Characterization of Dissolved Organic Matter in the Waters of Lomé Lagoon System (Togo)

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Abstract The aims of study is to distinguish the different origins of dissolved organic matter and emphasizes the spatial variations of dissolved organic matter quality in Lomé lagoon system composed by three lakes and Equilibrium canal. The results showed that, the three lakes of Lomé are dominated by biological dissolved organic matter (HIX < 4) except the site O_{11} (HIX = 5.75) with high biological activity (BIX included between 0.8 and 1). This high biological activity could due to the water contribution from north plateau and offshore bar. Apart from O_{11} and C_4 the information brought by the ratio $I\gamma/I\alpha$ shows that the dissolved organic matter of the lagoon is autochthonous and composed by labile organic compounds. Lomé lagoon system is composed in majority by humic substances with a small amount of microbial products.

Keywords: dissolved organic carbon, aromaticity, 3D fluorescence, fluorescence indexes

1. Introduction

In urban cities where naturals waters such as, lakes, rivers, lagoons are presents, the organic matter can have many origins: autochtonous or allochthonous or from to humans activities making it to be very complex. Several techniques such as XAD fractionation, ultrafiltration, GC-MS pyrolysis, UV Visible spectroscopy, mass spectroscopy, 3D fluorescence can helps to get much information about these organic matters. Spectroscopic techniques are widely used to have qualitative information of this kind of complex mixtures of organic compounds. The spectrometry UV Visible informs about the light absorption of a sample. The SUVA index (Specific Ultraviolet Absorbance) is used as an indicator of the chemical composition of dissolved organic matter. Nowadays, a new technique, 3D fluorescence is greatly used to characterize the OM [1]. About 70 % dissolved organic matter from water are able to emit a fluorescence signal. This technique (3D fluorescence), based on excitation and the emission of the molecules, give information about the energy emitted in response to the excitation. By this technique, it is easy to differentiate two molecules having the same emission wavelength and different excitation wavelength. 3D fluorescence excitation-emission matrix spectroscopy is a rapid, selective and sensitive technique. It has been proven to be a useful technique to characterize natural organic matters [2,3,4,5]. Because of it high sensitivity, good selectivity, and non-destructive nature, excitation–emission matrix is

also widely used to differentiate the changes and transformations of organic matter in natural environment. For the last decade, excitation–emission matrix and several indexes (HIX, BIX and $I\gamma/I\alpha$) have been developed to quantify humification degree and origin of humic materials [6,7]. The determination of these indexes is based on the fact that the progress of the humification process is associated with increased carbon and hydrogen (C/H) and the increase results in a shift of the spectrum fluorescence to longer wavelength emission wavelength [3,4,5]. In fact, the index of humification of MOD (index HIX) differentiates MOD sources such as between microbial cell lysis products and more humified compounds [4,5]. The BIX index that characterizes the supply of MOD of indigenous biological activity of an aquatic environment is linked to greater presence of fluorophore β in samples of natural waters [6,7,8]. As for the $I\gamma/I\alpha$, it allows the identification of protein compounds associated with biological activity mainly to the influence of MOD of marine origin [6,8]. The excitation–emission matrix diagrams of humic substances are scrutinized to establish a complete fluorescence fingerprint (number of peaks, their location and intensities) of this material as well as to identify potential correlations between features and properties of the samples. They can therefore be of great helps to differentiate complex mixtures of fluorophors, based on their specific peaks. The 3D fluorescence is used to study dissolved organic matter from sea waters [8], coastal and deep-sea sediments [9], landfill leachates [10], humic acid [11], farm wastes [3], natural waters [12,13], soil extracts [14], tropical wetlands [15], organic matter produced by algae [16], to trace the

origin of individual dissolved organic matter peaks [5,17,18,19,20,21], to monitor organic contamination [22] or the interaction between dissolved organic matter and metals [23]. In practice, the 3D Fluorescence requires a small quantity of volume with a low concentration of organic matter (< 20 mg.L^{-1}) [24,25]. However, the identification of fluorophors is difficult due to the changes in the pH, the temperature and ionic strength, which can affect the fluorescence emission [20,26]. Some fluorescence index such as HIX and BIX and the ratio of fluorescence intensities $I\gamma/I\alpha$ helps to get information about the origins and the characteristics of organic matters. The humification index (HIX) informs about the origins of dissolved organic matter [27,28,29]. It helps to appreciate the condensation degree of the organic matter, its complexity and stability towards the microbial activity [30]. The BIX index is the ratio between the maximum emission intensity at 380 nm and the maximum emission intensity at 430 nm for an excitation intensity of 310 nm. It shows the dissolved organic matter due to autochthonous biological activity in aquatic environment [27,29,31]. The $I\gamma/I\alpha$ helps to identify the proteics compounds due to the biological activity. This ratio can be defined as the ratio between the maximum emission intensity at 460 nm and the maximum emission intensity at 320 nm for an excitation intensity of 250 nm. In Togo, there is no data about organic matter characteristics of Lomé lagoon. So, the objective of this work is to distinguish the different origins of organic compounds and emphasizes the spatial variations of the dissolved organic matter quality.

2. Materials and Methods

2.1. Study Area

The studies were undertaken in Lomé lagoon with a length of 8 Km near the sea of Togo (Atlantic Ocean). The lagoon is composed by three lakes. West lake, East lake and lake of Bè. West lake and East lake are connected by Equilibrum canal. All the analyses was done in LCE (Laboratoire de Chimie des Eaux de l'Université de Lomé, Togo) and GRESE (Groupement de Recherche Eau Sol Environnement, Université de Limoges, France). Water samples were collected in September 2011 in Lomé lagoon system (West lake, East lake, lake of Bè and in Equilibrum canal). For each hydrological unit two representatives' samples were taken: sites O_{11} and O_5 for West lake, sites C_4 and C_2 for Equilibrum canal, E_3 and E_1 for East lake and B_6 and B_3 for lake of Bè. The location of each site is shown in Figure 1 and Table 1.

Table 1. Geographical location of sampled sites

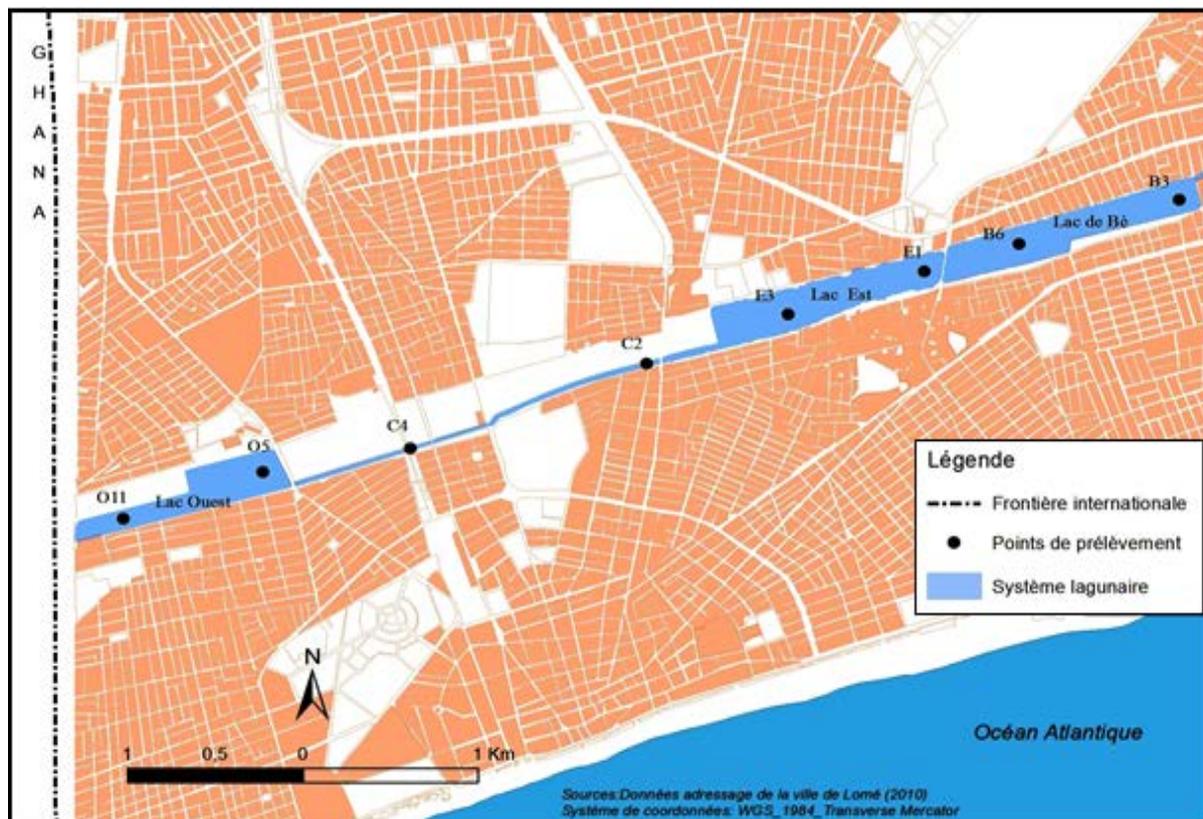| Stations	Samples	Location	Depth (m)
West lake	O_{11}	6° 8' 08"N ; 1° 12' 10"E	5.0
	O_5	6° 8' 16"N ; 1° 12' 29"E	3.0
Equilibrum canal	C_4	6° 8' 22"N ; 1° 13' 01"E	1.0
	C_2	6° 8' 31"N ; 1° 13' 24"E	1.0
East lake	E_3	6° 8' 49"N ; 1° 14' 11"E	2.5
	E_1	6° 8' 57"N ; 1° 14' 34"E	2.3
Lake of Bè	B_6	6° 9' 03"N ; 1° 14' 54"E	2.5
	B_3	6° 9' 09"N ; 1° 15' 12"E	6.0

Figure 1. Location of site in Lomé lagoon system

Water samples were collected in plastic bottles of 1.5 L, previously rinsed with distilled water and then with sampled natural freshwater. Smart et al., [32] and Patel-

Sorrentino et al., [26] reported that evolution of water samples may occur after collection. For this reason, once collected, the samples were immediately filtered and

acidified to avoid both coagulation and alteration of the characteristic peaks position of humics compounds. However, parameters such as temperature, pH and the electric conductivity were determined *in-situ* by a multimeter ''Type WTW Multi 3420'' and The redox potential was determined using a potentiometer ''PHM210 Type MeterLab''.

2.3. Characterization of Dissolved Organic Matter

Dissolved organic matter (DOM) were determined by a TOC-L analyser 5000 (Shimadzu) with a precision of $\pm$ 50µgC.L^{-1}. All the samples have been acidified with HCl 1M and sparged with high purity air (quality: 5.0) to removed inorganic carbon and volatile organic compounds. Non organic volatile carbon was then combusted at 720°C to produce CO_2 which is detected by infrared Spectroscopy. The SUVA is defined as the ratio of UV absorbance to DOC value (Absorbance /DOC). It helps to estimate the rate of aromatic and hydrophobic compounds found in the water [33; 34]. The absorbance at 254 nm which is characteristic of phenolics compounds was measured using a UV Varian Cary 50 Probe spectrophotometer. This measurement was performed on samples previously filtered at 0.45 µm. The precision was $\pm$ 0.005 cm^{-1} and the cell use was in quartz with double beam and 1 cm of length. The SUVA index, defined by the ratio UV_{254} nm and COD can be also expressed as a percentage of aromaticity (ARO) of the substance. The aromaticity of MOD in the waters was estimated using the following equation [33]:

$$\% \text{ aromaticity} = 6.52 + 3.63*SUVA_{254}$$

Where the $SUVA_{254}$ represents the UV absorbance at 254 nm of samples Standardized water to the organic carbon concentration dissolved (COD).

The 3D fluorescence was determined by a Shimadzu FP-5301 PC spectrofluorometer. The data was treated by Panorama Fluorescence 2.1 software. The samples were previously diluted by buffer phosphate pH 7 to obtain 5mgC.L^{-1}. HIX index was determined by taking the ratio of the areas defined between the emission wavelengths of 300 and 345 nm and those defined between 435 and 480 nm for an excitation wavelength at 254 nm [27,28,29,30]. The BIX index is the ratio between the maximum emission intensity at 380 nm and the maximum emission intensity at 430 nm for an excitation intensity of 310 nm. It shows that the dissolved organic matter due to autochthonous biological activity in aquatic environment [27,29,31]. The ratio Iγ/Iα can be defined as the ratio between the maximum emission intensity at 460 nm and the maximum emission intensity at 320 nm for an excitation intensity of 250 nm.

3. Results and Discussion

Table 2 shows the values of physicochemical parameters, permanganate index, dissolved organic carbon, the SUVA and aromaticity of samples lakes. It is found that C_4 site present higher levels of permanganate index (IP = 40 mg.L^{-1}) and dissolved organic carbon (DOC = 91.11 mg / L) follow to C_2 site (IP = 31.0 and COD = 20.83 mg.L^{-1}). However, the percentage of aromaticity of organic molecules for the two sites is the lowest and is located for C_4 and C_2 respectively between 14 and 16%. It was proved that, the aromaticity percent of the aromatics molecules such as humics substances were situated between 20 and 40% in opposite to microbial metabolites with about 16 % [35]. The low SUVA (< 2) of C_4 and C_2 is another parameter which confirms the humics acids absence [36; 37; 34]. It means that the dissolved organic matter of equilibrium canal (site C_4) is composed of microbial metabolites molecules. The COD of sites O_{11} and O_5 is low (11 mg.L^{-1}). But, aromaticity of the molecules is very high (22 %). This imply that, the dissolved organic matter of these points is characteristics of humics substances with bigs molecules. Some recent studies [34,37,38], reported that SUVA > 2.2 is characteristic of humics acids. For the sites O_5, E_3, E_1, B_6 and B_3, the values of dissolved organic matter and permanganate index are low. Their organic matter could come in part from microbial metabolites due to the percent of aromaticity (16 %). The production of microbial metabolites could due to the lyses of bacterial playing a rule in much ecological and biogeochemical process, like nutrients recycling (nitrogen fixation).

Table 2. Physicochemicals and spectrocopics parameters

Parameters	Unit	Sampling sites							
		O_{11}	O_5	C_4	C_2	E_3	E_1	B_6	B_3
T	°C	29	29	30	30	30	29	29	29
pH	-	7.7	7.3	6.5	6.5	8.5	8.2	7.9	7.9
EC	(µS/cm)	3153	3123	2697	3033	4277	4453	3882	3757
Eh	mV	261	126	16	40	115	187	229	244
IP	(mgO$_2$.L^{-1})	21	13	40	31	13	10	5	4
DOC	(mgC.L^{-1})	10,99	11,61	91,11	20,83	11,79	11,12	8,12	8,11
SUVA$_{254}$	(L.mg^{-1}.m^{-1})	5,86	2,91	1,59	1,86	2,23	2,14	2,21	2,24
Aro	%	41,83	22,6	14,02	15,77	18,18	17,61	18,07	18,21

T: Temperature; pH: potential hydrogen ; EC: Electric conductivity; Eh: redox potential ; DOC: dissolved organic carbon ; SUVA$_{254}$: Specific Ultraviolet Absorbance at 254 nm; IP: permanganate Index; Aro: Aromaticity.

So, the dissolved organic matter could be degrade in the lagoon (sites C_4, C_2, O_5, E_1 and B_3), characterized by the increases of the nutrients amount for microorganisms. For the site O_{11}, the lagoon deposits due to runoff waters could be rich in aromatics humics substances. Two maxima (peaks A and C) are observed with a remarkable constancy in all excitation-emission matrixes in this study.

The general fluorescence properties of samples are illustrated in Figure 2. Qualitatively, the 3D fluorescence matrixes show three intensities (I) excitation/emission (Ex/Em. They are I(285/310), I(230/280) and I(230/340) respectively in relation with microbial products, and proteins such as tyrosine and tryptophane likes. About, the peaks, the maximum fluorescence intensity are detected,

at the λ excitation 245 nm (peak A), and at 325 nm (peak C) and both have an emission maximum at 425 nm. Thus, the humic substances show at least, two kinds of fluorophores with different chemical and spectroscopic behaviors. These results are similar to those described in some previous studies [8,11,24,39]. Table 3 distinguishes the site where the fluorophores have been detected or not.

Table 3. Relation between the sites and the fluorophores

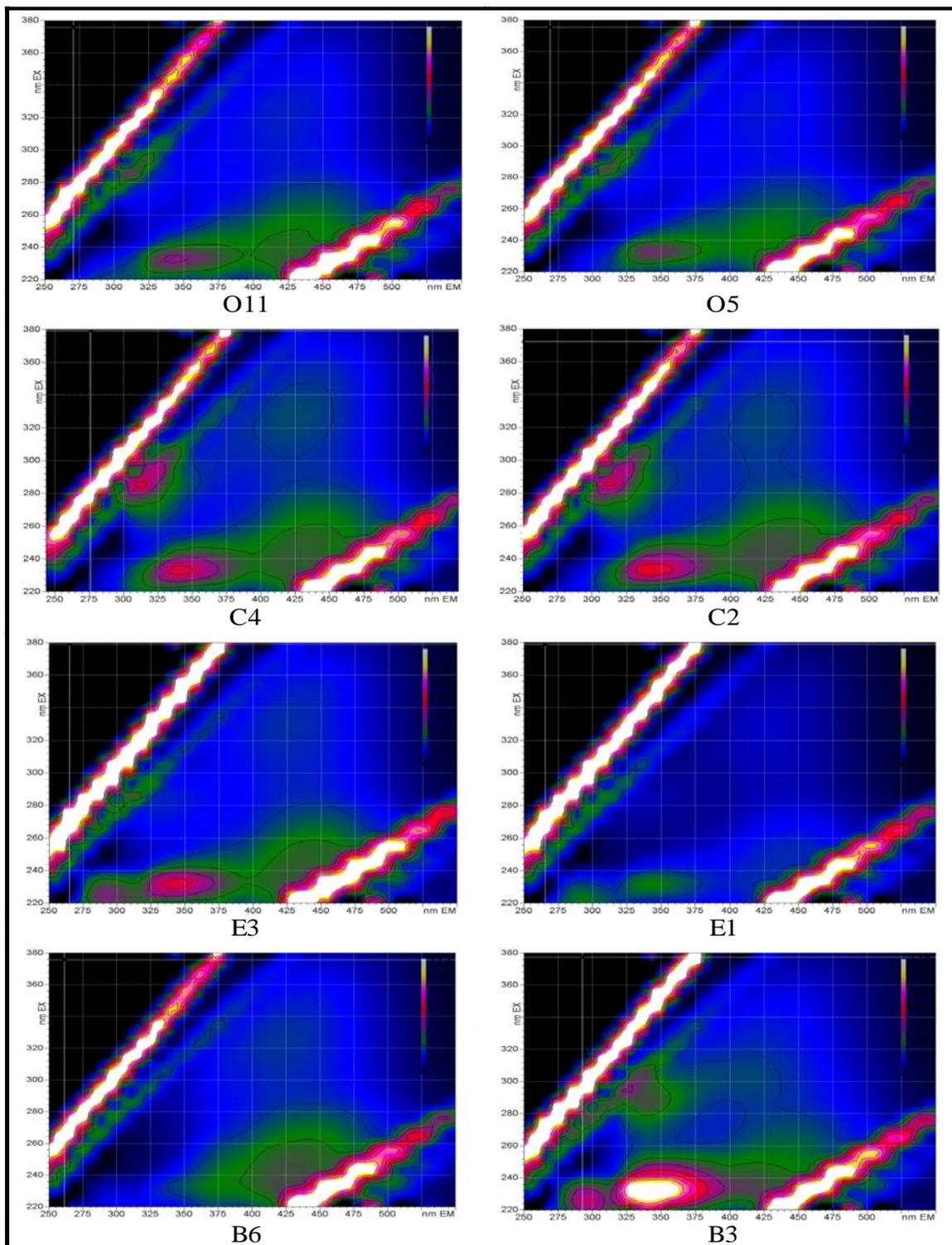| Maxima Ex/Em fluorescence	Compounds (Fluorophores)	Sampling sites							
		O_{11}	O_5	C_4	C_2	E_3	E_1	B_6	B_3
I (285/310)	Microbial metaabolits	-	-	+	+	-	-	-	+
I (230/280)	Protein-like (Tyrosine)	-	-	-	-	+	+	-	+
I (230/340)	Protein-like (Tryptophane)	+	+	+	+	+	+	-	+
I (240/425)	Pic A *(Coble, 1996)*	+	+	+	+	+	-	+	-
I (325/425)	Pic C *(Coble, 1996)*	+	+	+	+	+	-	+	+

Figure 2. Excitation/emission fluorescence matrix of the samples

Table 4. Fluorescence indexes values

Fluorescence indexes	O11	O5	C4	C2	E3	E1	B6	B3	Min	Max	Means
HIX	5,75	2	2	2	3	2	3	2	2	5,75	2,72
BIX	0,78	0,86	1	0,88	0,79	0,86	0,79	0,85	0,78	1,00	0,85
$I\gamma/I\alpha$	0,4	1,4	2	1,3	0,9	1	0,9	1	0,40	2,00	1,11

The fluorescence indexes and the ratio $I\gamma/I\alpha$ showing the spatial variations of dissolved organic matter (Table 4) will give more information about previous results.

The high HIX index (5.75 > 4) is only found in site O_{11}. This humification index means the low humic terrigenous nature with news autochtonous dissolved organic matter present in this lake. The others parts of the lakes shows HIX indexes of 2 and 3. This indicates that the dissolved organic matter is due to biological or bacterial activities. But, the BIX index prove that sites O_{11}, E_3 and B_6 situated between 0,7 and 0,8 revealed a low bacterial activity [27; 29] in opposite of the sites (O_5, C_4, C_2, E_1 and B_3). The dissolved organic matter of O_{11} is charcateristic of humic substances with a ratio $I\gamma/I\alpha < 0.75$ [29]. This result is also confirmed by the SUVA, Aromaticity and absorbance 254 nm. The ratio $I\gamma/I\alpha = 2 > 1.4$ confirmed that the organic matter of C_4 is due to aquatic biological or bacterial activities. The others sites are composed of labiles autochtonous organic compounds. The results illustrated that, the three lakes of Lomé are dominated by some biological dissolved organic matter (HIX < 4). This high biological activity may be influence by the water comes from north plateau and offshore bar.

4. Conclusion

The results showed that, the three lakes of Lomé are dominated by biological dissolved organic matter with high biological activity. This high biological activity may be due to contribution of water from north plateau and offshore bar. A part sites O_{11} and C_4, the information brought by the ratio $I\gamma/I\alpha$ showed that the dissolved organic matter of the lagoon is autochthonous and composed by labile organic compounds. The SUVA, aromaticity values and HIX, BIX and $I\gamma/I\alpha$ indexes are well-correlated.

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