Seasonal dynamics of dissolved organic matter in the Seine estuary (France) highlighted by multiple analytical and statistical approaches

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Introduction

Estuaries are unique ecosystems where the salt water of the ocean mix with the freshwater from rivers and create a brackish water zone directly conditioning by salinity and turbidity. In the north of France, the Seine estuary represents the link between the Seine river watershed and the English Channel. This watershed is characterized by natural and anthropogenic (agricultural, industrial and urban) influences. Furthermore a full dissolved organic matter (DOM) characterization in such environment is still very complex and needs a combination of analytical techniques. The aim of this study was to better understand the spatial and seasonal variability of DOM properties along this continuum between continental and coastal waters by using various descriptors and variables. For this purpose, environmental parameters such as water temperature, river discharge and salinity were confronted to the dataset of DOM properties obtained using UV/Vis spectrophotometry, Excitation-Emission Matrix (EEM) spectroscopy and Asymmetrical Flow Field-Flow Fractionation (AF4). The objective was to improve knowledge about DOM dynamics and environmental factors influencing it by exploring the dataset with different statistical approaches (Spearman correlation, model of linear regression (MLR), Parallel Factor Analysis (PARAFAC) and self-organizing maps (SOM)).

This work was conducted on 56 samples collected in summer 2015 and winter 2016 in the Seine estuary. The water samples were analysed to obtain the dissolved organic carbon concentration, DOM optical properties and apparent molecular weight.

Results

This work combining AF4, optical spectroscopy (UV/Vis and fluorescence) and statistical processing allowed us to discriminate DOM properties between seasons (summer and winter), tide periods and sample locations in the Seine estuary.
DOM can be characterized by higher aromaticity (a_{254}, $SUVA_{254}$ and HIX), lower biological activity (BIX) and molecular weight (MW) during the winter in link with the river discharge and water temperature (figure 1). Six components explaining the whole fluorescence dataset were determined by PARAFAC analysis and highlighted differences in DOM sources according to the seasons. Moreover, one peculiar component (C5), which could be an indicator of pulp mill inputs, was determined only in summer when the river discharge was the lowest. The Model Linear Regression (MLR) applied to the whole dataset showed all the interest to consider both DOM descriptors and environmental variables (salinity and water temperature). MLR has notably permitted to point out the influence of water temperature on the DOM variability in winter period.
The application of the SOM approach highlighted the spatiotemporal variations with very clear differences in DOM characteristics according to the seasons, tides and sampling sites. Moreover, SOM allowed us to link specific DOM descriptors to peculiar temporal or spatial

parameters, which permitted to separate the estuary according to specific characteristics such as low molecular weight and dissolved organic carbon for the lower estuary, or protein-like component, low temperature and high molecular weight for the fluvial estuary during the winter period.

Conclusions

The combined, analytical and statistical, approach, developed in this work, was shown to be very powerful for the study of DOM dynamics in complex environments.
Finally this approach allowed us to associate DOM properties, particularly in terms of size and type connected to its sources, with specific periods, positions of tide and the geographical zones.

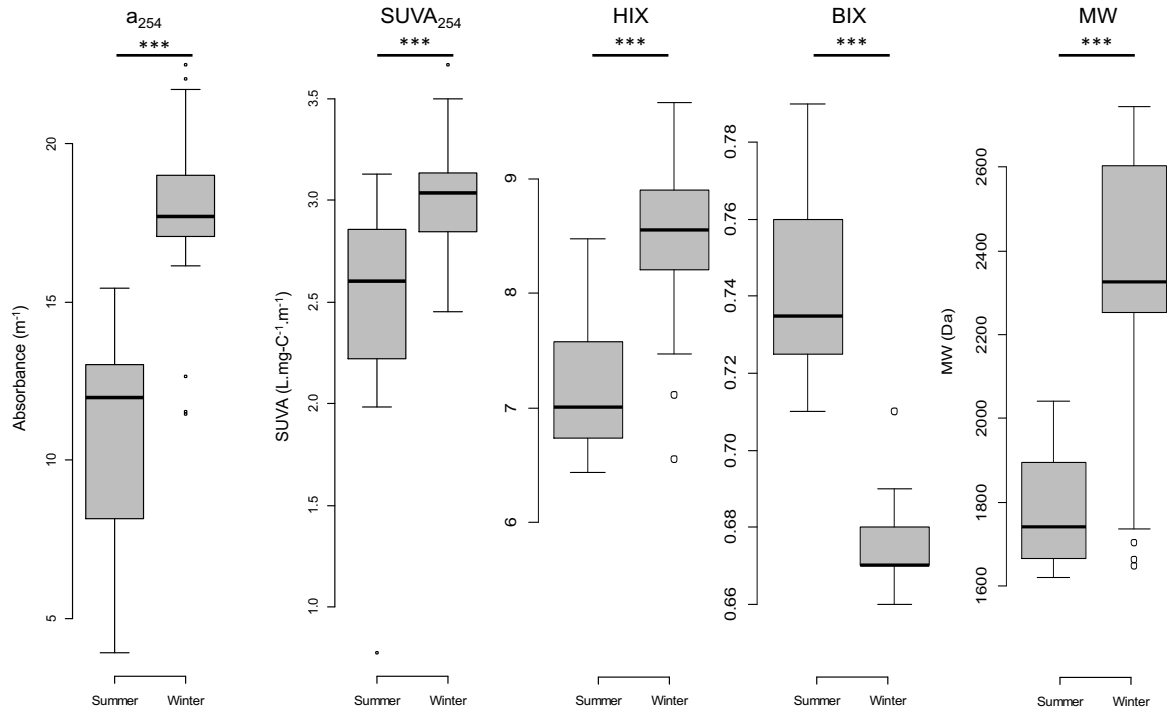

Figure 1 *Box plots comparing absorbance at 254nm (a_{254}), specific ultraviolet absorbance at 254nm ($SUVA_{254}$), humification index (HIX), biological index (BIX) and DOM molecular weight (MW) determined by AF4 between summer 2015 and winter 2016 (***= p<0.001).*