Monitoring dissolved organic matter in an urban watershed during one year by Excitation-emission matrix fluorescence spectroscopy: case of the Seine River (France)

A Goffin*, S Guérin, V Rocher, G Varrault

*Corresponding author: goffin.angel@gmail.com

Abstract: The aims of this study are to better understand dissolved organic matter (DOM) origins and variations observed in an urban watershed called the Seine River (France). For one year, DOM was weekly monitored at 12 locations from upstream to downstream of Paris (n=373). For each sample, Excitation-emission matrix fluorescence spectroscopy and water quality parameters measurements were made. A 10 PARAFAC components model was highlighted, which allowed to observe spatial and temporal variations of DOM quality and quantity. The monitoring also showed the impact of Paris wastewater treatment plants effluents in the Seine River DOM by highlighting specific fluorescence components. Finally, the observation of a 10-year return flood has given us a better understanding of the Seine River DOM quality and quantity changes during different flows periods. The highlighted fluorescence indicators can be used for future *in situ* DOM monitoring in this watershed.

Keywords: dissolved organic matter monitoring; excitation emission matrix fluorescence spectroscopy; receiving environment.

Dissolved organic matter (DOM) is well known to influence bioavailability and speciation of metallic and organic micropollutants into receiving waters (Matar, 2012). Knowledge of the quantity and quality of DOM in the receiving environment is an important issue for various actors in the field of water. An early characterization of DOM in water used for drinking water treatment could help to anticipate its treatability and the production of toxic disinfection by-products. Moreover, a fast DOM characterization could help to anticipate eutrophication phenomenon in receiving environment caused by wastewater treatment plants (WWTP) effluents. Current methods used to characterize organic matter are laborious, time consuming, and not applicable to directly monitor organic matter *in situ*. Excitation-emission matrix (EEM) Fluorescence spectroscopy is a good candidate to meet these requirements as it's a solvent-less, cost-less, *in situ* and rapid method. The present work has been carried out in the context of the MOCOPEE research program (www.mocopee.com) and the Piren-Seine research program (http:// www.metis.upmc.fr/piren/) in the aims to assess the use of EEM Fluorescence spectroscopy for monitor and characterize DOM in the Seine River watershed which is under strong urban pressure.

From July 2015 to June 2016, global parameters and EEM Fluorescence spectroscopy coupled with the PARAllel FACtor (PARAFAC) analysis have been investigated during a weekly monitoring of DOM in the Seine River watershed (n=373 samples). Dissolved organic carbon (DOC) measurements were also made in parallel of fluorescence measurements, immediately after sampling. The chosen sampling locations (n=12) cover the Marne/Oise/Seine Rivers and are parts of the measurement network "MeSeine" managed by the Greater Parisian Sanitation Authority (SIAAP). The studied zone also presents four WWTPs (SIAAP) with various treatment capacity from 300,000 to 1,700,000 m^3/day. This representing a total treatment capacity of 2,540,000 m^3/day.

This study highlighted a 10 components PARAFAC model (for the 12 sampling locations) which allowed to observe changes in DOM quality between the different rivers and seasons investigated. Three distinct class of fluorescent components were observed: humic substances-like components from different maturities, humic

substances-like components from a recent biological activity and protein-like components. Changes in DOM quality between the different rivers investigated and between the different seasons were observed. Impact of urban pressure was observed between upstream and downstream of Paris Conurbation by modification of DOM fluorescence proprieties. We also highlighted a wastewater effluent impact into the Seine river in downstream of Paris, resulting from maintenance operations in the largest Parisian wastewater treatment plant (1,700,000 m^3/day), with an increase in protein-like fluorescence intensity. Variations of fluorescence intensity between high and low flows was also measured with a predominance of humic-like compounds during a 10-year occurrence flood event. Spatio-temporal variations of DOM fluorescence quality and quantity was emphasized giving us important indications about DOM sources in this urban watershed. Correlations were found between fluorescence indicators and different water quality key parameters in the natural water. For example, dissolved organic carbon (DOC) concentration (r^2=0.800; $p<0.0001$; n=373) presents very good correlation with specific fluorescence peaks and indicators.

Thus, this study demonstrated the possibility to use the EEM fluorescence spectroscopy to highlight the impacts of the different Paris agglomeration WWTPs on the quality and the quantity of the Seine River DOM. A set of DOM sources tracers based on fluorescence measurements adapted to our watershed were also highlighted. These fluorescence indicators could be used for future *in situ* DOM monitoring.

REFERENCES

Matar, Z., 2012. *Influence de la matière organique dissoute d'origine urbaine sur la spéciation et la biodisponibilité des métaux dans les milieux récepteurs anthropisés.* PhD thesis, University of Paris-Est.