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## Spectroscopie de fluorescence de la matière organique dissoute pour la surveillance de la qualité de l'eau dans les plans d'eau urbains

### Fluorescence spectroscopy of dissolved organic matter for water quality monitoring in urban waterbodies

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### RÉSUMÉ

La matière organique dissoute (MOD) joue un rôle essentiel dans le fonctionnement des milieux aquatiques. La spectroscopie de fluorescence peut être utilisée pour la surveillance de la MOD en milieu aquatique. Dans les masses d'eau urbaines, les rejets d'eaux usées et le ruissellement pendant les événements pluvieux affectent la qualité de l'eau et modifient la composition de la MOD. Peu de données sont disponibles dans les eaux urbaines. Dans cet article, des mesures de fluorescence sur des échantillons collectés par temps sec et temps de pluie, dans des cours d'eau de la région métropolitaine de Paris (France), sont présentées. L'échantillonnage a été réalisé dans deux cours d'eau (rivière Marne et canal de la Villette), deux exutoires de réseau de drainage pluvial et le rejet d'une station d'épuration des eaux usées. Des index de fluorescence, utilisés dans la littérature pour estimer l'origine de la MOD, ont été calculés. Basés sur les données de fluorescence, ils ont permis d'émettre des hypothèses sur l'évolution de la MOD par temps de pluie et pourront servir d'indicateurs de contamination microbiologique dans les cours d'eau étudiés.

### ABSTRACT

Dissolved organic matter (DOM) plays a key role in the freshwater ecosystem function. Fluorescence spectroscopy can be used to monitor DOM in aquatic environments. In urban waterbodies, wastewater discharge and runoff during rainfall events affect the water quality and change the DOM composition. Few data are available in urban waters. In this paper, we present fluorescence data obtained through field campaigns conducted during dry and wet weather, in watercourses in the Paris metropolitan region (France). Samples were collected in two water bodies (Marne River and La Villette canal), two stormwater outlet and the outlet of a wastewater treatment plant. Fluorescence indices, used in the literature to estimate the DOM composition, were calculated. Based on these indices, assumptions on the DOM composition of the samples in wet weather were done. After further validation, they could be used as indicators of microbiological contamination in the studied watercourses.

### KEYWORDS / MOTS CLÉS

FDOM, humic-like fluorescence, tryptophan-like fluorescence, urban waters.

Fluorescence de la Matière Organique Dissoute, fluorescence de type humique, fluorescence de type tryptophane, eaux urbaines.

## 1 INTRODUCTION

In freshwaters, dissolved organic matter (DOM) plays a key role in the ecosystem function. In urban waterbodies, during rain events, wastewater discharge and runoff affect the water quality and change the DOM composition. Fluorescence spectroscopy can be used to assess DOM composition. Fluorescence data provide information about DOM source, type, and microbiological activity (Coble 1996).

Fluorescent dissolved organic matter (FDOM) contains molecular groups called fluorophores which, when excited by specific UV wavelengths emit fluorescence (Fellman et al. 2010). The fluorophores identified in natural freshwaters are associated with different types of dissolved organic matter and can be mostly attributed to humic-like (peaks A and C) and protein-like (peak T) fluorescence components (Coble 1996). Peak T may indicate microbial activity. The ratio between peaks C and T (C/T) may be used as a tracer of terrestrial DOM input. An increase of C/T values may indicate an increase of allochthonous sources of DOM (Zhou et al. 2017).

Fluorescence spectrophotometry has been widely used for characterizing DOM in surface waters (Cumberland et al. 2012), ground waters (Frank et al. 2018), and marine waters (Parlanti et al. 2000), in particular for microbial quality assessment (Baker et al. 2015). However, few data are available in urban waters.

In this paper, we present fluorescence data collected in watercourses located in the urbanized Paris metropolitan region. Field campaigns were conducted during dry and wet weather, in different types of surface waters.

## 2 MATERIALS AND METHODS

### 2.1 Sampling sites

Two watercourses, Marne River and La Villette canal, the outlet of two stormwater networks and the outlet of a wastewater treatment plant were sampled.

#### 2.1.1 Watercourses

La Villette canal, Paris, is 1500 m long and 3 m depth with a mean flowrate of 2 m<sup>3</sup>/s. Three sampling points, A, B and C are located respectively at the inlet of the canal, 1000 m downstream and between point A and B (Figure 1). The samples were collected from autumn 2020 to autumn 2022.

The studied stretch of the Marne River is around 30 km long. The summer mean flowrate is around 60 m<sup>3</sup>/s (HydroPortail 2022). The samples were collected during summer 2022. A total of 19 sampling points along the river stretch were collected. The point VGA is located in Saint-Maur-des-Fossés (VGA sailing club). The other 18 points are part of *Syndicat Marne Vive* monitoring program (points SMV) (Figure 1).

#### 2.1.2 Stormwater network and WWTP outlets

Two stormwater outlets were sampled, points SO-N and SO-S (Figure 1). In both catchments, with a surface area respectively of 500 ha and 1400 ha, the drainage network is separate.

Samples of the treated water of a wastewater treatment plant (WWTP, 40 000 m<sup>3</sup> treated per day) were collected before its release into river Marne (point WWTP-O in Figure 1).



Figure 1. Sampling points. La Villette (orange), Marne River SMV (dark green) and VGA (light green), stormwater outlets SO-N, SO-S (purple) and WWTP outlet WWTP-O (red).

## 2.2 Sampling methods

Two types of samples were collected, grab samples and 24-hour integrated samples, during dry and wet weather. Wet weather is defined as a rainfall episode higher than 2 mm/day. For the grab sampling, 100 mL of water were manually collected under the water surface at a pre-established schedule, covering wet and dry weather. The flasks were covered with aluminium foil and stored at 4 °C until the fluorescence measurement in laboratory, within the next 24 hours. The 24-hour sampling was made by an automatic sampler at an hourly time step. 24 samples (1L each) were collected under the surface during wet and dry weather. All the samples were stored at 5 °C and manually mixed on a 25 L flask before the lab analysis.

At La Villette, grab samples were collected at points A and B, twice a month from 2020 to 2022 (80 samples of each point). Eight rainy events were sampled, with sampling on the day of the rain and the next two to four days. At SMV points, grab samples were collected during summer 2022, three times a week in average, with a total of 164 samples. Three rainy events were sampled, with sampling on the day of the rain event and the next two days. Mean 24-hour samples were collected at La Villette point C (n=10), Marne River point VGA (n=15), the stormwater outlet points SO-N (n=9) and SO-S (n=8) and the WWTP outlet WWTP-O (n=8). A total of 374 samples were collected.

## 2.3 FDOM measurements

Fluorescence measurements were performed on a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies), at the laboratory. The absorbance at 254 nm was obtained by using a Lambda 35 spectrophotometer (PerkinElmer). The processing of the Excitation-Emission Matrix (EEM) spectra was conducted according to (Murphy et al. 2013), using the drEEM toolbox for Matlab R2022b. The absorbance was used for inner filter effect correction (Parker and Barnes 1957). The values were normalized to Raman Units (RU) according to Lawaetz and Stedmon (2009).

## 2.4 Fluorescence data

Three regions of the Excitation/Emission map were used for assessing the FDOM components: protein-like peak T, humic-like peaks A and C. Peak A corresponds to Excitation/Emission wavelengths respectively 260 nm and 400-460 nm; Peak C to Excitation/Emission wavelengths respectively 320-360 nm and 420-460 nm and Peak T is centred at Excitation/Emission wavelengths respectively 275 nm and 340 nm (Coble 2007).

BIX [-] is computed at an excitation wavelength of 310 nm (Equation 1).  $BIX_{ex\ 310} = \frac{I_{em\ 380nm}}{I_{em\ 430nm}}$  (Eq. 1)

Where  $I_{em\ 380nm}$  and  $I_{em\ 430nm}$  are the fluorescence at 380nm and 430nm emission wavelengths.

HIX [-] is calculated at an excitation 254 nm (Eq.2).  $HIX_{ex\ 254} = \frac{\sum(em\ 435,480\ nm)}{\sum(em\ 300,345\ nm) + \sum(em\ 435,450\ nm)}$  (Eq. 2)

Where  $\sum(em\ 435, 480\ nm)$  is the sum of the fluorescence between 435 nm and 490 nm of emission wavelength,  $\sum(em\ 300, 345\ nm)$  is the sum of the fluorescence between 300 nm and 345 nm and  $\sum(em\ 435, 450\ nm)$  is the sum of fluorescence between 435 nm and 450 nm emission wavelength.

## 3 RESULTS AND DISCUSSION

### 3.1 FDOM values of the study sites

The mean values of peaks T, A and C were calculated for all samples (Figure 2). The fluorescence values of the two groups of waters were clearly different. In La Villette and Marne River samples, peak T was around 0.15 RU. Humic-like peaks A and C were within the range [0.26-0.59 RU]. In stormwater networks and WWTP outlets, fluorescence was higher. At SO-N and WWTP-O, peak T was around 1.0 RU. At SO-S, peak T was higher (4.2 RU). In the stormwater network and WWTP outlets, humic-like peaks A and C were within the range [1.3 - 2.2 RU].

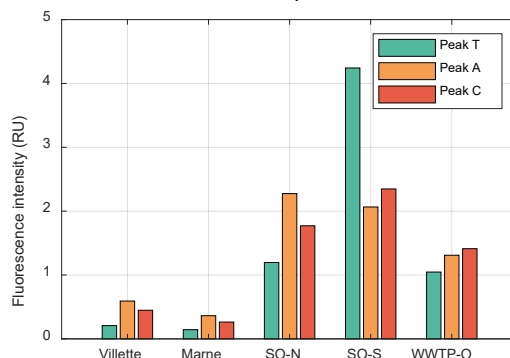


Figure 2. Fluorescence of La Villette and Marne River, stormwater network (SO-N and SO-S) and WWTP outlet (WWTP-O).

### 3.2 Dry and wet weather FDOM

The fluorescence values from dry and wet weather of all samples were plotted separately on Figure 3. In La Villette, peak T was higher in wet weather than in dry weather. Peaks A and C were lower in wet than in dry weather. In Marne River, peaks T, A and C were very close during wet and dry weather. In stormwater networks and WWTP outlets, peak T was higher in dry weather than in wet weather (Figure 3). In SO-S and WWTP-O, peaks A and C were close in dry and wet weather. In SO-N, peaks A and C were higher in wet than in dry weather.

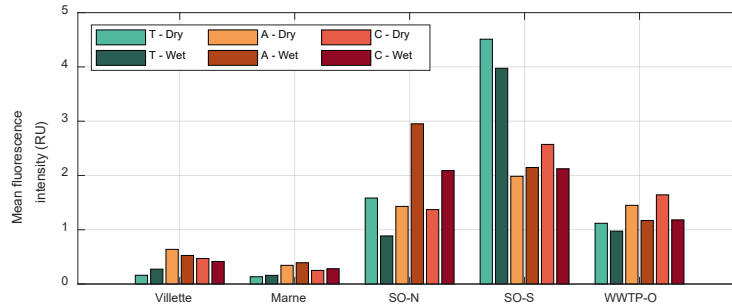


Figure 3. Peaks T, A and C at dry (light green, orange and red) and wet (dark green, orange and red) weather

The ratio C/T for all samples was plotted, separately for dry and rainy weather (Figure 4). In La Villette, C/T was lower in wet weather. C/T decrease during wet weather was mainly due to a twofold increase in peak T. A change in C/T ratio indicates a change in the proportion of allochthonous and autochthonous DOM, either a change in peak C value, or a change in peak T value. During wet weather, in La Villette DOM was probably from predominant autochthonous origin. In the Marne River, the C/T ratio remained unchanged during dry and wet weather. The C/T difference between La Villette and Marne River during dry and wet weather could be explained by the different sampling extension on the two watercourses, in spite of similar number of data. Marne River sampling covered only Summer 2022, with pre-defined collecting dates when La Villette sampling covered more than two years, comprising a targeted sampling during rainfall events. The Villette fluorescence values are probably more representative of the diversity of dry and wet weather conditions.

In SO-S and WWTP-O, the C/T ratio was close in dry and in wet weather. In SO-N, C/T was twofold higher in wet weather than in dry weather. Higher C/T value was associated to a decrease in peak T in wet weather. The low C/T value during dry weather, due to a higher peak T, suggested a misconnection of the wastewater network towards the stormwater network, leading to a microbiological contamination of the later.

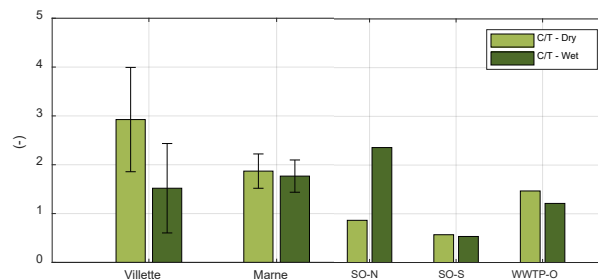


Figure 4. Mean C/T ratio in dry weather (light green) and wet weather (dark green).

The BIX and HIX indexes of all sampling sites were plotted in Figure 5. In La Villette, from dry to wet weather, BIX slightly increased and HIX slightly decreased. In Marne River, no difference of BIX and HIX was observed. In stormwater networks and WWTP outlets, BIX and HIX have similar values ([0.6 – 0.8]), except BIX in WWTP-O, around 1.1 in dry and wet weather. BIX close or higher than 1 may indicate a freshly produced DOM.

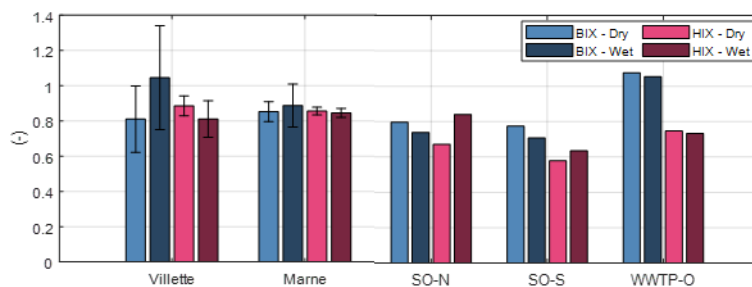


Figure 5. BIX and HIX indexes of dry and wet weather samples

## 4 CONCLUSION

Fluorescence values of dissolved organic matter were measured, during dry and wet weather, in different types of urban waters, two watercourses, two stormwater network outlet and a wastewater treatment plant outlet.

In the watercourses, La Villette and Marne River, the fluorescence of tryptophan-like peak T, and humic-like peaks A and C were low ( $\ll 1$  RU). In the outlet samples, peaks T, A and C were higher ( $> 1$  RU). Higher concentrations of humic-like and protein-like DOM were measured in outlets than in watercourses.

The comparison between dry and wet weather DOM was achieved through changes of C/T ratio and BIX index. During dry weather, C/T was lower in the outlet samples ( $< 1.5$ ) than in the watercourses ( $> 1.9$ ). This may indicate that less DOM of autochthonous origin is present in the watercourses in dry weather. In La Villette, in wet weather, a lower ratio C/T was related to an increase of peak T, due to a higher proportion of autochthonous DOM. The decrease of C/T might be related to a microbial contamination. This hypothesis could be validated through a comparison with microbiological water quality indicators, such as faecal indicator bacteria and ammonium.

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