

## Characterization by optical methods and high-resolution mass spectrometry of the Seine River dissolved organic matter (DOM)

Caractérisation par méthodes optiques et spectrométrie de masse à haute résolution de la matière organique dissous (MOD) de la Seine

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### RÉSUMÉ

La matière organique dissoute de la Seine a été caractérisée en termes de propriétés optiques (spectroscopie UV-visible et fluorescence) et de composition moléculaire, celle-ci étant obtenue à l'aide de spectres de masse à haute résolution. La traversée de grandes zones urbaines (Troyes et Paris) montre un changement dans la composition de la matière organique : la fluorescence de type protéinique (qui peut être liée à des apports d'eaux résiduelles domestiques) y augmente par exemple fortement. La présence d'atomes de soufre, chlore et phosphore confirme aussi la présence de substances anthropiques. La contribution finale permettra de relier les propriétés optiques, dont certaines peuvent être obtenues *in-situ*, à la composition moléculaire.

### ABSTRACT

The dissolved organic matter of the Seine is characterized in terms of optical properties (UV-visible spectroscopy and fluorescence) and molecular composition, which is obtained using high-resolution mass spectra. The crossing of large urban areas (Troyes and Paris) shows a change in the composition of organic matter: for example protein-type fluorescence (which can be linked to domestic wastewater inflow) increases strongly. The presence of sulfur, chlorine and phosphorus atoms also confirms the presence of anthropogenic substances. The final contribution will relate the optical properties, some of which can be obtained *in situ*, to the molecular composition.

### MOTS CLES

Caractérisation, fluorescence, matière organique dissoute, Seine, spectrométrie de masse

## 1 INTRODUCTION

Dissolved organic matter (DOM) is a significant component of freshwaters affecting biogeochemical cycling of metals and water resource. Various inputs (natural and anthropic) in aquatic ecosystems contribute to the chemical complexity and to the variability in composition and reactivity of dissolved organic matter, including fulvic acids (FA) (Fleury et al., 2017).

The aim of this study was to describe the DOM along the Seine River in order to gain insights into its various origins, based on its chemical characteristics (composition, structure and reactivity), by means of complementary approaches using optical method measurements (UV-visible spectroscopy and fluorescence spectroscopy) and ESI-FTMS analysis (electro-spray ionization Fourier Transform mass spectrometry).

## 2 MATERIALS AND METHODS

### 2.1 Sampling

Samples were collected in 10 L PTFE-lined polyethylene bottles in nine stations along the Seine River, from Nod-sur-Seine to Poses. The stations were characterized in terms of land use (CORINE-LC) and population (INSEE) in their up-stream sub-catchment. The samples were filtrated on pre-combusted GF-F filters within 24 hours and kept at 4°C in the dark until analysis. Ancillary analysis was performed for dissolved organic carbon and nitrogen, major anions (by ion chromatography for sulfates, nitrates, and chlorides, by colorimetry for phosphates) and cations (by ICP-OES).

### 2.2 DOM extraction

DOM was extracted by automated SPE after acidification at pH 2 by HCl on Oasis-HLB cartridges (elution with ultra-pure methanol).

### 2.3 Optical methods

Filtrated river samples and DOM extracts were analyzed by UV-visible spectrometry and fluorescence spectroscopy (emission-excitation matrices and synchronous fluorescence) with quartz cuvettes. Dilution by ultra-pure water was performed for fluorescence spectra, when the absorbance at 254 nm was larger than 0.1 cm<sup>-1</sup>.

Deconvolution in Gauss functions (up to four fluorophores) was applied on synchronous spectra (Assad et al., 2015). Indices (humification index, index of recent autochthonous contribution, etc.) were calculated from emission-excitation matrices.

### 2.4 High-resolution mass spectrometry

To obtain DOM solutions (pH 2.9), previous DOM extracts were evaporated under vacuum and dissolved in diluted nitric acid. A Thermo Scientific LTQ Orbitrap hybrid mass spectrometer was used for the analysis in ESI negative ionization mode of DOM solutions.

The samples were infused directly into the ESI source with a spray voltage of 3.5 kV at a flow rate of 10 µL.min<sup>-1</sup>, and were analysed in negative ion mode. Nitrogen was used as the drying and spraying gas. For each acquisition, 100 scans (2s/scan) were co-added using Xcalibur software. The Orbitrap MS was externally calibrated in negative ion mode on the 50-2000 m/z range using a LTQ/FT-Hybrid ESI Calmix solution, for a mass accuracy better than 3 ppm. Instrument operating parameters (capillary voltage: -50V and temperature: 275°C, tube lens voltage: -240V) were optimized for an optimal transmission of higher m/z ions. All ESI(-) mass spectra were recorded in the ranges 120-400 m/z and 400-798 m/z in order to improve the mass accuracy in the region of low masses as well as the signal-to-noise ratio (S/N) for compounds having the highest values of m/z in samples.

Molecular formula were determined as natural organic matter (C<sub>0-200</sub>H<sub>0-600</sub>O<sub>0-50</sub>N<sub>0-1</sub>S<sub>0-2</sub>) and possibly anthropic organic matter (C<sub>0-200</sub>H<sub>0-600</sub>O<sub>0-50</sub>N<sub>0-1</sub>S<sub>0-2</sub>P<sub>0-2</sub>Cl<sub>0-3</sub>) with a mass difference limit of 3 ppm. Based on the aromaticity index, three molecular classes were defined: condensed aromatics (AC), aromatics (A) and aliphatics (AL), plotted in Van Krevelen diagrams (H/C versus O/C atomic ratios).

## 3 RESULTS

The fluorescence spectra obtained on surface water samples indicate a change in the distribution of fluorophores when the river crosses large urban areas (Troyes, Paris). An increase of the protein-like

fluorescence (F1 in synchronous fluorescence spectra) whose origin could be anthropogenic, is especially noticeable on Figure 1 near these urban areas. Mass spectra are presented in figure 2. Some anthropic molecules are observed in collected samples downstream of Bar. Major sulphurous molecules are identified at  $m/z=183.01$ ,  $197.03$ ,  $209.03$ ,  $223.04$  and  $237.06$ . On another hand, chlorinated compounds are present on  $m/z$  ratio of  $311.11$  and  $325.11$ . The concentration of these molecules seem to increase along the river and reach a maximum at Triel. Identified molecules (~2470) at the most downstream sampling station (Poses) are mainly characterized by O/C ratios lower than 0.7. While nitrogen-containing molecules (80%) are found to be present in the three classes of compounds, phosphorous (8%) and sulfurous (6%) containing molecules fall only in the aliphatic region of VK diagrams. 'CHONPS' molecules (7%) are poorly-oxygenated (O/C <0.2) 'aliphatic like' molecules.

## 4 CONCLUSION

The data suggest an effect on dissolved organic matter of anthropic pressures depending on the type of land use and amount of population in the each sub-catchment studied. The final contribution will relate the optical properties, some of which can be obtained in situ, to the molecular composition as well as to land use and population.

## BIBLIOGRAPHIE

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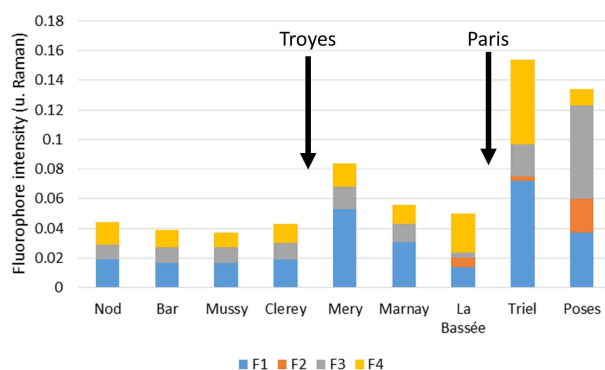


Figure 1 : Variability of the fluorophore distribution from upstream (Nod) to downstream (Poses) (synchronous fluorescence spectra on river samples) (F1=  $\lambda_{ex}=280/\lambda_{em}=330$ , F2=  $\lambda_{ex}=300/\lambda_{em}=350$ , F3=  $\lambda_{ex}=315/\lambda_{em}=365$ , F4=  $\lambda_{ex}=350/\lambda_{em}=400$ , wavelengths in nm)

Variabilité de la distribution en fluorophores de l'amont (Nod) à l'aval (Poses) (spectres de fluorescence synchrone des échantillons d'eau de surface) (F1=  $\lambda_{ex}=280/\lambda_{em}=330$ , F2=  $\lambda_{ex}=300/\lambda_{em}=350$ , F3=  $\lambda_{ex}=315/\lambda_{em}=365$ , F4=  $\lambda_{ex}=350/\lambda_{em}=400$ , longueurs d'onde nm)

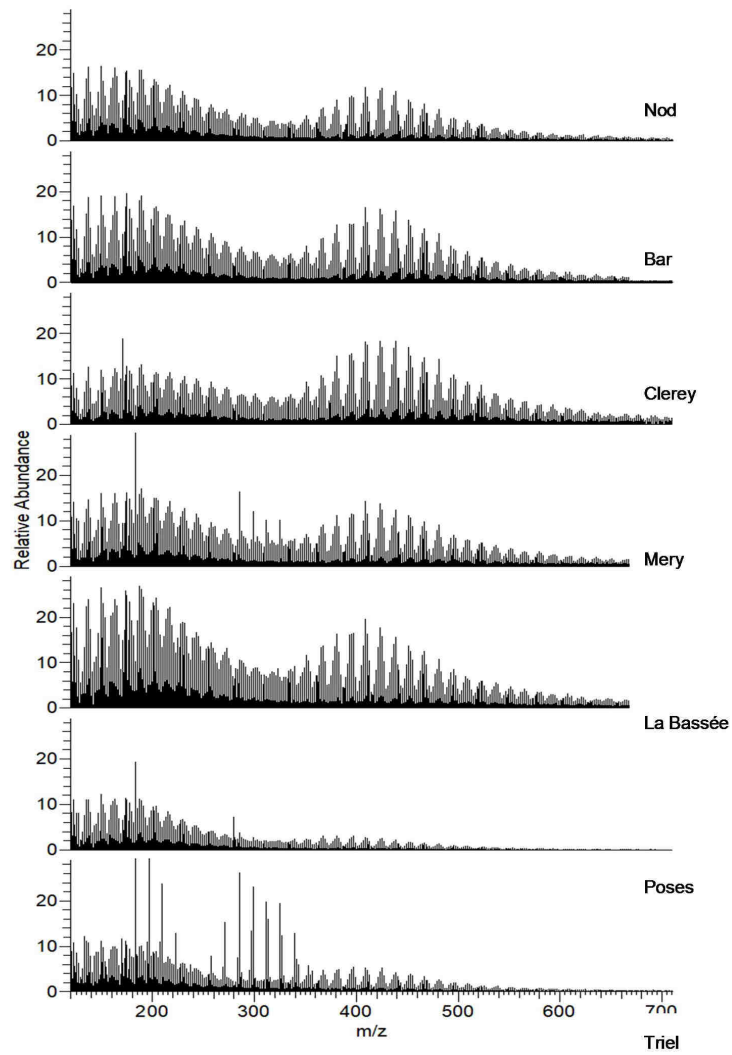


Figure 2. DOM mass spectra obtained along the Seine continuum.  
Spectres de masse de la matière organique dissoute le long de la Seine