Applications of Fluorescence Spectroscopy for dissolved organic matter characterization in wastewater treatments plants

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Introduction

Wastewater treatment plants (WWTP) efficiency is impacted by organic matter (OM) :

Organic matter in raw sewage water → Membrane fouling / Biological treatment efficiency / Foaming phenomenon → Need to monitor organic matter quality & quantity

Fluorescence Spectroscopy doesn't require the use of solvent, is rapid and can be used in situ and on-line for characterization of wastewater organic matter.

Aims of this research

- Obtain a **better knowledge of wastewater dissolved organic matter by fluorescence spectroscopy**.
- Identify **fluorescence indices who could be used for wastewater quality parameters prediction** in order to offer new monitoring tool to optimize wastewater treatment processes.

Material & methods

Sampling site

« Seine Centre » WWTP (240,000 m³/day) Paris, France Raw sewage, decantation, carbon elimination, nitrification and denitrification.

Analytical methods

After filtration (GF/F 0.7 µm), global parameters + **3D fluorescence spectroscopy** (JASCO, FP 8300) + **254 nm UV** (Uv-line Seconam) are analyzed at the same time.

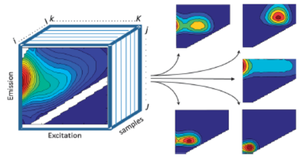
Data treatment

Fluorescence excitation-emission matrix (FEEM) are blank subtracted and Raman normalized.

- Method n°1: Fluorescence peaks (Coble, 1996; Parlanti et al., 2000)

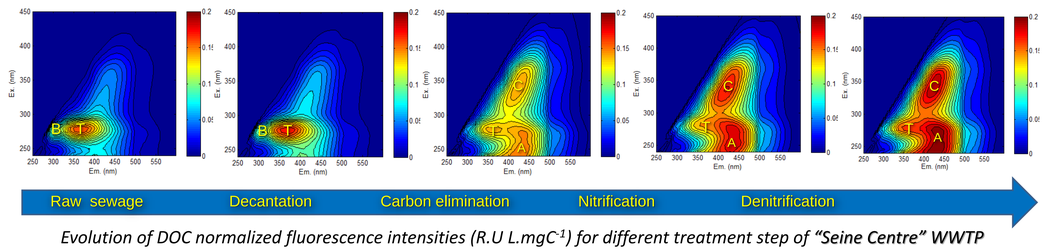
Fluorophore (Coble, 1996)	Fluorophore (Parlanti et al., 2000)	λex (nm)	λem (nm)	Fluorophore type
C	α	330-350	420-480	Humic-like
A	α'	250-260	380-480	Humic-like
M	β	310-320	380-420	Autochtonous production
B	γ	270-280	300-320	Protein-like (Tyrosine-like)
T	δ	270-280	320-380	Protein-like (Tryptophan-like)

- Method n°2: Parallel Factor Analysis (PARAFAC) (Murphy et al., 2013)



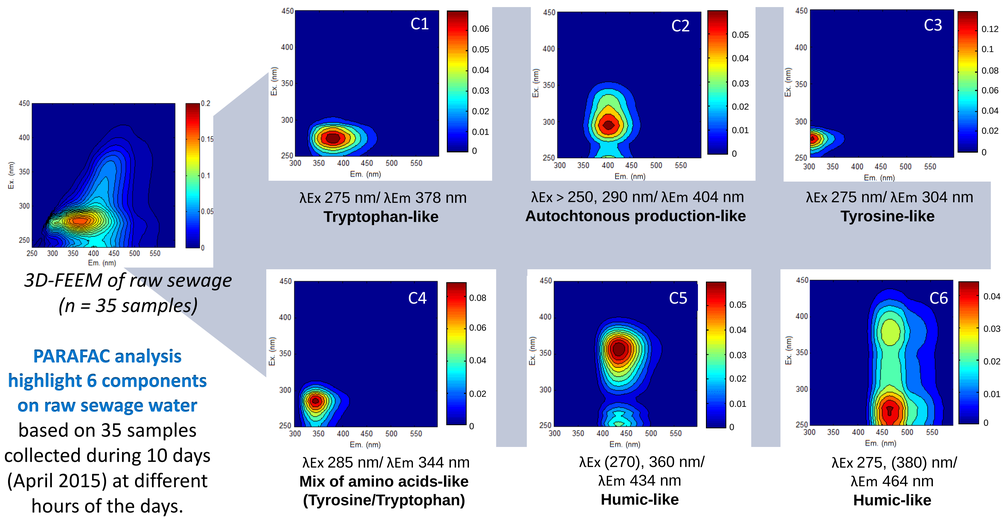
New fluorescence indicators more suitable for monitoring wastewater ?

A specific fluorescence signature at each treatment step



Evolution of DOC normalized fluorescence intensities (R.U L.mgC⁻¹) for different treatment step of "Seine Centre" WWTP

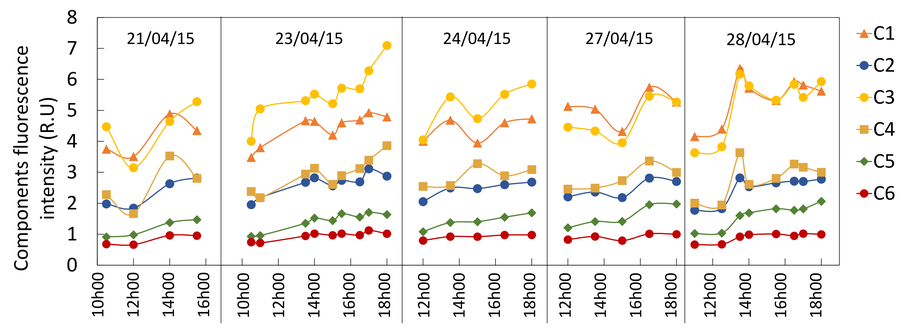
Focus on raw sewage organic matter composition



3D-FEEM of raw sewage (n = 35 samples)

PARAFAC analysis highlight 6 components on raw sewage water based on 35 samples collected during 10 days (April 2015) at different hours of the days.

Daily variations of organic matter fluorescence in WWTP influent



- Fluorescence intensity of all PARAFAC component follow a clear trend during the day.
- Protein-like component (C3, C1, C4) present the highest fluorescence intensities.
- Humic-like component C6 seem to show the smallest variations over time.

Fluorescence spectroscopy as a prediction tool for quantity of BOD_5 and NH_4^+ in raw sewage water

- *Quantity of BOD_5*

- BOD_5 simple linear regression

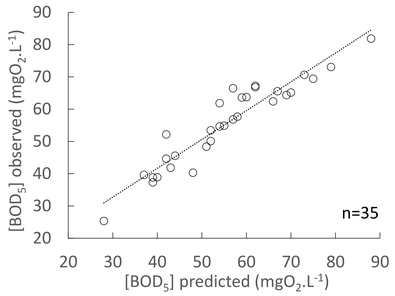
Absorbance 254 nm => r^2= 0.786

Component C3 => r^2= 0.745 (Tyrosine-like)

- BOD_5 multiple linear regression

BOD_5 ($mgO_2.L^{-1}$) = 103,317 + C3 * 9.980 – 27.368 * C2/C5 – 36.880 * HIX

r^2= 0.893 r^2_{ajt}= 0.881 p<0.0001



Correlation between [BOD_5] predicted with multiple linear regression and observed values in raw sewage water

- *Quantity of NH_4^+*

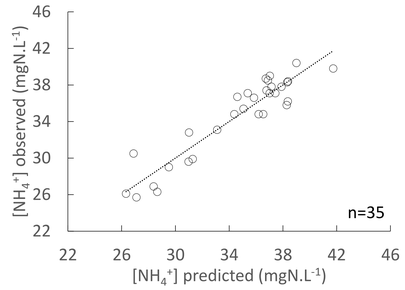
- NH_4^+ simple linear regression

Absorbance 254 nm => r^2= 0.752

Component C2 => r^2= 0.878 (autochthonous production-like)

NH_4^+ ($mgN.L^{-1}$) = 11.526 * C2 + 5.872

r^2 = 0.878 p<0.0001



Correlation between [NH_4^+] predicted with simple linear regression and [NH_4^+] observed values in raw sewage water

Conclusions and future research

- ***3D Fluorescence spectroscopy = fast characterization of dissolved organic matter in wastewater:***
  - Diminution of fluorophores quantity between influent and effluent.
  - Evolution of organic matter quality by dominance of certain fluorescent components.
    - Raw sewage is mainly composed of Protein-like component (C1+C3).
    - WWTP effluent is dominate by Humic-like fluorescence (peak A and C).
- ***3D FEEM allow us to build good prediction model of global parameters in raw sewage who will be used for process optimization.***

Future research

Exploration of different mathematical data treatment (like self-organizing maps) who will allow us to highlight other fluorescence indicators specific of wastewater and operational problems.

«Fluorescence spectroscopy a new prediction tool of fooling potential ? »

Henderson et al., (2011) highlight implication of tyrosine like component in fouling potential inside a tertiary wastewater treatment.

References:

Coble, P.G., 1996. Characterization of marine and terrestrial DOM in seawater using excitation–emission matrix spectroscopy.Mar. Chem. 51, 325–346.

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