Characterization of Dissolved Organic Matter at Different Stages of a Tropical Surface Water Treatment Using Fluorescence Spectroscopy (Agboville, Côte d'Ivoire)

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ABSTRACT

The quantitative and qualitative evolution of dissolved organic matter was followed at different stages of water treatment and in tap water to assess dissolved organic carbon (DOC) removal. Both DOC and 3- dimensional excitation emission matrix (EEM) fluorescence spectroscopy were used to evaluate the efficiency of the process. On the average, 53% of DOC was removed during the treatment process at the treatment plant. After water released in the distribution system, an increase of 27% DOC was observed in tap water, suggesting a production of organic carbon within the network. The EEM permitted to distinguish three main fluorophores, tryptophan-like (T) and humic-like (A and C) in raw water as well as in treated water. In tap water, an increase of fluorescence intensity (FI) was also observed, 31%, 34% and 59% on the average for fluorophores A, C and T, respectively. The tryptophan-like fluorophore is related to microbial activities and suggests an important development of microbial community within the distribution system due to the inefficiency of organic matter removal during the water treatment process.

Keywords: water treatment, DOC removal, EEM fluorescence, tap water, microbial activity

INTRODUCTION

The demand on water supply has increased over the last decades due to population growth and increase water use. People expect a secure, high quality, water supply and the water supply industry is governed by increasingly stringent water quality guidelines and legislation, ensuring that customers receive the highest quality drinking water at all times (Hurst *et al.*, 2004).

Among the undesirable water quality parameters, dissolved organic matter (DOM) defined as the complex matrix of organic material present in natural waters, significantly affects many aspects of water treatment, including the performance of unit processes (i.e oxidation, coagulation, and adsorption), application of disinfectants, and biological stability (Rizzo *et al.*, 2005). DOM has become increasingly important with regards to water supplies, because it reacts with chlorine during the disinfection process in drinking water treatment and produces disinfection by-products (DBPs) such as trihalomethanes (THMs) (Lee *et al.*, 2006; Sharp *et al.*, 2006). The formation of THMs is a huge concern because of their carcinogenic effects on humans (Tardiff, 1977, Krasner *et al.*, 1994). Aquatic humic substances, comprising fulvic and humic acids are the most common precursors of THMs. Organic matter in natural water can also cause

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bad odour, taste, colour, and bacterial regrowth problems (Yan *et al.*, 2006) within water distribution systems.

Of these DOMs, coloured humic substances (mainly humic and fulvic acids) generally predominate, and a large proportion of these substances are soluble. Coagulation is one of the most commonly used methods for the removal of DOM. Traditionally, the primary purpose of coagulation is to remove turbidity from water (Ye *et al.*, 2007). With the recognition of disinfection by-products, dissolved organic matter removal through enhanced coagulation is being widely adopted in the world. To evaluate the efficiency of DOM removal, dissolved organic carbon (DOC) is the principal parameter analyzed in water treatment plants. However, the determination of DOC does not give enough information about the nature of DOM because, DOM is a mixture of compounds with variable reactivity during water chlorination. DBPs are produced by natural organic matter (NOM), consisting mainly of humic substances, whereas DOC comprise NOM and also industrial and domestic wastewaters organic matters input.

Fluorescence spectroscopy has been widely used to investigate the chemical property and source of DOM in natural waters. In particular, 3-dimensional excitation emission matrix (EEM) fluorescence spectroscopy has been successfully used to probe the chemical structure of DOM because it can distinguish among different classes of DOM of different origins (Coble *et al.*, 1990; Wu *et al.*, 2003; Baker and Spencer, 2004). EEM spectra are acquired by sequential fluorescence emission scans at successively increasing excitation wavelengths, and consist of three-dimensional spectra showing excitation and emission wavelengths and fluorescence intensity. They are presented as contour maps of the fluorescence landscape with iso-intensity levels delineating various peaks. An EEM typically covers a range of excitation and emission wavelengths from 200 nm (short wavelength UV) through to 500 nm (visible blue-green light), and may contain fluorescence centres that are attributable to both natural DOM groups such as humic and fulvic-like material, as well as fluorescent protein-like material (Coble, 1996; Baker, 2001). Coble (1996) named the humic-like (mainly humic and fulvic acids) material fluorescence centres as fluorophores A and C, and protein-like material fluorescence centres as fluorophores T and B.

The objective of this study is to use both DOC and EEM to evaluate DOM removal and characterize DOM at different stages of water treatment.

MATERIALS AND METHODS

Water source and treatment

The raw water comes from the Agbo water reservoir, located in Agboville (Côte d'Ivoire) under tropical climate. This reservoir results from the construction of a dam on the Agneby river body in order to supply water to Agboville. The reservoir is colonized by aquatic plants and affected by municipal wastewaters. The raw water treatment process is shown in Figure 1. Owing to its low cost, chlorine is the chemical oxidant used at the treatment plant for pre-treatment (pre-chlorination) and for post-treatment (disinfection) to maintain a disinfectant residual in the system. After coagulation-flocculation using aluminium sulphate, sedimentation, in the filtration stage, homogeneous sand bed is used. At the end of the treatment process, before the release of

water to the distribution system, the pH is adjusted with lime to limit the corrosion of the distribution material.

Fig.1 - Stages of water treatment process in Agboville

Sampling

Raw, clarified, and treated water from the treatment plant and tap water samples were successively collected in January, February and March 2008. For raw, clarified and treated waters, only one sample was taken per month since the raw water characteristics remained fairly unchanged during the sampling period. The water treatment stages and reagents used were also unchanged during that period. On the other hand, 30 samples of tap water were collected at the rate of 10 samples per month from the same sampling points. The sampling points were spread out over the study area. The different samples were subjected to DOC, UV absorbance at 254 nm (UV_{254}), turbidity and EEM data analyses.

Analysis

Dissolved organic carbon analysis

A Shimadzu TOC-VCSH total carbon analyzer was used to analyse organic carbon in raw and treated waters by combustion at 680°C. Samples to measure organic carbon concentration were collected using amber glass bottles previously rinsed with nitric acidic solution (20%) and copious amounts of analytical grade water (Milli-Q) and then heated overnight at 500°C. Each sample was analyzed thrice and the average value was considered as the DOC data.

EEM data measurements

All samples (from raw and treated waters) were stored at room temperature (approximately 20°C), to minimize temperature influence. Furthermore, they were filtered through a micro-filtration membrane (0.45 µm) prior to analysis, to remove all the insoluble organic particles.

An RF – 5301 PC Shimadzu spectrofluorometer equipped with a 150 W xenon lamp was used. Excitation (Ex) wavelength was set from 220 to 500 nm, and emission (Em) wavelength from 250 to 600 nm. Ex and Em increment were 10 nm and 1 nm, respectively, with a slit of 10 nm for both Ex and Em. EEMs were measured using 1-cm path length quartz cells. In order to confirm the consistency of measurement conditions, scans of quartz cell containing analytical grade water (Milli-Q) were run systematically and the intensity of the Raman line of water at 348 nm excitation wavelength was recorded. The mean Raman value during the study period was 10.5 ± 0.6 intensity units (required value = 10 ± 2). All the fluorescence intensities were corrected to a Raman peak intensity of 10 units. TOC values from raw water (10.66 ± 0.27 mg/L) were such that an inner-filter correction was applied. Sample dilution to a concentration at which the inner-filter effects are negligible was used following Baker *et al.* (2004). The dilution factor was varied from 1 to 10.

UV absorbance and turbidity measurements

UV₂₅₄ absorbance was measured by Hitachi U – 2001 spectrophotometer. The specific ultraviolet absorbance (SUVA) was calculated as the UV absorbance at 254 nm (cm⁻¹) per mass of carbon (DOC in mg/L). Differences in SUVA for water samples collected at different locations or times reflect inherent structural differences in the material containing the DOC. According to Imai *et al.* (2001) and Weishaar *et al.* (2003), the SUVA is a very useful parameter for evaluating the characteristics of DOM in waters. Turbidity, on the other hand, was measured with a Hach 2100 P turbidimeter.

RESULTS AND DISCUSSION

Raw water characteristics

The chemical characteristics of the water from Agbo reservoir are summarized in Table 1.

Table 1 - Chemical characteristics of raw water from Agbo reservoir

	Raw water
TOC (mg C/L)	10.66 ± 0.27
DOC (mg C/L)	9.93 ± 0.34
POC (mg/L)	0.73 ± 0.61
SUVA (m⁻¹ L mg⁻¹)	3.75 ± 0.49
pH	6.57 ± 0.04
Turbidity (NTU)	14.21 ± 6.86
Temperature	26.32 ± 1.02

SUVA values are used to distinguish autochthonous and allochthonous sources of DOM. When $SUVA \geq 4 \text{ m}^{-1} \text{ L mg}^{-1}$, terrestrially-derived DOM are admitted to be dominant (Edzwald and Van Benschoten, 1990; Westerhoff and Anning., 2000). The SUVA of the Agbo reservoir ($3.75 \pm 0.31 \text{ m}^{-1} \text{ L mg}^{-1}$) indicates that autochthonous DOM production prevails within the reservoir. Autochthonous DOM results mainly from microbial activity and algal bloom.

The concentration of particulate organic carbon accounting for TOC is weak, implying that the organic matters from the Agbo reservoir are rather soluble.

Raw water samples were then subjected to EEM fluorescence spectroscopy to distinguish the different classes of DOM.

An example of EEM spectrum (Figure 2) qualitatively indicates the DOM composition. Three peaks have been detected in all samples. Peak T is present at $\lambda_{ex} = 230 - 240$ and emission $\lambda_{em} = 350 - 400$. Peak A is observed at $\lambda_{ex} = 240 - 250$ and emission $\lambda_{em} = 440 - 450$. A third fluorescence centre (Peak C) is observed at $\lambda_{ex} = 330 - 340$ and emission at $\lambda_{em} = 440 - 450$. These peaks have been widely identified in previous studies (Coble, 1996; Parlanti *et al.*, 2000; Hudson *et al.*, 2008).

Fig.2 - Fluorescence EEM of the Agbo reservoir raw water (Sample diluted 8 fold).
Fluorophores A and C = Humic-like; Fluorophore T = Tryptophan-like

Peak T is identified as Tryptophan-like. Tryptophan-like fluorescence may be exhibited by natural waters where tryptophan is present as 'free' molecules or bound in proteins, peptides or humic structures. It is related to microbial activity or algal bloom within the system.

Peaks A and C are related to humic-like (mainly humic and fulvic acids) and derived from the catchments mainly through the decay of terrestrial plant material and subsequent leaching of partial decomposition products. Humic and fulvic acids are the most common fluorophores in natural surface waters.

Treated water characteristics

Characteristics of water at different stages of treatment

The water treatment process at Agboville leads to about 46% of organic matter removal at the treatment plant before the release of water to the distribution system. However, within the distribution system (tap water), the DOC concentration increases from 5.01 ± 0.57 in treated water at the treatment plant to 6.87 ± 1.23 (27%) in tap water (Table 2). The turbidity also increased during the course of water within the distribution system whereas chlorine was consumed. This suggests a source of organic matter within the distribution system.

Table 2 - Chemical characteristics of water at different stages of treatment

	DOC (mg/l)	Cl ₂ (mg/l)	SUVA (m ⁻¹ l mg ⁻¹)	Turbidity (NTU)	pH
Clarified water (not disinfected)	5.73 ± 0.62	0.08 ± 0.03	2.1 ± 0.10	0.84 ± 0.31	5.74 ± 0.09
Treated water (Treatment plant)	5.01 ± 0.57	2.83 ± 0.92	2.02 ± 0.08	0.89 ± 0.33	6.33 ± 0.39
Tap water	6.87 ± 1.23	1.06 ± 0.80	2.01 ± 0.10	2.01 ± 1.67	6.39 ± 0.42

The SUVA value remains practically constant, indicating no qualitative change in the DOM composition since SUVA increases with aromatic carbon containing more carbon-to-carbon bonds (Weishaar *et al.*, 2003, Izbicki *et al.*, 2007). Edzwald and Van Benschoten (1990) and Uyak *et al.* (2007) demonstrated that SUVA relates closely to the amount of dissolved aromatic organic matter removed, because aromatic humic substances have a great affinity with aluminium during coagulation. The increase of organic matter within the distribution system is the evidence that the treatment process at the treatment plant is inefficient. Indeed, by optimizing the coagulation-flocculation process of raw water from the same reservoir (Agbo), Gone *et al.* (2008) obtained 70 % of organic matter removal. These authors showed that pH and aluminum dose were the most important parameters controlling the efficiency of DOM removal. In all water treatment plants in Côte d'Ivoire, the variation in pH of the coagulation-flocculation process is the consequence of aluminium sulphate addition responding to variable water turbidity and organic matter content, rather than the result of deliberate pH adjustment. The role of pH is particularly significant insofar as it determines at the same time the electrical charge of organic and inorganic colloids, and it is a major factor in the hydrolysis of aluminium salts (Ye *et al.*, 2006).

It is likely that the poor organic matter removal may lead to microbial activity increase, biofilm formation and sludge deposit within the distribution system. This hypothesis may be confirmed since the water turbidity also increases in tap water. Gauthier *et al.* (1999) showed that deposits within water distribution systems contain a reserve of organic matter which can contaminate the water carried by the distribution system. Transfer of organic matter from deposits to water occurs with the change in water flow rate within the water distribution network (Gauthier *et al.*, 2001). When the chlorination is not applied correctly, bacterial growth within the network can also release organic

matter, thereby increasing its concentration in water (Fass *et al.* 2002). The organic matter resulting from microbial activities is well known to be less light-absorbing (Weishaar *et al.*, 2003) and may justify the SUVA value remaining constant.

EEM characterization of finished water at the treatment plant

Treated water and tap water samples were also subjected to EEM fluorescence spectroscopy. An example of each type of water (treated and tap water) is presented in Figure 3.

The EEM spectrum of treated water (Figure 3a) highlights the different fluorophores that remained in water after the treatment process. Three compounds are identifiable as raw water, humic-like (C and A) and tryptophan-like (T). Except for the variation of the different fluorophores intensities, no significant difference occurred in the treated water spectrum compared to the raw water one. The EEM spectrum of tap water (Figure 3b) also presents the same three fluorophores. The particularity of the tap water spectrum is that the peak T is well individualized, giving evidence of an increase of tryptophan-like material within the water distribution network. As stated above, peak T is related to bacterial activity and may represent the presence of a bioavailable, labile organic substrate or the product of microbial activity (Cammack *et al.*, 2004; Nguyen *et al.*, 2005; Elliot *et al.*, 2006; Urban-Rich *et al.*, 2006). For this reason, it is considered that analysis of the fluorescence intensity of the tryptophan-like region can be used to indicate the size and activity of the microbial community (Hudson *et al.*, 2008). Waste waters including sewage effluents (Reynolds, 2002; Chen *et al.*, 2003), farm wastes (Baker, 2002) and landfill leachates (Baker and Curry, 2004) have been found to be rich in microbial derived peak T fluorescence and this peak has been used as tracer of waste waters in natural waters (Baker and Inverarity, 2004; Baker *et al.*, 2004). However, the peak T has not been used to investigate microbial activity within water distribution network. The increase of peak T within the distribution network is the evidence of microbial community development due to the inefficiency of organic matter removal during the water treatment process.

Fig. 3 - Fluorescence EEMs of treated water at the treatment plant before water release in the distribution system (a) and in tap water (b).

In order to better characterize the evolution of each fluorophore from the raw water treatment to tap water, the fluorescence intensities (FI) were used to calculate the removal or increasing percentage of each fluorophore (Figure 4). Indeed, the intensity of a peak can be used as a relative measure of the concentration of the fluorophore depending upon the fluorophore (Hudson *et al.*, 2008). It appears that the different fluorophores are removed significantly during the water treatment process whereas they increase again within the distribution network, suggesting a production of organic matter within the distribution system. Cammack *et al.* (2004) and Elliot *et al.* (2006) indicate that observation of the peak T is actually an observation of the balance of decline in substrate and increase in microbial community. However in this study, humic-like (A and C) and tryptophan-like (T) peaks increase (31.13%, 34.34% and 59.51% for peak A, peak C and peak T, respectively). This suggests a continuous accumulation of organic matter due to the inefficiency of organic matter removal at the water treatment plant as stated above.

Fig. 4 - Quantitative evolution of the different fluorophores from raw water to tap water using fluorescence intensities (FI).

At Agboville, small particles are frequently observed in glasses of water when they are allowed to stand, confirming the hypothesis that deposits occur within the network. This leads to frequent complaints of consumers. Thus, some consumers prefer drinking limpid water from wells even if well waters are not protected from contamination.

The remaining organic matter above all the humic-like compounds in water after treatment is of great concern since humic-like compounds are the main source of

precursors that contribute to the formation of disinfection by-products (DBPs) during water treatment (Yang *et al.*, 2008). Chlorine and its related species react with organic matter in water to produce DBPs (Hamidin *et al.*, 2008). DBPs in water system are of great concern due to their potentially adverse health effects (Krasner *et al.*, 2006).

For this reason, effective removal of DBP precursors is one of the major challenges in modern drinking water treatment (Uyak *et al.*, 2007).

Several epidemiological studies have revealed that there is an association between health effects and exposure to DBPs. King *et al.*, (2000a) and Wright *et al.* (2003) noted a relationship between THMs and adverse birth outcomes. King and Marrett (1996) and King *et al.* (2000b) identified an association between THMs (a DBP) and the risk of bladder and colon cancer, respectively. Also, Hinckley *et al.* (2005) and Wright *et al.* (2004) found that exposure to dichloroacetic acid and trichloroacetic acid (all DBPs) was linked to a risk of growth reduction in infants. It also resulted in pregnancy loss (Bielmeier *et al.*, 2001) and decrease in sperm mobility (Klinefelter *et al.*, 1995).

CONCLUSIONS

The aim of this paper was to evaluate DOM removal and characterize DOM at different stages of water treatment. Investigation results revealed that the 3-dimensional excitation emission matrix (EEM) fluorescence spectroscopy has the potential to be a powerful tool in the measurement and characterization of organic matter in water with particular application in organic matter monitoring from the treatment plant to the distribution network system. The EEM permitted to distinguish three main fluorophores: humic-like (A and C) derived from the breakdown of plant material and tryptophan-like (T) related to microbial activity.

The removal of these organic compounds is not sufficient at the water treatment plant and a production of organic matter is identified within the distribution network. The remaining organic matter in water after treatment is of great concern since organic matter and particularly humic-like compounds are the main source of precursors that contribute to the formation of disinfection by-products (DBPs) during water chlorination. Moreover, DBPs have potential adverse health effects. For the succeeding experiments, we will analyze the DBPs in tap water to evaluate the risk of their consumption.

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