A year of dissolved organic matter monitoring by excitation-emission matrix fluorescence spectroscopy, case of an urban watershed: the Seine River

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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 (Buffle, 1988). 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 the formation of carcinogenic disinfection byproducts (Awad et al, 2017). Current methods used to characterize organic matter quality are laborious, time consuming, and not applicable to directly monitor organic matter *in situ*. This stresses the need of a new methodology with a high analytical frequency and usable *on site* to follow variations of DOM quality and quantity in freshwater. 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/). 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.

From July 2015 to June 2016, 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 12 sampling points from upstream to the downstream of Paris and in its two main affluent (Marne and Oise rivers). A 10 component PARAFAC model allowed us to observe changes in DOM quality between the different rivers investigated and between the different seasons. 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. 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.

Finally, this study highlight a set of DOM sources tracers and DOC concentration indicators based on fluorescence measurement adapted to our watershed. These fluorescence indicators can be used for future *in situ* DOM monitoring.

References:

Buffle, J., 1988. Complexation Reactions in Aquatic Systems: An Analytical Approach., Ellis Horwood. ed. New York.

Awad J., Van Leeuwen, J., Chow, C.W.K., Smernik, R.J, Anderson, S.J, Cox, J.W., (2017). Seasonal variation in the nature of DOM in a river and drinking water reservoir of a closed catchment. Environmental Pollution Part B 220, 788-796. https://doi.org/10.1016/j.envpol.2016.10.054.