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Variability of pH in the Ogooué and M'passa rivers (Gabon)

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Abstract

We consider here pH time series which recorded at high frequency and at fixed points during 2 hours on July 2013. These data from Ogooué and M'passa rivers located in Gabon. The M'passa River is one of tributary of Ogooué in France Ville. The Ogooué River rises in Congo and flows through Gabon and crosses France Ville town and the river flows into Atlantic in Port-gentil. These locations are subject to human activities (here kinds of waste generated by human activities, industrial effluents).The wastes coming from domestic consumption and industrial activities are discharged into rivers. In order to detect pollution degree caused by such waste, the sampling sites are selected according to pollutants along the courses. The first time, we consider the data from M'passa River in France Ville. Two sets data were recorded along the course. The second time, two sets data were also recorded along in the Ogooué River. The pH time series reveals high fluctuations and these fluctuations indicate the possible influence of natural factors (biological and chemical activity) and of pollution. We also considered the pH distribution using box whisker plot and we estimate also their probability density function (pdf). The pdfs reveal a variable repartition in pH dynamic. The comparison of sampling sites reveals large variability and the smaller pH values are found in polluted areas and according to degree of pollution. We find also that the pH values depend on sites thus pollutants.

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Introduction

The study of physical parameters dynamic is important in the field of ecology focusing water quality and climate change (Schmitt *et al.,* 2008) and it receives a great attention in the last few years (Combes, 2008; Zongo and Schmitt, 2011a). The case study was realized through in the Ogooué river basin in France Ville, which is the third largest town in Gabon. This study is the first study demonstrating the water quality in the France Ville using pH. The Ogooué dynamic is greatly characterized by the freshwater from its tributaries. Here we focus on the river quality and the impact of human activities on the temporal variability of pH parameter, using data sets recorded at fixed points.

The Ogooué River is situated in tropical region which is in a warm-temperate and humid climate (an equatorial climate). Water masses are globally transported along the Ogooué and this zone is among the most productive systems of the country. The fishing and commercial ship are principal activities and mainly between Lambaréné and Port-Gentil. Many studies have been carried out in this ecosystem in Gabon (Mahé *et al.*, 1990; Biscara *et al.,* 2011). However, there are a few studies about the physico-chemical parameters and water qualities of these rivers of Gabon have been published. Presently there is no information available about the France Ville area. To our knowledge Lambaréné remains the most studied region (Mahé *et al.,* 1990). Most studies have already considered the variability of some fish along the Ogooué River, focusing on the diversity of fish and sedimentary dynamic evolution of the river (Biscara *et al.*, 2011). Here an important question is to characterize the response of aquatic environment to natural perturbations or human activities. The pH is an important indicator of water quality and is very important for coastal waters studies and physico-biology couplings. Furthermore, marine pH values are also more and more cited as a key issue in the framework of climate change (Caldeira and Wickett, 2003, 2005). The variability in marine pH is observed in today's ocean while this pH variability has been shown long-past in lake and in rivers (Philip, 1927). Some researchers have shown that CO_2 elevated concentrations will accompany reduced pH in sea water and then an ocean acidification (Blackford and Gilbert, 2007; Iglesias-Rodriguez *et al.*, 2008). Cole *et al.* (2007) have shown that rivers are also source and sink of Carbone and high variability of CO_2 flux driven to pH changes. The Aquatics ecosystems have a role in global Carbone cycle in response to climate changes. Moreover domestic waste and industrial effluent can also affect and alter the chemical and physical characteristics of water under influence of toxic substances and corrosive. Like physico-chemical parameters, the plankton may respond quickly to changes in pollution levels. However in the ecology framework, the physical parameters variability of river may induce ecological disturbances (Cótrim Marques *et al.*, 2007; Badjeck *et al.*, 2010). And a strong modification can be responsible for many changes in the composition and structure of an ecosystem.

We characterize here the pH fluctuations. The pH was measured at high frequency in Ogooué and M'passa rivers in the town of France Ville. M'passa River is a tributary and joins the ogooué in France Ville. We analysis here a pH data of the Ogooué and M'passa sampled on July 2013 focusing on the variability and comparison of study zones. The aim of the present study is: to characterized the pH dynamic; to evaluate the pollution degree caused by such waste using the pH distribution in each area.

Materials and methods

Presentation of study area

Gabon is situated on the west coast of central Africa bordered by the Atlantic Ocean. This tropical rainforest country is crossed by the equator and has a total land-surface area of 267, 667 km². Gabon shares borders with some countries, in the North with Cameroon and Equatorial Guinea, in the East and South with the Republic of Congo and in the West with the Atlantic Ocean. This country is "housed" in the Gulf of Guinea.

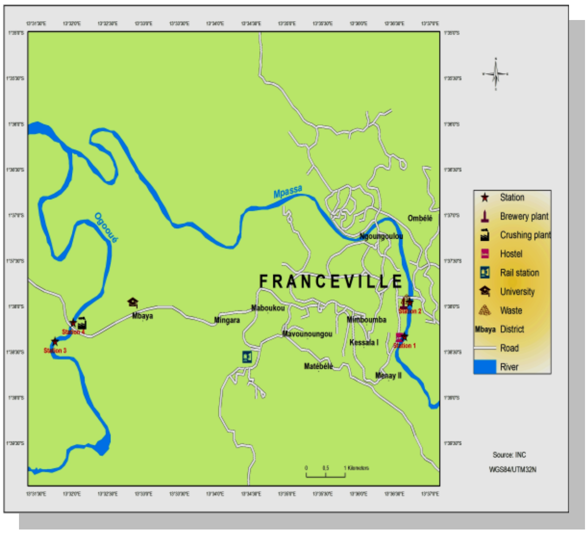

Fig. 1. Map of Ogooué and M'passa rivers: sampling sites along of courses (stations 1 and 2 in the M'passa; stations 3 and 4 in the Ogooué). The M'passa River passes into the city and The Ogooué River passes around the city.

The Ogooué River rises on the Massif du Chaillu in the Republic of Congo and flows through Gabon. In Gabon, the Ogooué is formed by the confluence of many rivers: the Ngounié, the Ivindo, the M'passa, the Sébé, the Djadié, the Okano, the Obanga, the Lolo, and the Offoué. The Ogooué river drains nearly the whole of Gabon and this basin covers 215, 000 km^2 (6000 km^2 in Congo) (Richard and Léonard, 1993). This river crosses France Ville and the river flows into the Gulf of Guinea in the south of Port-gentil (Mahé and Olivry, 1995). The mouth of Ogooué River forms a delta and is heavily influenced by currents from ocean (Mahé *et al.*, 1990).

The Ogooué river is considered as the largest in Gabon and is longest river in Gabon about 1,100 km and navigable for about 310 km, between Ndjolé and Port-Gentil (Richard and Léonard, 1993). The M'passa River is the principal tributary of the Ogooué that rises in the "Plateaux Batéké". The M'passa is about 150 km and passes into the city, while the Ogooué River passes around the city (see Fig.1.). The local people use water river for bathing and domestic uses (washing clothe, dishwashing etc).

The region is influenced by four seasons: a short dry season from December to February; a rainy season from February to May, a long dry season from June to August and other rainy season period from September to December. The Ogooué was strongly influenced by flow variability. The annual mean temperature is around 28°C and ranges from 20°C to 28 °C in summer. Some researchers have also shown that river flows were highly variable and the rainfall changes according to years (Mahé *et al.*, 1990; Mahé and Olivry, 1991). However the flow varies seasonally and reaches 979 m^3/s and 11300 m^3/s in dry and rain respectively, the river flow are high between Ndjolé and Port-Gentil (Richard and Léonard, 1993). Generally, these extreme events are due to intense rainfall and to drought and annual pluviometry varies between 1400 and 1600 mm on the Ogooué basin. The investigations have generally shown that rainfall variability was often related to climate regime. Olivry *et al.* (1993) study has shown that central Africa rivers flows are more and less abundant.

In France Ville town has a total surface area of 60 km^2 and the population has increased from 31,000 to 56,000 people between 1993 and 2010. The exploitation of manganese in Moanda and Uranium in Mounana, both in the northwest has greatly stimulated growth and commerce in the area. Furthermore, we find in the town some factories, the brewery plant, the crushing plant, and we find also the rubbish dump (the human waste, bags, oil, bottles, cans, excrements, waste from hospitals etc....). The town is characterized by small agriculture activities. These solid and liquid wastes coming from industrial activities and domestic consumption are discharged into rivers.

Sampling sites

The sampling stations are located in the part of South-East of Gabon in France Ville. In order to evaluate the effects of the pollutants on the quality of the Ogooué and M'passa rivers, four monitoring stations were selected along its both courses: two stations along each river. pH parameter in the stations are measured as follow as:

- Station 1 and station 2, in the M'passa River;
- Station 3 and station 4 in the Ogooué River.

Table 1. Shows description of each station.

Table 1. Sites description: areas characteristics.

Sampling sites	M'passa		Ogooué	
	Station 1	Station 2	Station 3	Station 4
Characteristics area Activities human and pollutants type	-Hotel -Bathing -Waste domestic -Washing clothe -Artisanal fishing -Without vegetation on bank	-Rubbish dump (excrements, bottle, bags, can, bottle, human waste), -Brewery plant, -Artisanal fishing -Vegetation on bank	-Forest -Artisanal fishing	-Forest -Crushing plant -Artisanal fishing

The pH was measured in surface by a sensor during month of July; this month corresponds to the end of the rainy season. The pH sensor covers measurement from 0 up to 14 with accuracies of 0.01 units of pH. The calibration was done in the laboratory before the measurements.

Table 2. Data description.

Stations	1	2	3	4
available data	10h20-12h21	12h38-15h17	9h55-11h44	9h33-11h35
Time resolution (second)	10	10	10	10
Number of data	720	954	753	732

In the present study (see table 2.), for station 1, pH database goes from 9h 35 to 12h 21: 720 values recorded on 15 July 2013, for station 2, the pH database goes from 12h 38 to 15h17: 959 values were recorded on 15 July 2013, for station 3 and 4, the pH data has 753 and 732 data values recorded on 13 July 2013 and 12 July 2013 respectively.

Results

pH Distribution

The pH of 4 stations on the rivers are sampled then analyzed and the results of sample analysis show in table 1. as follow as:

This table shows some representative comparisons: a local mean of pH vary 5.28 $\pm$ 0.73 to 6.66 $\pm$ 1.28 UpH for station 1 and 2 respectively (M'passa river) while a local mean of pH vary 6.78 $\pm$ 0.12 to 7.09 $\pm$ 0.35 UpH in stations 4 and 3 respectively for the Ogooué river. A local minimum of pH about 4.80 UpH(station 1 in the M'passa River) which may reflect the effect of the acidification process. Here we obtain a local minimal pH about 6.43 UpH for Ogooué River in station 4 precisely. The largest Minimum value is found for the Ogooué River whereas, the stations situated in M'passa, have much smaller mean values. Comparison between

M'passa and Ogooué monitoring sites reveal changes in the pH concentration. These results show that the pH values decrease or increase according to pollutants. The mean temperature values in M'passa (24.6°C) and in the Ogooué (23.4 °C) were also recorded during dry season (on July).

In fact during the measurements, increases in water temperature occur concomitantly with the increase in water pH in each station.

The portions of pH time series show important irregular fluctuations (Fig.2.)

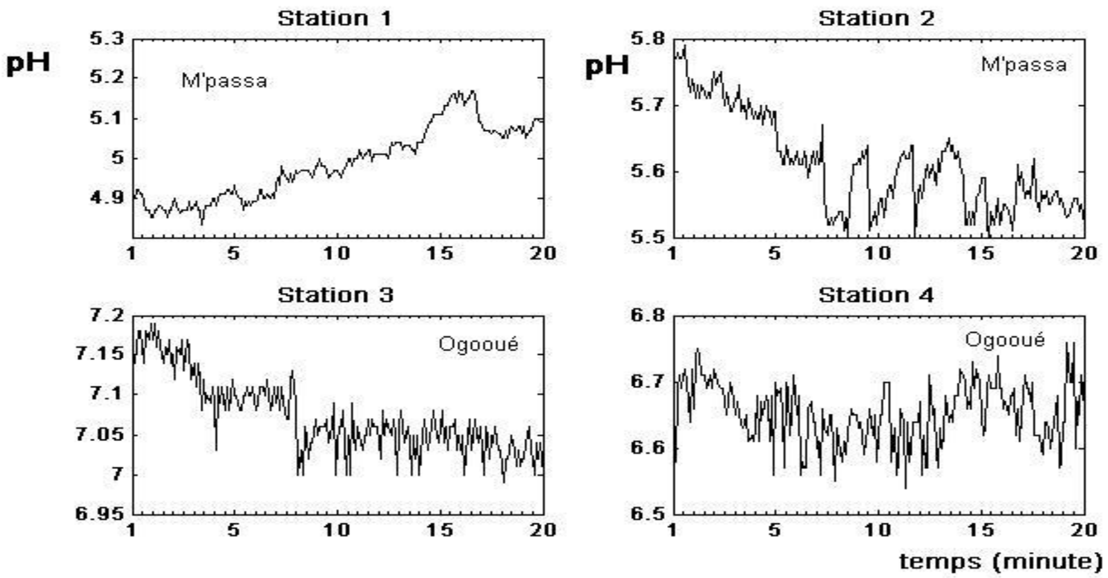

Fig. 2. A 20 minutes portions of pH time series: stations 1, 2, 3 and 4 show important and irregular fluctuations.

This figure gives an example of the data collected on each station, the pH dynamics are visually intermittent and these figures indicate a trend quite similar. Fig.3. Shows fluctuation amplitude indicating also intermittency in the data and amplitudes vary quite widely. In station 3 (the Ogooué bordered by forest) indicate the amplitude average of fluctuations about $6.9.10^{-4}$ and for stations 1, 2 and 4 the amplitude mean of fluctuations are 6.10^{-3}, $3.2.10^{-3}$ and $2.6.10^{-3}$ respectively. This shows that locally aquatic organisms are subject to pH variations at a rate which is minus 3 in polluted areas compared to unpolluted area which is minus 4 (station 3).

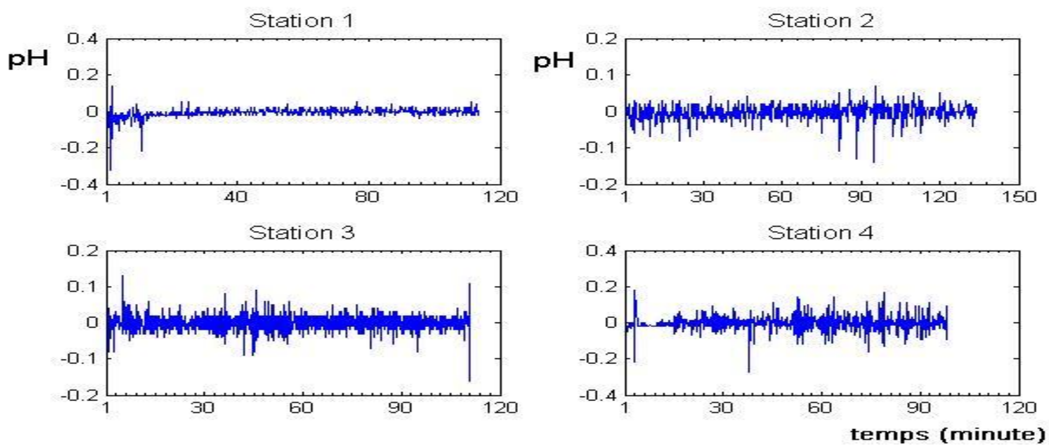

Fig. 3. A 2 hours portions of pH amplitude fluctuations of each station showing intermittent behaviour.

The amplitude average $(pH_{station1} - pH_{station2})$ in M'passa is about 0.19 UpH while the amplitude average $(pH_{station3} - pH_{station4})$ in the Ogooué is around 0.32 UpH which could be explained by characteristics of each zone. The M'passa stations receive the rubbish and industrial effluents whereas in the Ogooué, there is a station that receives industrial effluents and second station is bordered by forest which is away from pollutants. The amplitude average between station 1 and Station 3 $(pH_{station1} - pH_{station3})$ about 1.85 and the amplitude mean between station 2 and station 3 $(pH_{station2} - pH_{station3})$ amounts to 0.30 which indicated that station 1 have more important variation.

Whereas, we have also described the distribution of pH we used a box-whisker plot (Fig.4.). Each box and whisker plotted corresponds to each station. The median of data is not centered (red horizontal line) and the 25th and 75th quartiles correspond to the top and bottom of the box. The whiskers are the 5th and 95th quartiles located inside the defined region. The outliers correspond to the lowest and highest data outside the defined region (<5th and > 95th quartiles) are visualised in station 1 (M'passa) and station 4 (Ogooué) which reveal the local extremes.

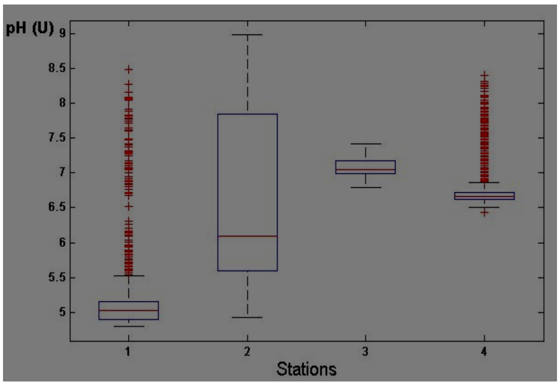

Fig. 4. Spatial evolution of pH. The 25th, 75th percentiles and the interquartile ranges of each station show variability. The median of each box (line red) is not centered for some station. The crosses red correspond to outliers.

Fig. 4. reflects the effect of high variability. The median values are highly variable with locally huge variations for each station. The median position indicates that samples are skewed and significantly different. In addition to the shape of distribution, statistics description has been made which allows a numerical comparison of distributions, there are the quartiles values (25th, 50th, 75th quartiles) (see table 3.).

Table 3. The mean, minimum, maximum, variance and standard deviation (STD) of pH values of the rivers.

pH (UpH)	M'passa		Ogooué	
	Station 1	Station 2	Station 3	Station 4
mean	5.28	6.66	7.09	6.78
min	4.80	4.92	6.79	6.43
max	8.49	8.98	7.41	8.40
var	0.53	1.64	0.01	0.12
std	0.73	1.28	0.12	0.35

Calculations were carried out using Matlab software. Our numerical results show that there is considerable variation in four databases. The interquartile range Q_{25}-Q_{75} differs for each parameter and indicates the extent to which the central 50% of values within the dataset are dispersed.

In the Ogooué, the interquartile range for station 4 is 0.08 and for station 3 is equal to 0.18 suggesting a greater dispersion. The distribution of pH data in station 3 water is clearly more spread out than of pH data in polluted water. However the 50th quartile value (median) differs for the mode value which suggested an asymmetric distribution. The smaller values of pH are encountered during the pollution.

Concerning the M'passa River, the interquartiles are 0.18 and 0.35 in station 1 and station 2 respectively. The pH is more spread in station 2 than in station 1. The modes values are also different from median values which suggested an asymmetric distribution (see Fig .4.). In comparison, the pH measured in the M'passa River (station 2) is more spread than the pH in the Ogooué.

pH pdfs

In order to analyse the pH data dynamic, we used probability density function (pdf). The probability density function of pH and all data together is displayed in Fig.5.

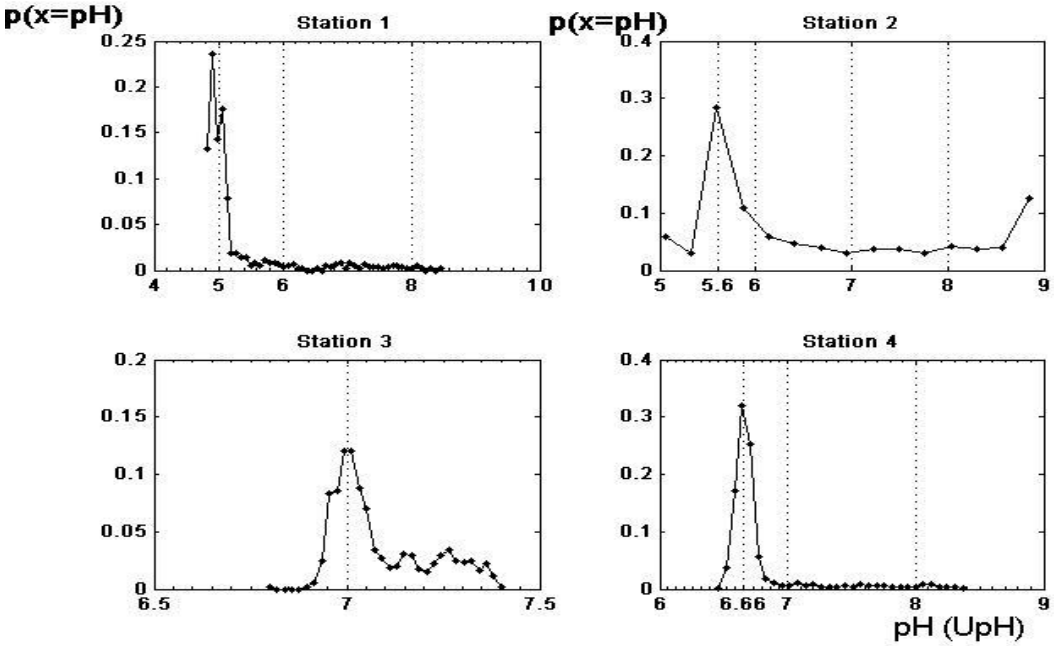

Fig. 5. The probability density function (pdf) of pH for each station: the pdf shape corresponds to pollution degree.

The pdfs show a non-Gaussian distribution with strong asymmetry. First, let us discuss the shape of pH pdfs (Fig.5.). The pH pdf in station 1 displays an asymmetric distribution and principal mode is equal to 4.90 UpH. In station 2, the pdf is skewed to the right; there are many high values, whereas small values are limited in the left. The pH pdf exhibits a mode to 5.6 UpH. The highest pH values are associated with low probabilities. Following their pdfs, 4.90 and 5.6 UpH are highly encountered in stations 1 and 2 respectively.

In pH of Ogooué exhibit quite the same shape but station 3 is more widely distribution. Station 3 shows many modes with principal mode amount to 7 UpH and small modes superior with 7 UpH. The lowest pH concentrations associated with high probabilities were found in station 3. The second modes may be due to the influence of M'passa flow. According to Mosley *et al.* (2010) during estuarine mixing, the pH shows a trend increase due to bicarbonate and carbonate system. pH distribution is skewness and the pdf indicates an increase of this parameter during flow discharge.

In Station 4, the pdf of pH also displays a non-Gaussian distribution showing the nice and unimodal repartition with a strong mode visible at 6.66 UpH. The lowest and highest pH values are associated with low probabilities. This pH value is highly encountered in this station. The pdfs shape seems to depend on the site location.

Such shape is much heavier than Gaussian indicating that extreme events are frequent (Schmitt *et al.*, 2008).

In the Second part of the study, it was interesting to examine the duration of the lowest and highest pH values. Here we are computerized the duration for extremes values when the values are below and above 5 UpH and 8 UpH respectively for station 1 et 2. For station 1, data greater than 8 UpH exhibit duration about 2 minutes and data smaller than 5 UpH is about 55 minutes. For station 2, the duration of high values (8 UpH) about 51 minutes against 8 minutes for low pH values.

Overall, it can be summarized that the durations of these extreme values were very variable and correspond to each sampling site.

Discussion and conclusion

In this study, the pH dynamics of the Ogooué and M'passa rivers has been characterized, as for ecology application it is crucial to highlight or detect the impact of pollution on the aquatic ecosystem (Fisher and Wad Leigh, 1986; Gray *et al.*, 1990; Osenberg and Schmitt, 1996). Generally, one can note that pollution is always associated with environmental changes (Peters and Meybeck, 2000; Florescu *et al.*, 2010).

The analysis of pH time series has revealed very large fluctuations showing intermittency in their dynamics with many fluctuations at all scales (Schmitt *et al.*, 2008; Bensoussan *et al.*, 2009; Zongo and Schmitt, 2011a). The analysis of the pH brings to light variability along both rivers and the fluctuations range exhibits quite high important variation. Yoo (1991) found that pH values may change over very small pH units and consequently affected aquatic plankton grown or distribution. However most estuarine organisms are adapted to live within narrow range of pH, so changes in pH can affect the population and distribution of estuarine inhabitants (Devreker *et al.*, 2004).

In the study, we were interested in the pH variability. The distribution of this parameter is described by using the probability density function which is often used to estimate the repartition of biogeochemical parameters in geophysical fields (Schmitt *et al.*, 2008; Zongo *et al.*, 2011b). Some environmental variables chosen allow to characterize in part the dynamic of an aquatic ecosystem and also to link the biotic factor to plankton assemblage (Harrison and Whitfield, 2006). The parameter treated here was pH and like the other parameters, pH is an indicator of water quality or as health indicators of river ecosystem (Millero, 1996; Howland *et al.,* 2000). However variation in pH also occurs and can be caused by photosynthesis and respiration cycles of algae in eutrophic waters. pH water is regulated by carbonate system and photosynthesis increases water pH and CO_3^{2-}.

Table 4. The quartiles of each distribution: M'passa and Ogooué rivers.

Quartiles of pH	M'passa		Ogooué	
	Station 1	Station 2	Station 3	Station 4
Q1 (0.25)	4.89	5.56	6.99	6.62
Q2 (0.50)	4.97	5.64	7.04	6.65
Q3 (0.75)	5.07	5.91	7.17	6.70
Interquartile range (Q3-Q1)	0.18	0.35	0.18	0.08

In our study, pH appears to be more sensitive to the perturbations. These pdfs exhibit temporal and spatial patterns quite different. Nevertheless, the pdfs shapes could yield information on the dissemination mode of certain aquatic species such as fish and or the type of pollution they could encounter. The information of each station given by their pdfs and the pH pdfs clearly show the distribution of pH in relation to river dynamic.

Our results show a mode below 5 UpH and other above 5 UpH in station 1. The acid condition is characterized by pH concentrations below 5 UpH. However, the thresholds of pH values have been determined to identify the pollution level of aquatic ecosystem (EPA, 1996). Nonetheless, the pH below 5 UpH may indicate a scarcity of fish food and low pH values of less than 5 affected behaviors and reproduction of some aquatic species. However Petrin *et al.* (2007) have shown also that some macro invertebrate freshwater are capable also to adapt to low pH. According to EPA (1996), for rivers where aquatic life is expected, the pH has to be within the range of 6.5 to 8.7 UpH.

In stations 2, 3 and 4, the pH mode is above 5 UpH, in station 2, the mode is 5.6 UpH, which is associated to pollution. The waste and brewery effluent increase acidity in the environment. In human health, pH levels above recommended values are associated with microbial growth. In station 3, where there is not human housing, the mode amounts to 7 UpH and the pH of most fresh waters is relatively well buffered or neutral (Dallas *et al.*,1994). In station 4, where there is industrial activity, the amounts to 6.66 UpH and we suggest that the pH reduction may be linked to pollution by the industrial effluent. Our results reveal that freshwater variation produces an increased pH gradient along each river.

For each station, the pdfs were not close to Gaussian and pdfs reveal a much heavier tail. These results show that pdfs had a similar asymmetric shape. The tail of distribution indicates intermittent behaviour characterizing extreme pH during dry period (Zongo and Schmitt, 2011a).

In conclusion, we can mention here some perspectives opened by this work. First, to have a long time series; to detect disease encountered in bathing zone; to show the relation between water quality and disease, to study other parameters such as river discharges, oxygen, and turbidity.

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