Excitation-emission matrix Fluorescence spectroscopy to assess quality and quantity of dissolved organic matter in the Seine River from the upstream to the downstream of the Paris agglomeration during a hydrological year

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Dissolved organic matter (DOM) is ubiquitous in surface water is well known to influence bioavailability and speciation of metallic and organic micro-pollutants into receiving waters. DOM also represents a challenge for drinking water management as its treatability is subject to inter-seasonal variations (high/low flow-winter/summer) and could induce formation of carcinogenic disinfection by products. Current methods used to characterize organic matter quality are laborious, time consuming, and not applicable to directly monitor organic matter \textit{in situ}. This stresses the need of a new methodology with a high analytical frequency and usable \textit{on site} to follow variations of DOM quality and quantity in freshwater. The present work has been carried out in the context of MOCOPEE research program (www.mocopee.com) and Piren-Seine research program (http://www.metois.upmc.fr/piren/). It aims to assess the use of optical techniques, such as UV-Visible absorbance and Fluorescence spectroscopy in order to monitor and characterize DOM in the Seine River watershed which is under strong urban pressure.

Since July 2015, global parameters, UV-Vis absorbance and Excitation-emission matrix Fluorescence spectroscopy coupled with PARAFAC analysis have been investigated during a weekly monitoring of DOM at several locations in the Seine River watershed (n=373 samples). This measurement network includes 13 sampling points from upstream to the downstream of Paris and in its two main affluents (Marne and Oise rivers).

A 10 component PARAFAC model allowed us to observe change in DOM quality between the different rivers investigated. Impact of urban pressure was observed between upstream and downstream of Paris Conurbation by modification of DOM fluorescence properties. 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\textsuperscript{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.

Finally, correlations were found between fluorescence indicators and different water quality key parameters in the natural water. For example, dissolved organic carbon concentration ($r^2=0.800; p<0.0001; n=373$) presents good correlation with specific fluorescence peaks and indicators.