Excitation-emission matrix fluorescence spectroscopy applications to monitor variations in the quality and quantity of dissolved organic matter in six Paris wastewater treatment plants influents: towards a better optimization of the wastewater treatment process

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Abstract: The online monitoring of dissolved organic matter (DOM) in sewage is expected to result in a better control of wastewater treatment processes. Three-dimensional fluorescence spectroscopy combined with parallel factor analysis (PARAFAC) has been investigated as a fast and alternative methodology to conventional wastewater quality measurement indicators. This study also presents the first to attempt using EEM-PARAFAC to characterize DOM quality and quantity in sewage, at the hourly sampling scale and to follow variation of PARAFAC components scores over 14 full days monitoring of domestic sewage. Relationships were highlighted between DOM fluorescence indicators identified using PARAFAC and measurements of soluble biological oxygen demand (BOD_5) (r^2=0.846; adjusted r^2=0.839; p<0.0001; n=83) as well as with soluble chemical oxygen demand (COD) measurements (r^2=0.785; p<0.0001; n=83) for a dataset of 6 Paris wastewater treatment plants influents.

Keywords: wastewater dissolved organic matter; quality monitoring; biochemical and chemical oxidation demand.

The regulatory context in the field of urban wastewater treatment has evolved considerably in the last two decades by presenting a significant increase in the requirements on the water quality returned to the receiving environment. In this context, the main French agglomerations conducted a policy of construction and modernization of sanitation facilities. However, to maintain a high quality of treatment, wastewater treatment plants (WWTP) management requires a high level of technical and scientific expertise. Current methods used to characterize dissolved organic matter (DOM) quality, like biological oxygen demand in five days (BOD_5) or chemical oxygen demand (COD), are laborious, time consuming (few hours to several days) and are not applicable to monitor organic matter *in situ*. An improvement of online monitoring and characterization of sewage DOM is one of the ways considered to optimize control and management of treatment facilities (Carstea et al., 2016; Goffin et al., 2018). In the context of the MOCOPEE research program (www.mocopee.com), this study aims are: (1) to assess the use of fluorescence spectroscopy to characterise sewage DOM and (2) to developed fluorescence indicators which can be used to monitor and to optimize WWTP efficiency.

Excitation-emission matrix (EEM) Fluorescence spectroscopy coupled to PARAFAC analysis was used on 69 domestic sewage samples from the "Seine Centre" WWTP (240,000 m^3/day; sewage from the western Paris basin) located near to Paris in France. All samples were collected at different hours in order to highlight temporal variations (daily and hourly) of DOM fluorescence during April 2015 and between June and July 2016. Soluble COD and BOD_5 measurements were also made directly after sampling. Predictive models of soluble BOD5 and COD using PARAFAC score were investigated. Since the PARAFAC approach cannot be used *in situ* at the moment, a "peak-picking" approach based on the maximum fluorescence intensity localization of PARAFAC components has been applied to all the 62

samples from the "Seine Centre" WWTP. Finally, in order to take into account the variability of influents between different WWTPs, the possibility of transposing the first prediction models of soluble COD and soluble BOD_5 was tested for a second set of 83 sewage samples from 6 Paris WWTPs (Marne Aval WWTP: 75,000 m^3/day; Seine Morée WWTP: 50,000 m^3/day; Seine Centre WWTP: 240,000 m^3/day; Seine Grésillons WWTP: 300,000 m^3/day, Seine Valenton WWTP: 600,000 m^3/day, Seine Aval WWTP: 1,700,000 m^3/day).

A six PARAFAC components model was obtained: three components were related to humic substances-like components and three others were related to protein-like components. Fluorescence signature of sewage DOM from the "Seine Centre" WWTP was mainly composed of protein-like components, which exhibit the highest fluorescence intensities and humic substances-like components showed the lowest fluorescence intensity. The soluble COD of wastewater can be predicted by using a simple linear model with the tyrosine-like component scores (r^2=0.829; $p<0.0001$; n=62). The soluble BOD_5 can be predicted by a multiple linear model based on various fluorescence indices (r^2=0.863; adjusted r^2=0.857; $p<0.0001$; n=62). Since the PARAFAC methodology cannot currently be automated (to date), prediction models based on the location of fluorescence maximums (Ex-Em) of the identified PARAFAC components have been developed. The Pearson determination coefficient obtained for the prediction of soluble COD is equal to 0.825 ($p<0.0001$; n=62). For soluble BOD_5, r^2 equal 0.803; with an adjusted r^2 of 0.792; ($p<0.0001$; n=62). Thus, the potential for *in situ* application of these prediction models has been successfully demonstrated for sewage from the western Paris basin. These models were generalized to sewage from the entire Paris basin (6 Paris WWTPs; n=83). A Pearson determination coefficient of 0.785 ($p<0.0001$; n=83) was obtained for soluble COD and for soluble BOD_5, a Pearson determination coefficient of 0.846 with an adjusted r^2=0.839 ($p<0.001$; n=83) were obtained.

Use of EEM fluorescence spectroscopy coupled with PARAFAC analysis allowed to better characterize temporal variability of DOM quality and quantity in sewage. A Six fluorescent components model showed useful information about sewage fluorescent DOM quality. The peak-picking method highlighted, derived from the PARAFAC components identified above, is simple, easy to automate and applicable to the operational area of wastewater treatment for high-frequency and ecological online monitoring of soluble COD and soluble BOD_5 in order to reduce the energy costs of WWTPs (chemical reagents, pumping and aeration) and to better control treatment processes. The models highlighted by this study can also be used for fast, simple and inexpensive laboratory measurement.

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