Hi 736: total phosphorus, Hi 701: free chlorine, Hi 711: total chlorine and Hi 733: ammonium). The nitrate was determined ex situ using a spectrophotometer type Hi 83200 Hanna Mark. At each sampling site, 35 mL of water was taken from the surface in a sealed plastic bottle to avoid exchange with the surrounding environment. The principle of the method is based on Beer Lambert’s law (Rodier et al., 2009) which indicates the proportionality of the optical density with the thickness of the solution (sample analysed) and the concentration of the desired chemical element. After adding the appropriate reagent, the
water-reagent sample mixture is poured into the spectrometer which displays the concentration of the ions as compared to a control solution consisting of a sample of the water to be analysed without the reagent.

**Data analysis**

A rapid assessment based on the available research studies coupled with a principal component analysis (PCA) were carried out to establish the typology of the sites (natural, transition and impacted sites). For each sampling site, the mean values considering all seasons were used. Software XLSAT 2016 for multivariate analyses. The different categories resulting from the rapid assessment and ACP were characterized by a univariate descriptive analysis (minimum, maximum, mean and standard deviation). An inferential analysis by the Kruskall-Wallis test, with multiple comparisons Dunn posterior test from the STATISTICA 7.1 software, was applied to compare the spatial variation of the physico-chemical parameters among the three groups. The results were considered significant when \( p \) was less than 0.05. Two methods were used to define the reference conditions. The first method, BJP, is based on the calculation of the median values of natural stations). As for the second a trisection method (Buck et al., 2000), the median of the lower third (1/6th) for each variable was calculated from the whole dataset, including both impacted and natural sites.

![Figure 1: Map of Taï national Park with indication of the sampling sites. Ha: Hana River; Me: Meno River; SP: San Pedro River.](image)
Table 1: Principal characteristics of rives of Taï National Park.

| Rivers   | Length (km) | Watershed (km²) | Source                  | River mouth                |
|----------|-------------|-----------------|-------------------------|----------------------------|
| Hana     | 105         | 4300            | Outside the park        | Cavally                    |
|          |             |                 | - Soubre area           |                            |
| Meno     | 70          | 1895            | TNP                     | Hana                       |
| San Pedro| 117         | 3317 whose 17% in TNP | TNP                     | Atlantic Ocean             |

TNP: Taï National Parc

Table 2: General analysis of the ecological status on the basis of research studies from Grell et al., (2012), Diarrassouba (2014) et Kamelan (2014).

| Rivers   | Sites        | Codes | Grell et al., 2012 | Diarrassouba 2014 | Kamelan 2014 |
|----------|--------------|-------|--------------------|--------------------|--------------|
| Hana     | Mont Nienonkoué | Ha2   | Good               | Good               | -            |
|          | Ecotel       | Ha3   | Good               | Good               | Good         |
|          | Point O      | Ha1   | Degraded           | Degraded           | Menaced      |
| Meno     | Source       | Me1   | -                  | -                  | -            |
|          | Point 13     | Me2   | -                  | -                  | -            |
|          | Djouroutou   | Me3   | Degraded           | Degraded           | Degraded     |
| San Pedro| Source       | SP1   | Good               | Good               | Degraded     |
|          | Palabod      | SP2   | Degraded           | -                  | Degraded     |
|          | City         | SP3   | -                  | -                  | -            |

:-: No data.

RESULTS
Water physical and chemical characteristics

The descriptive analysis of water variables is shown in Table 3. Water temperature varied from 24.2 to 35.6°C, pH from 6.23 to 9.10, dissolved oxygen between 1.3 and 10.2 mg L⁻¹, electric conductivity from 26.9 to 162 µS cm⁻¹, and TDS from 19.2 to 89.7 mg L⁻¹. Nitrates varied from 0.12 to 2.22 mg L⁻¹, nitrites from 0.003 to 0.03 mg L⁻¹ while reactive phosphorus and total phosphorus ranged between 0.007-0.420 mg L⁻¹ and 0.04-6.50 mg L⁻¹, respectively. Significant spatial variations in temperature, conductivity, TDS, nitrite, nitrate, total phosphorus and free chlorine (Kruskall-Wallis, p <0.05) were found at all the sites. The site SP3, located in San Pedro, an urban area, reported higher values of temperature (28.9°C), conductivity (89.8 µS/cm), TDS (64.135 mg/L), and lower values of dissolved
oxygen (4.35 mg/L) compared to the other stations located in the park. Inside the park, the site SP1 registered the lowest value of water temperature (25°C), conductivity (37.135 µS/cm) and TDS (26.515 mg/L), and the highest dissolved oxygen value (6.765 mg/L) of Taï National Park. Very high total phosphorus values were measured in site SP2 (3 mg/L) compared to other stations (0.094-1.8 mg/L).

Sites typology

The classification of the sampled sites based on previous works (Grell et al., 2012; Diarrassouba, 2014; Kamelan, 2014) shown in Table 4 indicates that. The sampled sites can be grouped in three categories including natural, transition and impacted sites. Principal component analysis was performed using 12 abiotic variables to test the classification reported in the literature. The first axis (F1) in the PCA ordination explained 32.56% of data variability (Figure 2). This axis indicated a gradient degradation from left to right. On axis I (F1), sites Ha1 and SP3 were associated with high values of nutrients (nitrate, nitrite, and chlorine), pH, water temperature, conductivity and total dissolved solids while sites SP1 and Me1 showed low values of these parameters and high values for dissolved oxygen. Water temperature (r = 0.86), chlorine (r = 0.81), and conductivity (r = 0.71) registered the most important values (r>0.7) for axis I ordination. These results demonstrate the PCA confirms the existence of three categories of sites: Natural (Me1 and SP1), Transition (Me 2, Me3, Ha2, Ha3 and SP2) and Impacted (Ha1 and SP3).

Physicochemical characteristics of the categorized sites

Average values and standard deviations of water variables in each sites category (natural, transition and impacted) are shown in Table 5. Natural, transition and impacted sites were statistically different (Kruskall-Wallis, p < 0.05) for water temperature, dissolved oxygen, electricity conductivity, total dissolved solids, total phosphorus, free and total chlorine. The impacted sites recorded the highest values for water temperature, electricity conductivity, total dissolved solids, total phosphorus, free and total chlorine, followed by transition sites and natural sites. As for dissolved oxygen, the natural sites recorded significant higher values than the ones in transition and impacted sites. Higher values were observed in the impacted sites for nitrate, nitrite and phosphate compared to those measured in the other sites. However, this spatial variation is not statistically different (Kruskall-Wallis, p > 0.05).

The reference values of the physicochemical parameters of Taï National Park determined based the BJP method and the trisection method can be seen in Table 6. This result indicated relatively similar values. Except the electrical conductivity, the BJP method produces higher values compared to the trisection method. The reference values of the Tai National Park stream waters are for the temperature: 25.1 – 25.3°C ; pH : 6.86 – 7.04 ; DO : 6.33 – 6.40 mg/L ; EC : 37.13 – 38.20 µS/cm; TSD : 27.50 – 29.03 mg/L ; NO₂⁻ : 0.005 – 0.009 mg/L ; NO₃⁻ : 0.450 – 0.625 mg/L; PO₄³⁻ : 0.053 – 0.054 mg/L ; TP : 0.123 – 0.134 mg/L ; FCl : 0.03 – 0.04 mg/L ; TCl : 0.04 – 0.05 mg/L.
Table 3a: Median, average, maximal and minimal values of physicochemical parameters of studied sites in Taï National Park.

| Parameters | Ha1 (a) | Ha2 (b) | Ha3 (c) | Me1 (d) | Me2 (e) | Me3 (f) | SP1 (g) | SP2 (h) | SP3 (i) |
|------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| **Physical parameters** |         |         |         |         |         |         |         |         |         |
| Temperature (°C) | Min 24.630 | 25.300 | 24.800 | 24.300 | 24.170 | 25.030 | 24.160 | 22.530 | 26.300 |
|               | Max 35.600 | 28.200 | 29.200 | 26.970 | 28.700 | 29.830 | 28.900 | 27.400 | 31.770 |
|               | Median 27.100 | 26.370 | 26.500 | 25.760 | 25.770 | 25.730 | 25.000 | 25.700 | 28.900 |
|               | Mean 27.864 | 26.514 | 26.597 | 25.784 | 26.046 | (g) 27.362 | (fi) 25.332 | (g) 26.618 | |
|               | SD 0.973 | 0.320 | 0.393 | 0.290 | 0.458 | 0.458 | 0.467 | 0.382 | 2.471 |
| **pH** | Min 6.520 | 6.570 | 6.250 | 6.230 | 6.310 | 6.340 | 6.330 | 6.850 | 6.710 |
|               | Max 8.480 | 8.480 | 8.080 | 8.480 | 8.060 | 8.500 | 8.880 | 8.730 | 9.180 |
|               | Median 7.100 | 7.100 | 7.085 | 7.070 | 7.255 | 6.925 | 7.225 | 7.305 | 7.320 |
|               | Mean 7.223 | 7.258 | 7.140 | 7.266 | 7.231 | 7.065 | 7.376 | 6.825 | 7.676 |
|               | SD 0.155 | 0.168 | 0.165 | 0.254 | 0.159 | 0.182 | 0.256 | 0.640 | 0.246 |
| **DO (mg/L)** | Min 3.370 | 5.200 | 5.330 | 4.680 | 4.630 | 4.800 | 4.800 | 3.600 | 3.600 |
|               | Max 7.570 | 7.930 | 8.700 | 7.250 | 7.800 | 8.200 | 9.170 | 10.230 | 6.430 |
|               | Median 5.785 | (i) 6.235 | (i) 6.285 | 6.235 | 6.010 | 6.100 | (i) 6.765 | (ai) 7.185 | (begh) 4.35 |
|               | Mean 5.387 | 6.296 | 6.417 | 6.085 | 6.073 | 6.207 | 6.518 | 7.668 | 4.567 |
|               | SD 0.384 | 0.210 | 0.294 | 0.218 | 0.312 | 0.291 | 0.539 | 0.367 | 0.228 |
| **Conductivity (µS/cm)** | Min 39.500 | 38.500 | 33.300 | 29.100 | 26.900 | 35.000 | 31.070 | 38.300 | 65.130 |
|               | Max 125.600 | 62.300 | 59.770 | 55.330 | 55.700 | 65.830 | 43.170 | 60.870 | 162.200 |
|               | Median 53.580 | 49.285 | (i) 45.35 | (i) 38.67 | (i) 36.115 | (i) 40.35 | (i) 37.135 | (cdefg) 89.8 | |
|               | Mean 61.192 | 50.090 | 46.712 | 39.847 | 39.366 | 45.315 | 45.315 | 51.550 | 93.290 |
|               | SD 7.510 | 2.770 | 2.419 | 2.582 | 2.482 | 3.102 | 1.107 | 2.273 | 7.679 |
| **TDS (mg/L)** | Min 28.210 | 27.500 | 23.780 | 27.500 | 19.210 | 24.990 | 22.190 | 27.350 | 46.520 |
|               | Max 89.710 | 44.490 | 42.680 | 44.490 | 39.780 | 47.020 | 30.830 | 43.470 | 85.400 |
|               | Median 35.665 | (g) 35.200 | (i) 32.385 | 34.990 | (i) 25.795 | (i) 28.65 | (ai) 26.515 | (i) 36.845 | (adfg) 64.135 |
|               | Mean 43.271 | 35.532 | 33.195 | 35.483 | 27.690 | 32.228 | 26.457 | 33.433 | 63.780 |
|               | SD 5.411 | 2.067 | 1.764 | 1.870 | 1.789 | 2.246 | 0.882 | 3.419 | 3.825 |
| **Redox (mV)** | Min 31.330 | 36.670 | 21.670 | 48.670 | 39.330 | 41.330 | 57.670 | 0.000 | 31.330 |
|               | Max 123.700 | 138.000 | 198.500 | 148.000 | 112.000 | 108.670 | 120.000 | 132.670 | 172.700 |
|               | Median 54.500 | 93.665 | 70.500 | 70.670 | 60.815 | 57.000 | 77.000 | 67.335 | 81.665 |
|               | Mean 64.228 | 87.667 | 80.958 | 84.696 | 66.772 | 69.806 | 84.800 | 72.223 | 77.322 |
|               | SD 8.625 | 11.610 | 15.157 | 10.821 | 7.444 | 6.890 | 8.151 | 10.809 | 11.428 |
Table 3b: Median, average, maximal and minimal values (mg/l) of physicochemical parameters of studied sites in Taï National Park.

| Parameters       | Ha1 (a) | Ha2 (b) | Ha3 (c) | Me1 (d) | Me2 (e) | Me3 (f) | SP1 (g) | SP2 (h) | SP3 (i) |
|------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Nitrites (NO$_2^-$) |         |         |         |         |         |         |         |         |         |
| Min              | 0.005   | 0.000   | 0.003   | 0.004   | 0.003   | 0.004   | 0.007   | 0.006   | 0.002   |
| Max              | 0.030   | 0.013   | 0.019   | 0.017   | 0.020   | 0.016   | 0.024   | 0.022   | 0.020   |
| Median           | (b) 0.013 | (a) 0.001 | 0.006   | 0.007   | 0.017   | 0.011   | 0.011   | 0.010   | 0.006   |
| Mean             | 0.016   | 0.003   | 0.008   | 0.009   | 0.012   | 0.011   | 0.015   | 0.012   | 0.009   |
| SD               | 0.004   | 0.002   | 0.002   | 0.002   | 0.003   | 0.001   | 0.003   | 0.003   | 0.002   |
| Nitrites (NO$_3$N) |         |         |         |         |         |         |         |         |         |
| Min              | 0.400   | 0.150   | 0.250   | 0.425   | 0.250   | 0.325   | 0.525   | 0.450   | 0.125   |
| Max              | 2.225   | 1.000   | 1.425   | 1.250   | 1.500   | 1.175   | 1.775   | 1.625   | 1.525   |
| Median           | (b) 1.000 | (a) 0.375 | 0.450   | 0.800   | 0.550   | 0.788   | 0.825   | 0.750   | 0.450   |
| Mean             | 1.189   | 0.505   | 0.636   | 0.833   | 0.793   | 0.814   | 1.095   | 0.932   | 0.650   |
| SD               | 0.266   | 0.169   | 0.150   | 0.153   | 0.205   | 0.088   | 0.244   | 0.158   | 0.188   |
| Phosphates (PO$_4^{3-}$) |         |         |         |         |         |         |         |         |         |
| Min              | 0.028   | 0.062   | 0.013   | 0.026   | 0.027   | 0.029   | 0.007   | 0.085   | 0.057   |
| Max              | 0.098   | 0.399   | 0.166   | 0.184   | 0.254   | 0.418   | 0.160   | 0.163   | 0.232   |
| Median           | 0.056   | 0.090   | 0.075   | 0.099   | 0.111   | 0.108   | 0.047   | 0.104   | 0.116   |
| Mean             | 0.060   | 0.138   | 0.074   | 0.105   | 0.113   | 0.131   | 0.064   | 0.114   | 0.124   |
| SD               | 0.010   | 0.053   | 0.020   | 0.030   | 0.029   | 0.031   | 0.022   | 0.011   | 0.020   |
| Total Phosphorus (TP) |         |         |         |         |         |         |         |         |         |
| Min              | 0.029   | 0.000   | 1.000   | 0.126   | 1.000   | 0.404   | 0.045   | 1.800   | 0.103   |
| Max              | 0.171   | 0.449   | 5.700   | 0.443   | 6.000   | 1.250   | 1.800   | 6.500   | 0.320   |
| Median           | (ceb) 0.114 | (ceb) 0.094 | (ab) 1.8141 | (ab) 2.213 | (h) 0.138 | (h) 0.1375 | (abeg) 3 | 0.154   |         |
| Mean             | 0.110   | 0.117   | 2.543   | 0.193   | 3.171   | 0.330   | 0.129   | 3.729   | 0.170   |
| SD               | 0.017   | 0.045   | 0.598   | 0.051   | 0.820   | 0.126   | 0.019   | 0.632   | 0.027   |
| Free Chlorine (CLF) |         |         |         |         |         |         |         |         |         |
| Min              | 0.103   | 0.010   | 0.030   | 0.017   | 0.013   | 0.033   | 0.053   | 0.017   | 0.057   |
| Max              | 0.470   | 0.040   | 0.250   | 0.050   | 0.100   | 0.123   | 0.130   | 0.120   | 0.190   |
| Median           | (b) 0.147 | (b) 0.0215 | 0.107   | 0.034   | 0.083   | 0.099   | 0.107   | 0.040   | 0.120   |
| Mean             | 0.201   | 0.023   | 0.121   | 0.034   | 0.061   | 0.087   | 0.097   | 0.049   | 0.116   |
| SD               | 0.068   | 0.006   | 0.033   | 0.007   | 0.018   | 0.015   | 0.023   | 0.018   | 0.024   |
| Total Chlorine (CLT) |         |         |         |         |         |         |         |         |         |
| Min              | 0.033   | 0.040   | 0.020   | 0.033   | 0.033   | 0.040   | 0.000   | 0.027   | 0.047   |
| Max              | 0.163   | 0.110   | 0.160   | 0.140   | 0.103   | 0.120   | 0.720   | 0.110   | 0.160   |
| Median           | 0.110   | 0.069   | 0.075   | 0.060   | 0.052   | 0.070   | 0.097   | 0.035   | 0.083   |
| Mean             | 0.100   | 0.072   | 0.080   | 0.068   | 0.060   | 0.075   | 0.170   | 0.048   | 0.094   |
| SD               | 0.020   | 0.012   | 0.016   | 0.010   | 0.009   | 0.012   | 0.069   | 0.010   | 0.014   |
**Table 4:** Sites categories of the Taï National Park of this study.

| Rivers | Sites       | Codes | RAH                | PAA | Categories      |
|--------|-------------|-------|--------------------|-----|-----------------|
| Hana   | Mont Nienonkoué | Ha2   | Good condition     | F   | Natural         |
|        | Ecotel      | Ha3   | Good condition     | C   | In Transition   |
|        | Point O     | Ha1   | Menaced            | VC  | Impacted area   |
|        | Source      | Me1   | Good condition     | F   | Natural         |
|        | Point 13    | Me2   | -                  | C   | In Transition   |
|        | Djouroutou  | Me3   | Menaced            | VC  | Impacted area   |
| Meno   | Source      | SP1   | Good condition     | F   | Natural         |
|        | Palabod     | SP2   | Good condition     | C   | In Transition   |
|        | Ville       | SP3   | -                  | VC  | Impacted area   |

RAH: Rapid assessment of habitats on the basis of previous research studies, PAA: Proximity of anthropogenic actions; F: Far; C: Close to the peripheral area; VC: Close to the peripheral area; - : No data.
2a: Correlation graph of physicochemical parameters.

CLL: Free Chlorine; CLT: Total Chlorine; O₂: Dissolved oxygen; NO₂⁻: Nitrites; NO₃⁻: Nitrates; PO₄³⁻: Phosphates; PT: Total Phosphorus; NH₄⁺-N: Ammonium; Cond: Conductivity; TDS: dissolved solids; Redox: Oxidation reduction potential.

2b: Factorial map showing the distribution of the 9 sampling sites.

Figure 2: PCA for water abiotic variables and sampling sites of Taï National Park.
Table 5: Median, average, maximal and minimal values of physicochemical parameters according to river classification.

|                  | T (°C) | pH    | OD (mg/L) | EC (µS/cm) | TDS (mg/L) | NO\textsubscript{2} (mg/L) | NO\textsubscript{3}–N (mg/L) | PO\textsubscript{4} (mg/L) | TP (mg/L) | (CLL) mg/L | (CLT) mg/L |
|------------------|--------|-------|-----------|------------|------------|---------------------------|----------------------------|---------------------------|------------|------------|------------|
| **Natural (n)**  |        |       |           |            |            |                           |                            |                           |            |            |            |
| Number           | 72     | 72    | 72        | 72         | 72         | 72                        | 72                         | 72                        | 72         | 72         | 72         |
| Minimum          | 24.160 | 6.230 | 1.500     | 29.100     | 22.190     | 0.002                     | 0.150                      | 0.007                     | 0.045      | 0.010      | 0.020      |
| Maximum          | 28.900 | 8.880 | 9.170     | 55.330     | 44.490     | 0.022                     | 1.625                      | 0.184                     | 0.443      | 0.250      | 0.160      |
| Mean             | 25.558 | 7.319 | 6.302     | 38.746     | 31.185     | 0.010                     | 0.733                      | 0.084                     | 0.161      | 0.069      | 0.066      |
| Median           | 25.100 | 7.045 | 6.330     | 37.135     | 29.030     | 0.009                     | 0.625                      | 0.054                     | 0.134      | 0.040      | 0.057      |
| 10th percentile  | 24.272 | 6.331 | 4.788     | 31.208     | 23.526     | 0.003                     | 0.230                      | 0.010                     | 0.059      | 0.013      | 0.029      |
| 90th percentile  | 26.778 | 8.402 | 7.388     | 48.480     | 40.910     | 0.018                     | 1.365                      | 0.177                     | 0.180      | 0.130      | 0.111      |
| **Transition (t)** |       |       |           |            |            |                           |                            |                           |            |            |            |
| Number           | 180    | 180   | 180       | 180        | 180        | 180                       | 180                        | 180                       | 180        | 180        | 180        |
| Minimum          | 22.530 | 6.250 | 2.200     | 26.900     | 19.210     | 0.004                     | 0.425                      | 0.013                     | 0.061      | 0.017      | 0.013      |
| Maximum          | 29.200 | 8.730 | 8.730     | 62.300     | 48.490     | 0.024                     | 1.775                      | 0.398                     | 6.500      | 0.013      | 0.720      |
| Mean             | 26.206 | 7.265 | 5.045     | 46.686     | 33.048     | 0.012                     | 0.952                      | 0.108                     | 2.492      | 0.061      | 0.119      |
| Median           | 26.030 | 7.145 | 4.900     | 45.770     | 31.590     | 0.009                     | 0.800                      | 0.091                     | 1.800      | 0.044      | 0.069      |
| 10th percentile  | 24.846 | 6.515 | 3.648     | 33.600     | 23.995     | 0.004                     | 0.430                      | 0.026                     | 0.147      | 0.027      | 0.033      |
| 90th percentile  | 27.494 | 7.945 | 5.930     | 59.085     | 42.200     | 0.021                     | 0.513                      | 0.164                     | 5.420      | 0.144      | 0.149      |
| **Impacted (i)** |       |       |           |            |            |                           |                            |                           |            |            |            |
| Number           | 72     | 72    | 72        | 72         | 72         | 72                        | 72                         | 72                        | 72         | 72         | 72         |
| Minimum          | 24.630 | 6.520 | 1.870     | 39.500     | 28.210     | 0.002                     | 0.124                      | 0.028                     | 0.029      | 0.057      | 0.033      |
| Maximum          | 35.600 | 9.180 | 6.430     | 162.200    | 89.710     | 0.030                     | 2.225                      | 0.232                     | 0.320      | 0.470      | 0.163      |
| Mean             | 28.451 | 7.450 | 4.227     | 77.241     | 58.525     | 0.012                     | 0.920                      | 0.092                     | 0.140      | 0.158      | 0.097      |
| Median           | 27.530 | 7.170 | 4.300     | 71.130     | 50.740     | 0.011                     | 0.800                      | 0.090                     | 0.138      | 0.123      | 0.083      |
| 10th percentile  | 25.342 | 6.626 | 2.090     | 39.782     | 28.410     | 0.002                     | 0.175                      | 0.032                     | 0.052      | 0.057      | 0.036      |
| 90th percentile  | 31.722 | 8.594 | 5.550     | 109.060    | 77.894     | 0.025                     | 1.870                      | 0.126                     | 0.173      | 0.190      | 0.157      |

n: Significant statistical difference to n; t: Significant statistical difference to t; i: Significant statistical difference to i.
Table 6: Comparison of the reference values of physico-chemical parameters of TNP water with other river of several countries.

| Parameters | This Paper | Camara et al. (2012) | Konan (2014) | Glüker et al. (2009) | Fonseca et al. (2014) | Silva et al. (2011) | Pardo et al. (2012) | Lock et al. 2011 | Newal and Tiller (2002) | USEPA (2001) | Smith et al. (2003) | Dodds and Oakes (2004) |
|------------|------------|----------------------|--------------|----------------------|-----------------------|---------------------|---------------------|------------------|------------------------|--------------|-------------------|-------------------------|
| BJP | Tris. | BPN | TESF | Côte d'Ivoire | Brazilia | Europe | Australie | United States |
| **T (°C)** | 25.10 | 25.33 | 25.57 - 27.33 | 24.4 - 31.3 | - | - | - | - | - | - | - | - |
| **pH** | 7.04 | 6.86 | 4.98 - 6.27 | 5.1 - 6.8 | 6.2 | 6.42 | - | 7.8 | - | - | - | - |
| **DO (mg/L)** | 6.33 | 6.40 | 1.8 - > 3.41 | 5.27 | 2.6 | 5.27 | 6.98 - 7.79 | 9.73 | - | - | - | - |
| **EC (µS/cm)** | 37.13 | 38.2 | 21 - 40.16 | 27.5 - 48 | 30.9 | 7.3 | 3.99 - 4.03 | 183 | - | - | - | - |
| **TDS (mg/L)** | 29.03 | 27.5 | - | - | - | - | - | - | - | - | - | - |
| **NO₂⁻(mg/L)** | 0.009 | 0.005 | - | - | - | 0.005 | 0.012 - 0.032 | - | - | - | - | - |
| **NO₃⁻N (mg/L)** | 0.62 | 0.45 | - | - | 0.004 | 0.04 | 0.007 - 0.009 | 2.0 - 6.0 | - | - | - | - |
| **PO₄³⁻(mg/L)** | 0.054 | 0.053 | - | - | - | - | - | 0.14 | - | - | - | - |
| **PT (mg/L)** | 0.13 | 0.12 | - | - | 0.04 - 0.03 | - | 0.1 | 0.04-0.08 | 0.003 | 0.015-0.048 | 0.010-0.0130 | 0.006-0.08 | 0.020-0.151 |
| **CLL (mg/L)** | 0.04 | 0.03 | - | - | - | - | - | - | - | - | - | - |
| **CLT (mg/L)** | 0.05 | 0.04 | - | - | - | - | - | - | - | - | - | - |

BJP: Best Judgement Professional; Tris: Trisection method; BNP: Banco National Park; TESF: Tanoé-Ehy Swamp Forest, DO: dissolved oxygen (milligrams per liter), EC: electrical conductivity (micro-Siemens per centimeter), PT: total phosphorus, TDS: Total dissolved solid, CLL: Free chlorine; CLT: Total chlorine.
DISCUSSION

The analysis of the physicochemical characteristics of the different rivers showed significant variations in water temperature, dissolved oxygen, electrical conductivity, dissolved solids, total phosphorus and total chlorine. According to Cherbi et al. (2008), this spatial variation in physico-chemical characteristics indicates the existence of a particular environment for each of the sites visited. Indeed, the water temperature of each river is higher in areas near to human activities compared to sites located in the park. This spatial variation in temperature is related to the presence of the forest which creates a particular microclimate within the Taï National Park. The increase in temperature, particularly in the anthropogenic areas of the Hana and San Pedro Rivers (Ha1 and SP3 respectively), is responsible for the decrease of dissolved oxygen levels in these sites. The interaction between these parameters can be explained by the existence of a high microbial activity in these sites and, as result the decrease of dissolved oxygen level (Rossetti et al., 2004), an increase of the total dissolved solids and the electrical conductivity of sites near to anthropogenic actions. On the other hand, the sites located in the park have well oxygenated waters with low value of the conductivity and the rate dissolved solids. However, the sites located in the park are well oxygenated with low value of electric conductivity and total dissolved solids. Specifically, the high concentration of nitrate observed at site Ha1 is linked to an exogenous supply. This site located downstream of the cocoa plantations, receives water runoff from the catchment area dominated by agricultural activities around this site. Total phosphorus showed significant variability across all sites visited with a higher value in the San Pedro River. This availability of phosphorus in this river would be determined by the internal charge of phosphorus from sediments. Indeed, San Pedro River has a rocky substrate whose erosion by runoff would contribute to the mobilization of phosphorus in the San Pedro River.

Establishing reference nutrient conditions for rivers and streams is necessary to assess the human impacts on aquatic ecosystems and to protect water quality and biotic integrity (Dodds and Oakes, 2004; Cunha et al., 2011). Thus, the identification of appropriate sites is the cornerstone of this study. According to Dodds and Oakes (2004), the identification of reference conditions is a particularly tough question due the different sources of pollution that are either natural or anthropogenic (Mokaya et al., 2004; Kotti et al., 2005; Singh et al., 2005). To circumvent all these difficulties, two methods were applied in this study to determine the most appropriate sites close to natural environment.

The BPJ method based on bibliographic research allowed isolating initially three natural sites (Me1, SP1 and Ha2). The statistical approach from the principal component analysis confirmed this method by determining the Me1 and SP1 sites as close to the natural state. This result of the statistical analysis is confirmed by the observation of Hawkins et al. (2010) which reveals that the greatest weakness of the BJP method is its subjectivity. Hence the need to associate more objective statistical methods. The withdrawal of site Ha 2 could be explained by its position on the Hana River. In fact, the quality of the water downstream of the river is affected by the agricultural activity of the upstream watershed. The reclassification Ha2 could be explained by its position on the Hana River. In fact, the water quality of the downstream of the Hana River is affected by the agricultural activity localized in the upstream of watershed.

The sites typology showed that the natural sites are located upstream of streams that take their sources in the Taï National Park. This position gives them a natural barrier against agricultural pollution caused by the anthropised actions implemented in the peripheral zone of the park. In fact, the forest reserve of the park ensures the maintenance of the biophysical processes of the watersheds of these rivers. This improves the quality and flow of water (Brummett et al., 2008). Therefore, the physicochemical data of these sites are therefore quality data that should be
used for a rigorous and objective monitoring of the aquatic environment of the TNP. This result is confirmed by the work of Kamelan (2014) which indicates that the headwaters of the San Pedro River contain more than half of all Mormydae captured in the TNP. This family of fish is well known as a bio-indicator species of water quality (Hugueny et al., 1996; Kamdem-Toham and Teugels, 1998). Moreover, the Kruskall-Wallis test does not indicate any significant variation between the data of the two natural sites (Me1 and SP1).

The reference values from the two methods indicate relatively close especially for temperature (BJP: 25.10°C – Trisection: 25.33°C), the dissolved oxygen (6.33 mg/L – 6.40 mg/L), le phosphate (0.054 mg/L – 0.053 mg/L), total phosphorus (0.13 mg/L – 0.12 mg/L), the free chlorine (0.004 mg/L – 0.003 mg/L) and total chlorine (0.005-0.004 mg/L).

The reference values of the temperature proposed in this study are close to those obtained in the Banco National Park (Camara et al., 2012) and in the Tanoé-Eby swamp forest (Konan 2014). The temperature around 25°C is ideal for good quality water. This value is confirmed by Lemoalle (2006), who indicates that the average temperature of African tropical waters is high and most often above 20°C.

The proposed pH value is slightly above the values obtained by Camara et al. (2012) and Konan (2014) in Côte d’Ivoire as well as in Brazil (Glücker et al., 2009; Fonscesa et al., 2014). However, Chapman et al. (1996) indicated that the pH of natural waters is between 6 and 8.5. Moreover, Mounjid et al. (2014) and Tohozin et al. (2018) have argued that the pH optimal conditions are obtained for values close to neutral or slightly alkaline. The reference value of the dissolved oxygen content obtained is comparable to those obtained in Brazilian waters (Silva et al., 2011; Fonsceca et al., 2014).

The analysis of the physicochemical parameters of the various sites visited on the basis of the values of the natural sites reveals two sites of poor quality. This is the Ha1 site (Point O on the Hana river) and the SP3 site (San Pedro river). At site Ha1, there is a high temperature (27.74 ± 3.11°C), a low dissolved oxygen level (3.89 ± 1.33 mg/L), and a high conductivity (61.19 ± 26.01 μS/cm). This site is located upstream of the Hana river, near the cocoa plantations. The factors that determine the change in water temperature of aquatic ecosystems are latitude, degree of sunshine, substrate composition, precipitation, wind and vegetation cover. Thus, the increase in temperature is fully related to the removal of vegetation cover in favour of plantations. It results in the reduction of oxygen levels observed in this site (IBGE, 2005). In addition, its position makes the Ha1 site a real receptacle for runoff that drain the topsoil mixed with fertilizer. This will cause a natural cleaning reaction by the river, thus involving aerobic bacteria. All this would contribute to a decrease in dissolved oxygen levels (CCME, 2001). Moreover, the high conductivity observed in this site is an indicator of high mineralization in the environment (Morbit et al., 2012). At the SP3 site of the San Pedro River, the observed high mineralization associated with the increase in temperature is due to the combined pressure of the farm and the effect of urbanization (household and industrial pollution). The Hana River, Main River of the TNP, constitutes the most problematic aquatic environment for the conservation of this park. In fact, it takes its source out of the park in the peripheral zone of the park. However, this part of the peripheral zone is an important agricultural area for cash crops (cocoa and coffee). It is therefore an important source of diffuse pollution that negatively impacts the physicochemical quality of this important aquatic ecosystem.

**Conclusion**

This study has highlighted the environmental characteristics of the main rivers of the largest area of primary forests under strict protection in West Africa. The results showed a well-preserved aquatic environment in comparison with the values obtained in the Ivorian rivers and other countries in the world. Despite the negative impact of deforestation and farms on the water quality of sites located on the periphery of the
Park, the sites located inside the park indicated physicochemical values which showed a positive impact of the forest on the water quality. Thus, the typology of the sites visited made it possible to group these study stations into three classes: natural, transition and impacted. The water quality reference values reported from natural sites are an essential tool for the management and monitoring of African rivers. This is a real first for Africa and is a significant step towards the establishment of ecoregions and the rivers typology for a rigorous and objective monitoring of water quality in West Africa.

COMPETING INTERESTS
The authors declare no competing interests.

AUTHORS’ CONTRIBUTIONS
MTK: Conceptualization; Data curation; Formal analysis; Funding acquisition; Investigation; Methodology; Resources; Validation; Writing - original draft; Writing – review & editing. AD: Data curation; Formal analysis; Investigation; Methodology; Validation; Writing - original draft; Writing - review & editing. MYK: Data curation; Formal analysis; Investigation; Methodology; Validation; Writing - original draft; Writing - review & editing. BS: Data curation; Formal analysis; Investigation; Methodology; Validation; Writing - original draft; Writing - review & editing. PEK: Data curation; Formal analysis; Writing - original draft; Writing- review & editing. Project administration, Supervision.

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