



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

Angélique Goffin, Sabrina Guérin, Vincent Rocher, Gilles Varrault



Organic matter influence

Drinking water treatment plant

- Organic matter quality
- Disinfection by-products

Ground water

- Organic matter quality

Biochemistry of aquatic environment

- Spatial and temporal change of organic matter origin/quality

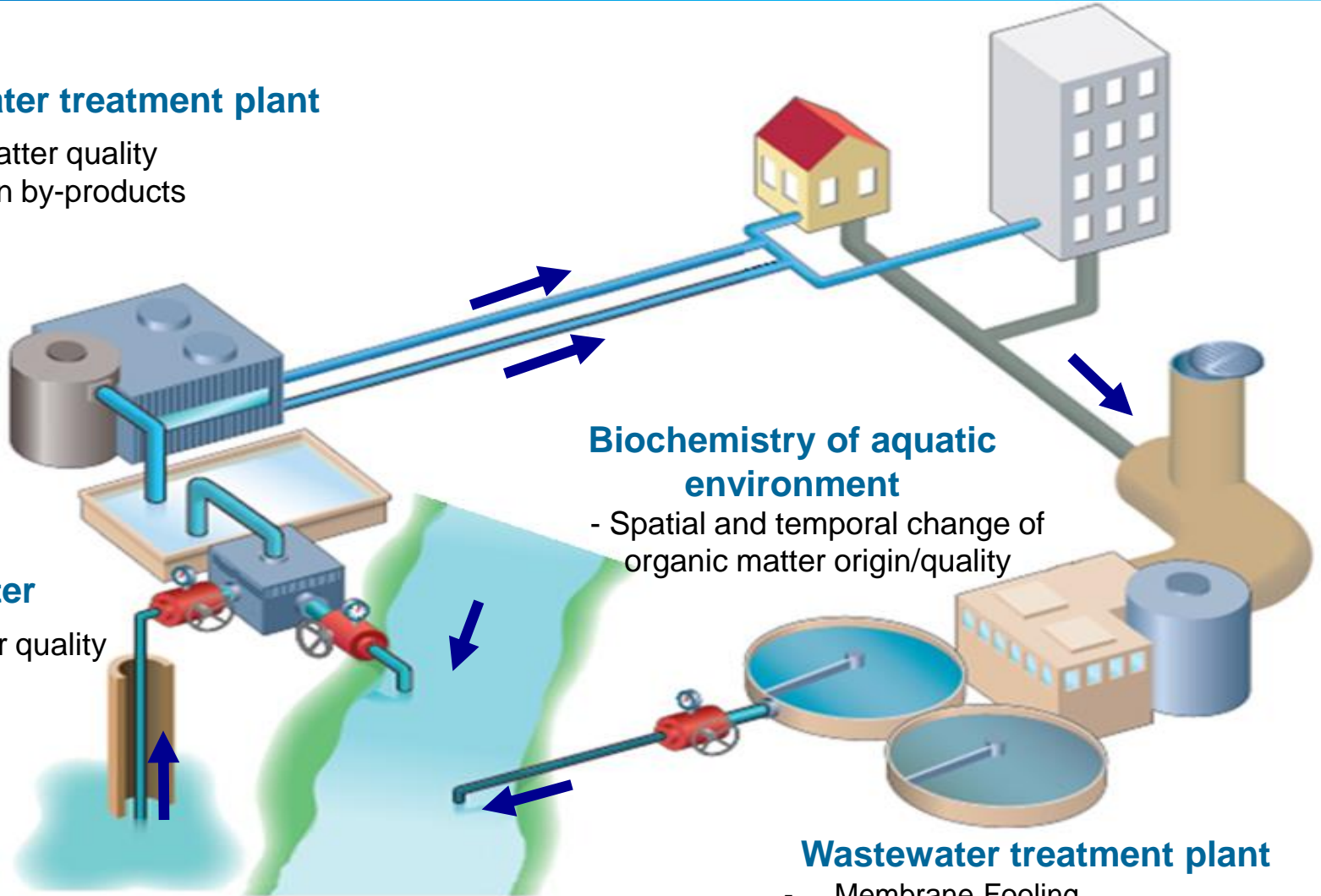
Receiving environment

- Eutrophication
- Organic and metallic pollutants biodisponibility

Wastewater treatment plant

- Membrane Fouling
- Foaming events
- Organic matter quality

➡ Water



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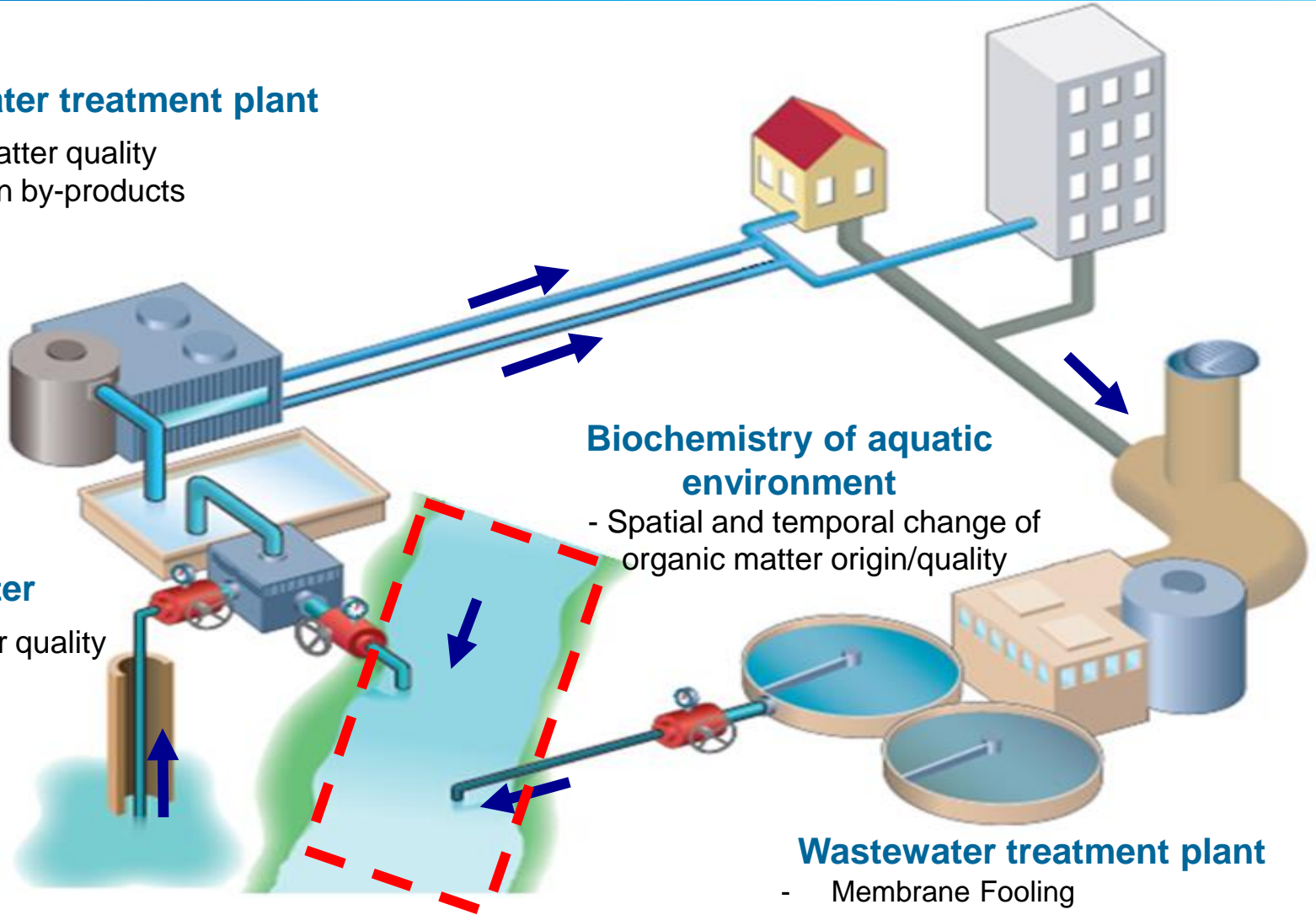
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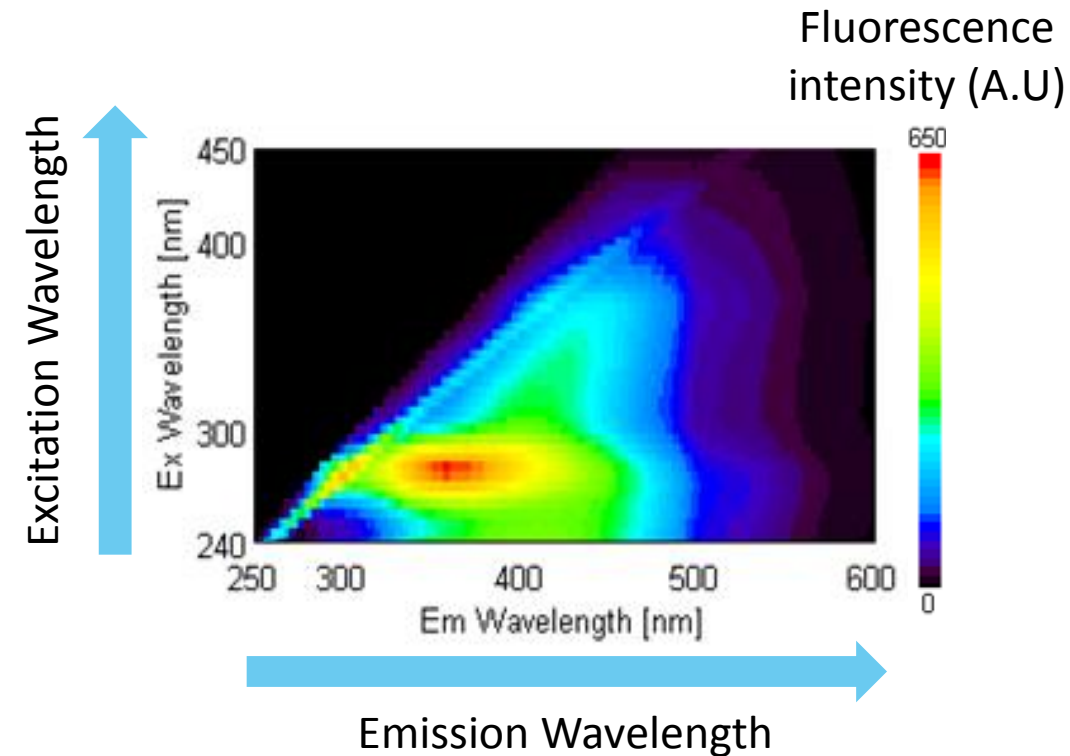
Wastewater treatment plant

- Membrane Fouling
- Foaming events
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➔ Water

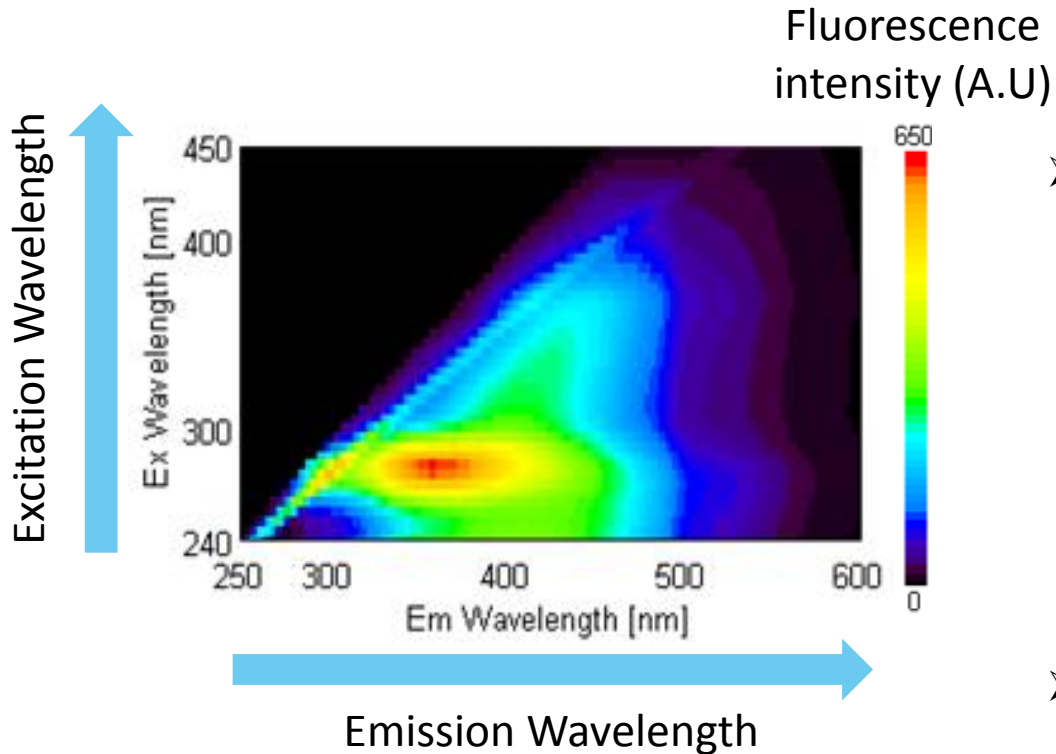


What is 3D EEM-Fluorescence Spectroscopy ?



3D Excitation-Emission matrix (EEM) fluorescence spectra of wastewater influent

What is 3D EEM-Fluorescence Spectroscopy ?

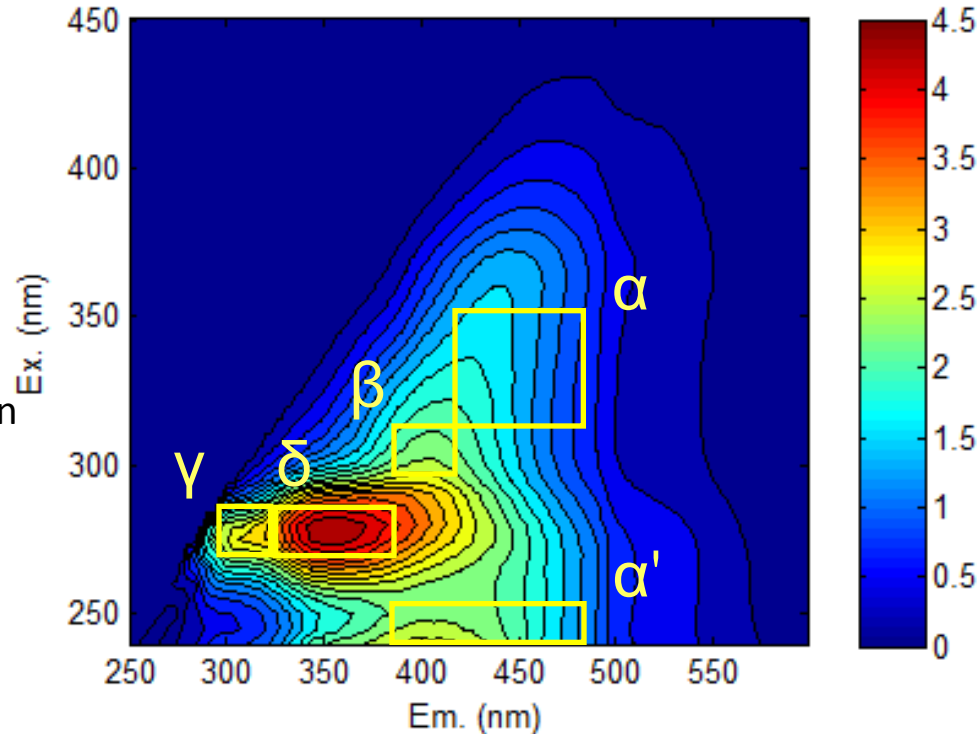


3D Excitation-Emission matrix (EEM) fluorescence spectra of wastewater influent

- *3D EEM Fluorescence spectroscopy:*
 - Fluorophore number
 - Relative concentration (intensity)
 - Fluorophores type ($\lambda_{ex}/\lambda_{em}$)
- *Parameters :*
 - Spectrofluorimeter FP-8300, JASCO (Japan)
 - Excitation 240 - 450 nm (5 nm)
 - Emission 250 - 600 nm (2 nm)

Data interpretation

by Coble (1996), Parlanti et al., (2000)



β

λ Ex 310 – 320 nm
 λ Em 380 – 420 nm

Autochthonous production

α

λ Ex 330 – 350 nm
 λ Em 420 – 480 nm
Humic-like substances

α'

λ Ex 240 – 260 nm
 λ Em 380 – 480 nm
Humic-like substances

γ

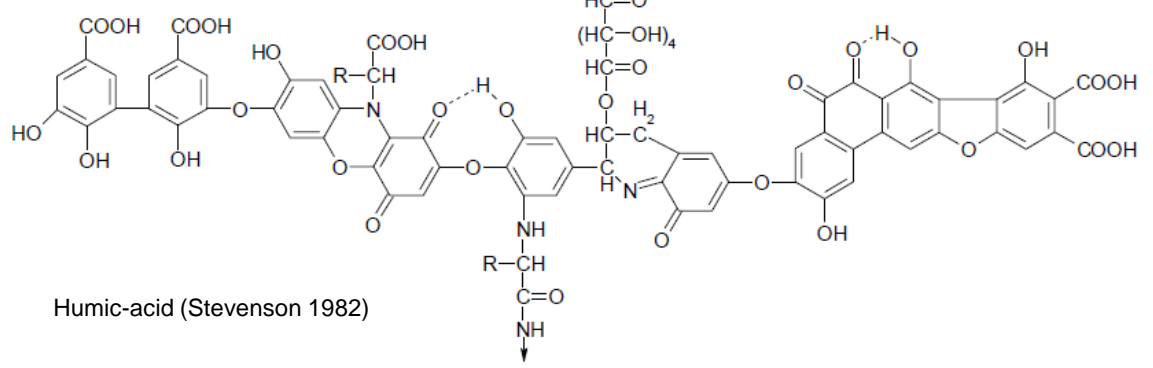
λ Ex 270 – 280 nm
 λ Em 300 – 320 nm

Protein-like
(Tyrosine)

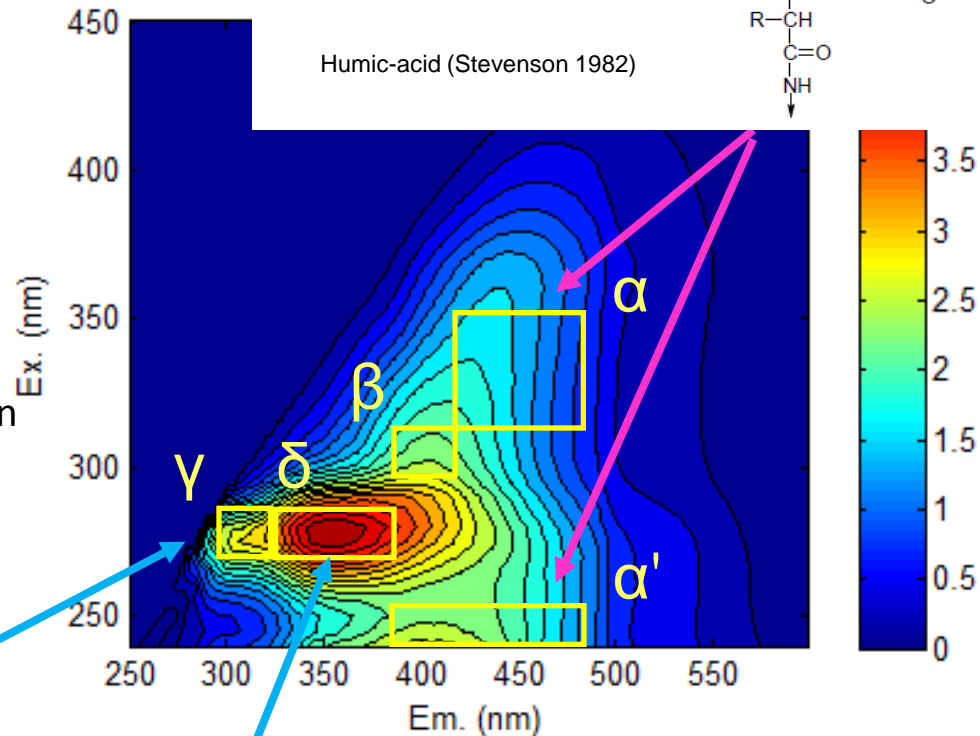
δ

λ Ex 270 – 280 nm
 λ Em 320 – 380 nm

Protein-like
(Tryptophan)

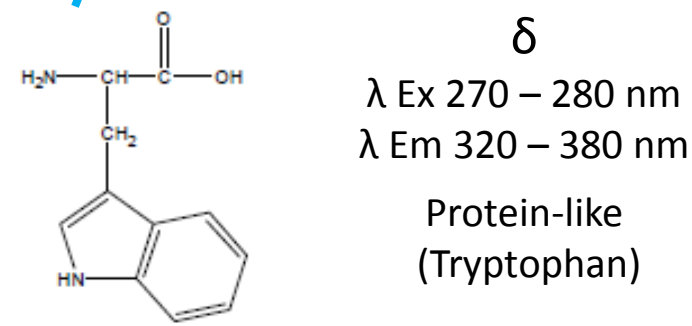
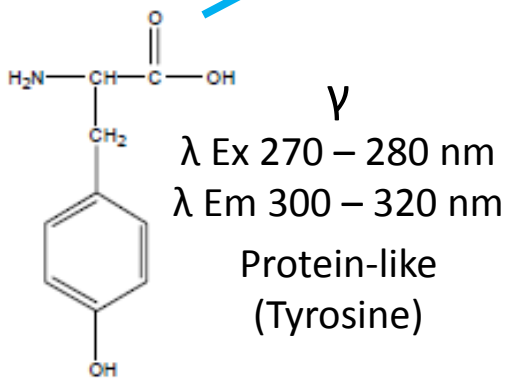


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Parallel factor analysis (PARAFAC)

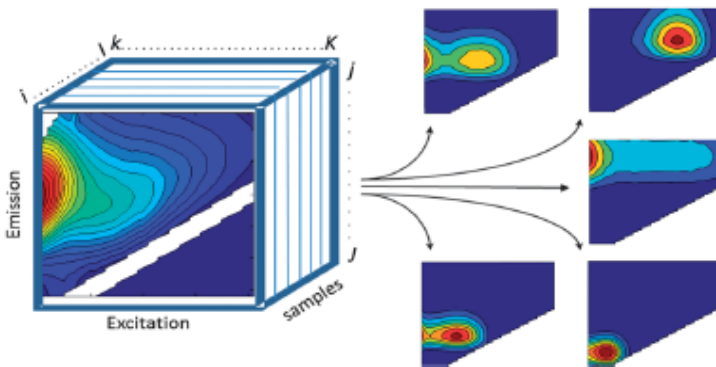
- Parallel factor analysis =
Multivariate data analysis (Bro, 1997)

$$x_{ijk} = \sum_{f=1}^F a_{if} b_{jf} c_{kf} + \varepsilon_{ijk}$$

Measuring data
i sample
j emission wavelength
k excitation wavelength

Modeled Data
Components concentrations
Emission propriety
Excitation propriety

Residues
Unexplained data (Residual
fluorescence, interferences....)

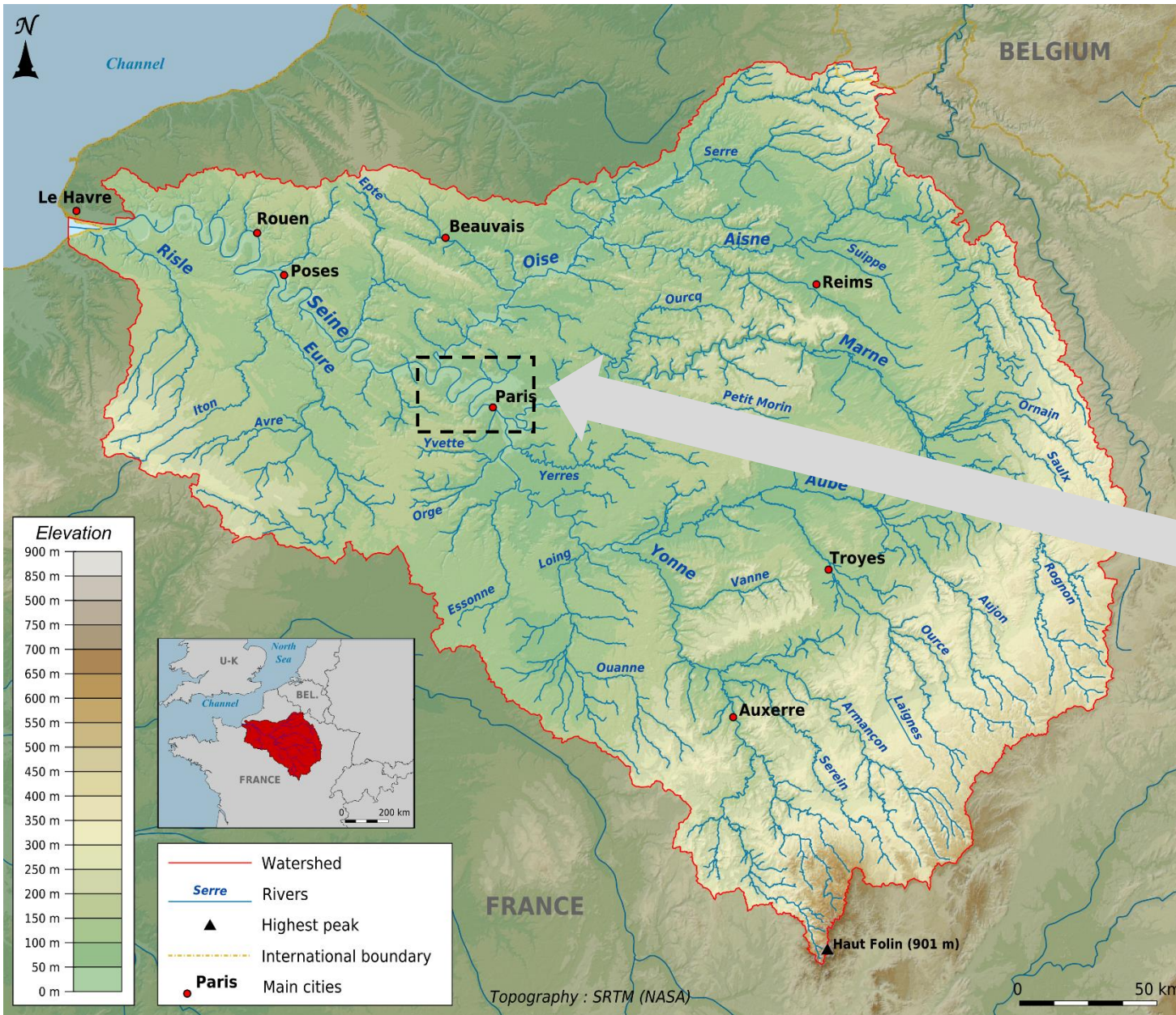


(Murphy et al., 2013)

Data validation by split half analysis

Residues < 5% on EEM after
deconvolution

The Seine River catchment in France



75,000 km²

16 million inhabitants

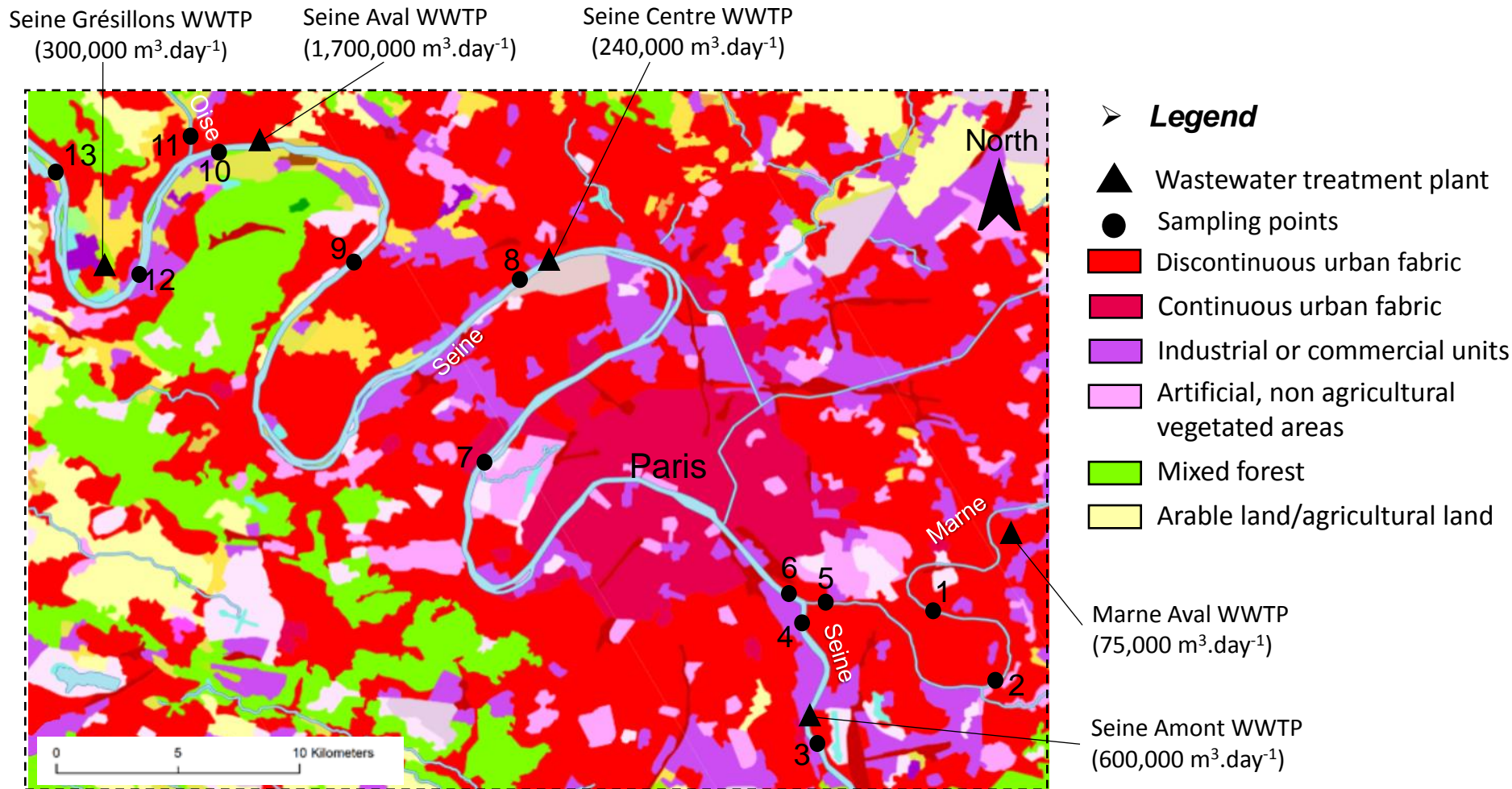
28% French population

=

Anthropogenic impacts ?

Dynamic of organic matter through the time ?

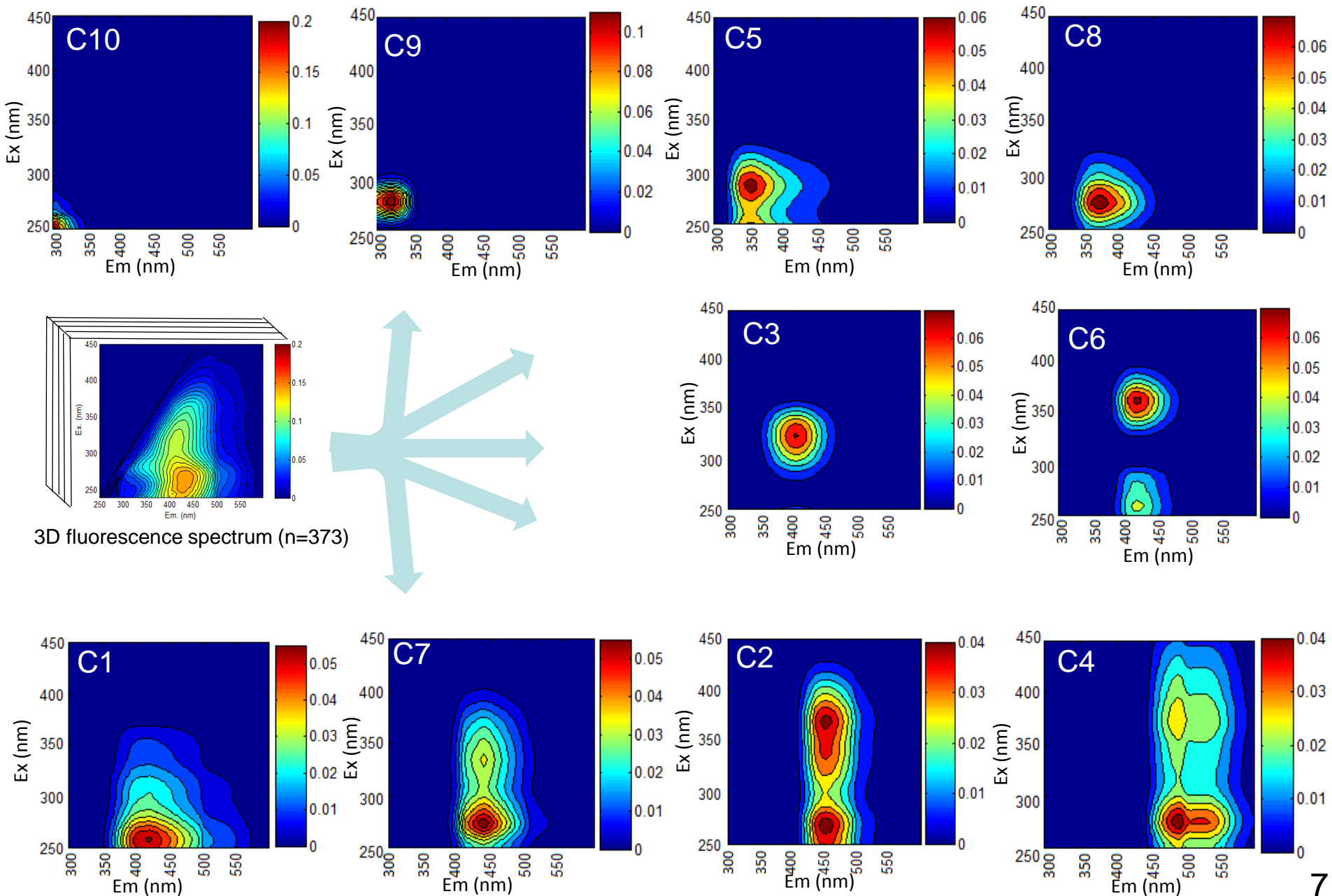
Sampling points



Sampling point map and land use of Parisian conurbation

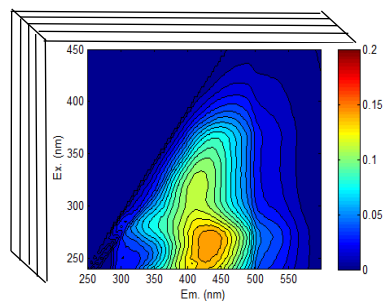
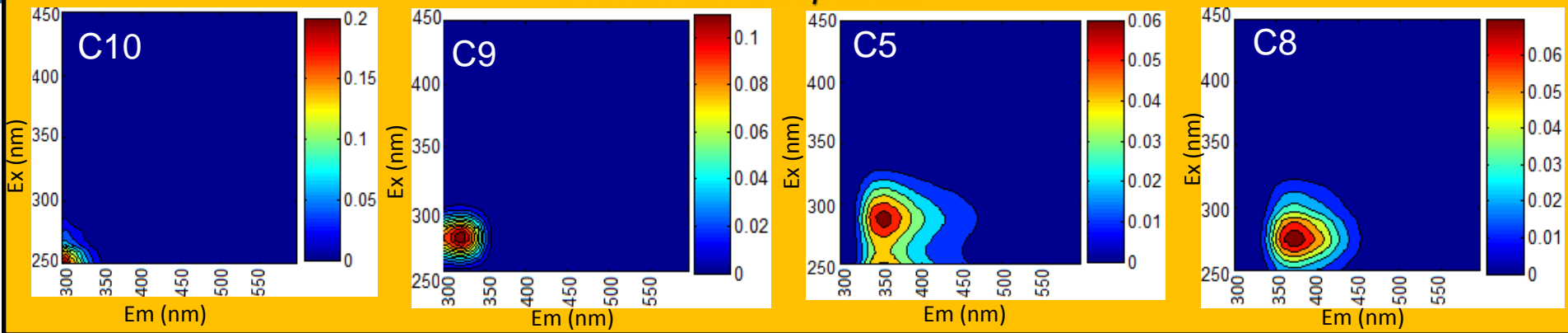
- **One year of sampling July 2015 - June 2016: Weekly sampling** on 13 spots (n = 373)
- 3D EEM fluorescence spectroscopy + UV-Vis spectroscopy 254 nm (Filtration 0.7µm, GF/F)
- Global parameters: SS, COD, soluble COD, BOD₅, soluble BOD₅, TOC, DOC, NH₄⁺, NO₃⁻, NO₂⁻

PARAFAC model



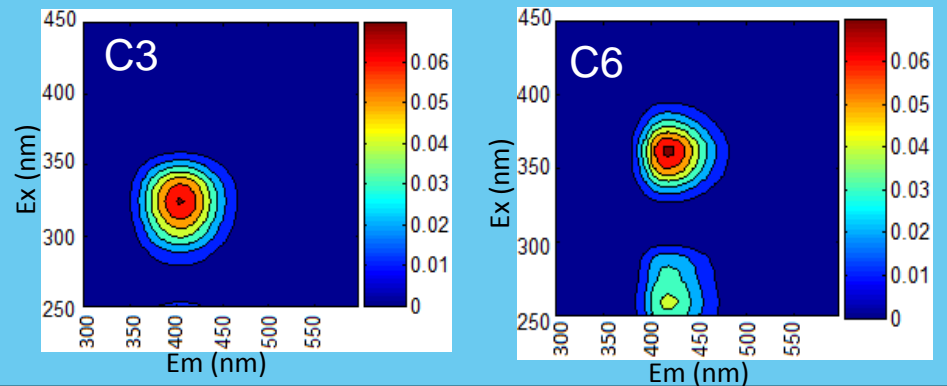
PARAFAC model

Protein-like component

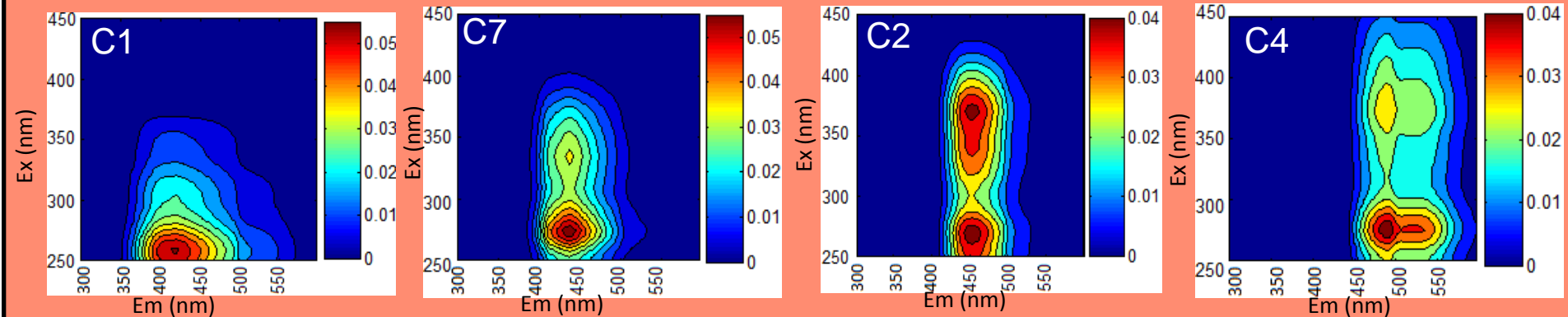


3D fluorescence spectrum (n=373)

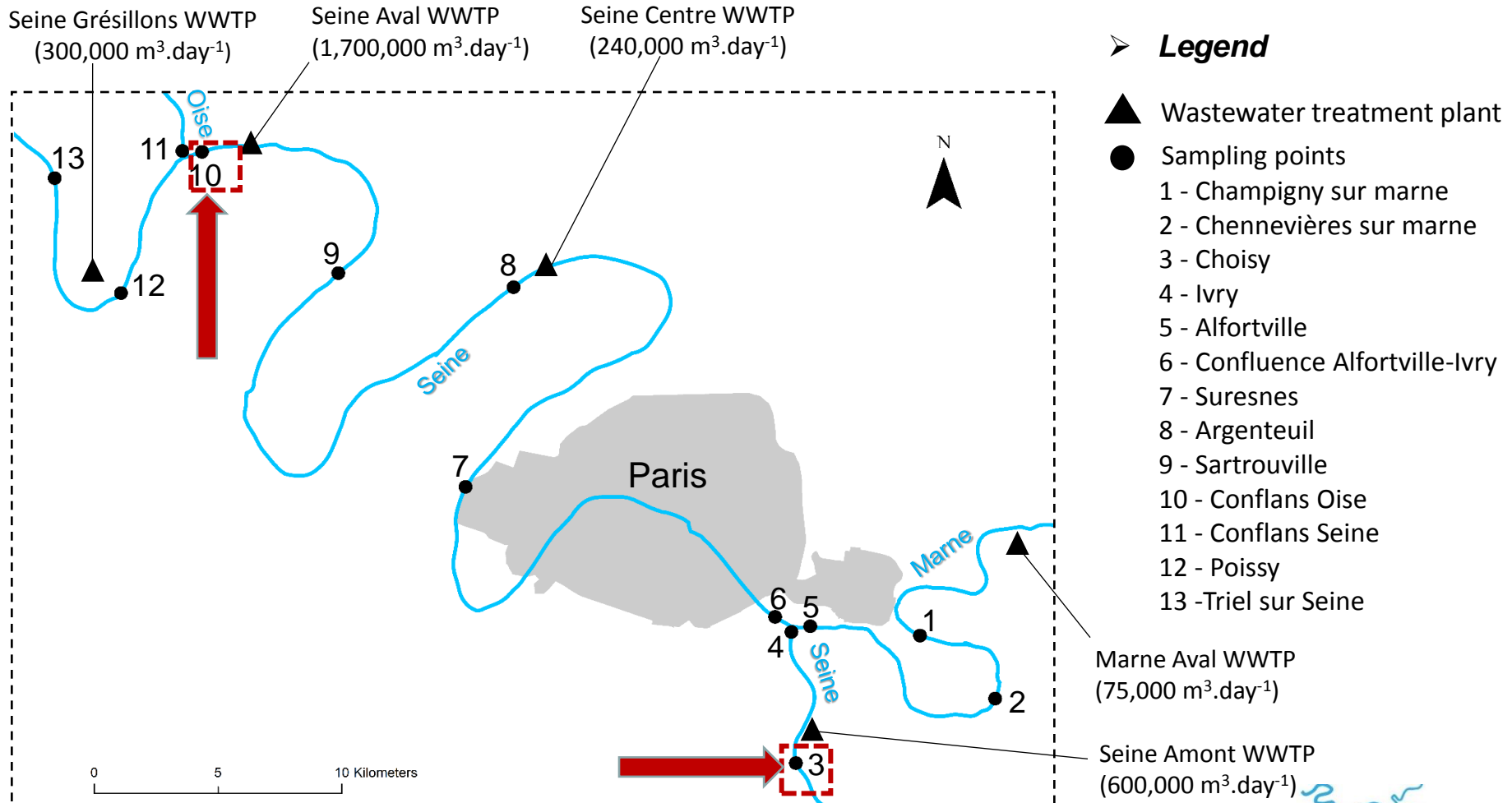
Recent Humic-like component



Humic-like component

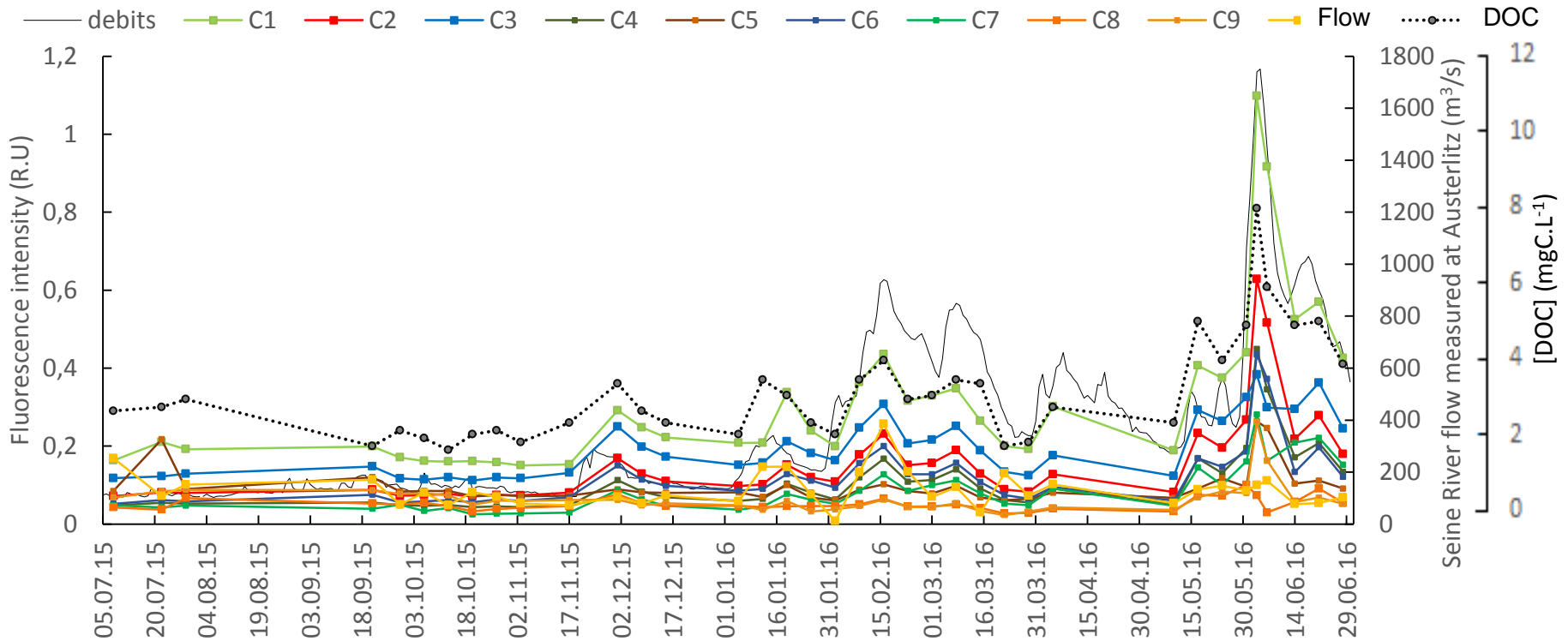


Upstream vs downstream



Sampling point map of upstream-downstream Parisian conurbation

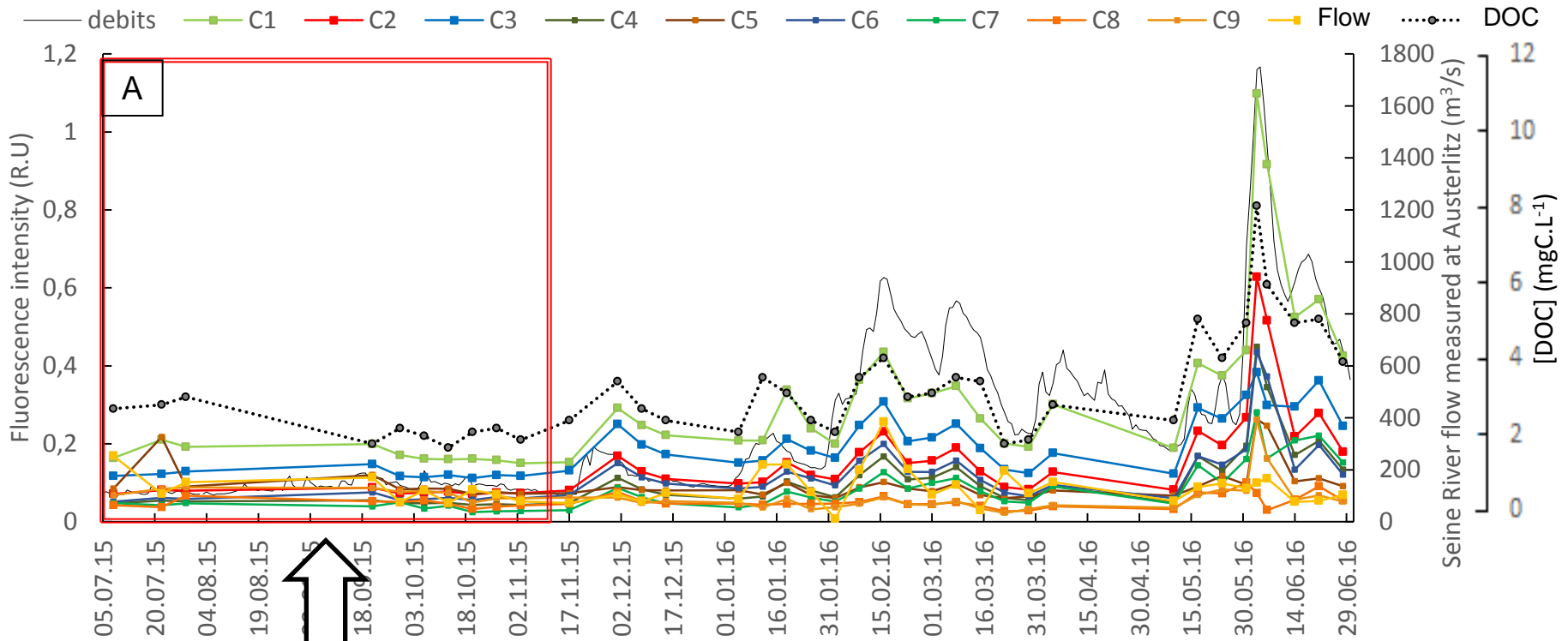
Focus on upstream of Parisian conurbation (Choisy)



*Chronic of fluorescence intensity, DOC concentration and measured flow in the Seine River
For Upstream of Paris between July 2015 and June 2016*

- DOM fluorescence intensity change with the Seine River flow
- Fluorescence spectroscopy can be used to follow **quantity** of fluorescence material

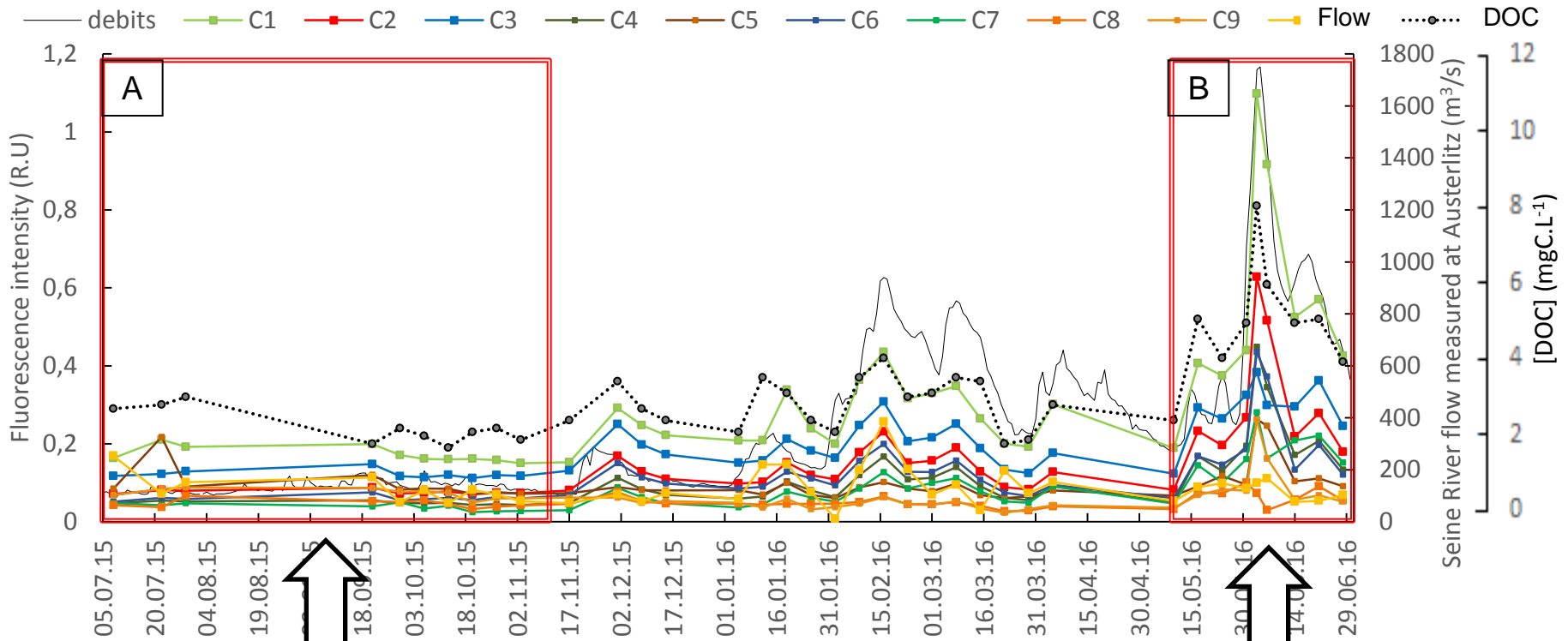
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Low flow period
June-November 2015

Focus on upstream of Parisian conurbation (Choisy)



Chronic of fluorescence intensity, DOC concentration and measured flow in the Seine River For Upstream of Paris between July 2015 and June 2016

Low flow period
June-November 2015

Exceptional high flow (Paris flood)
June 2016
=> 10 years occurrence event

June 2016

Last week

Paris under water: Following a 10-year occurrence flood event



Alma Bridge



2016 6.10 m

1910
8.62 m

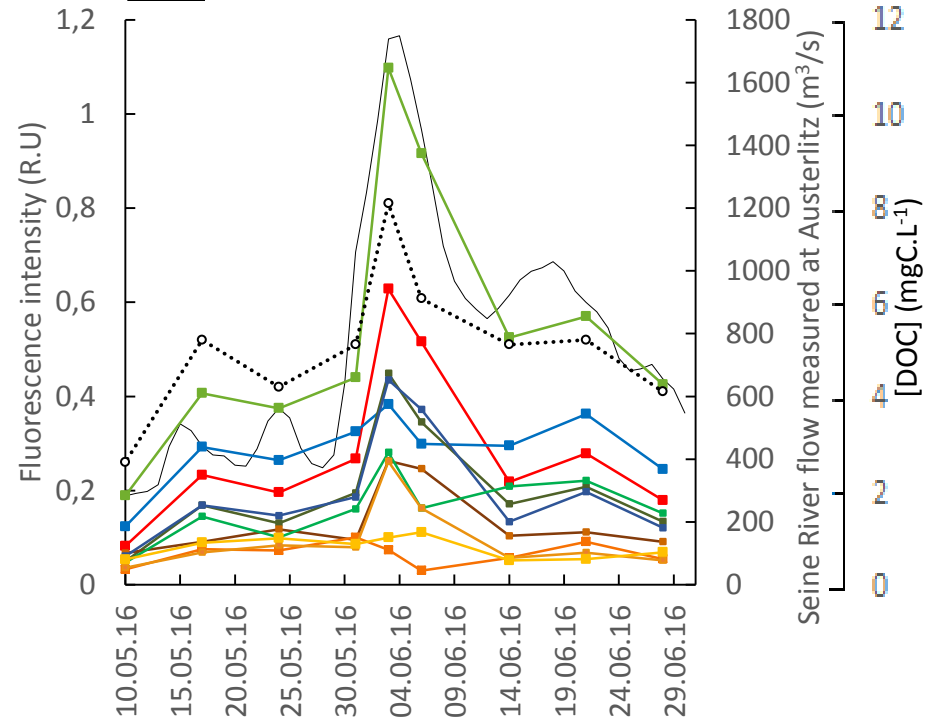
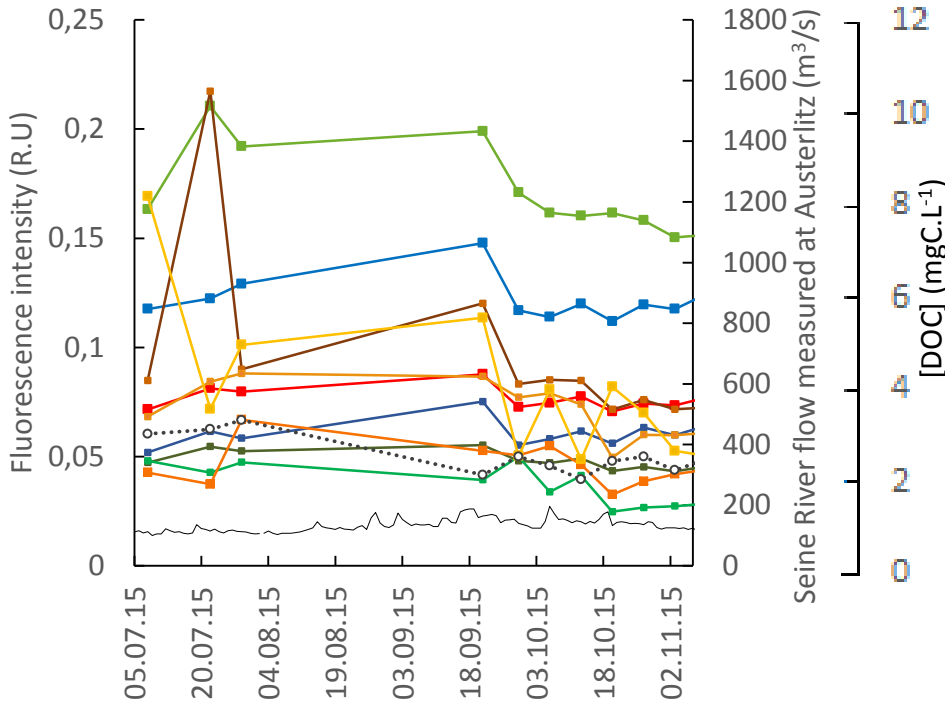
Bridge of Arcole

Focus on upstream of Parisian conurbation (Choisy)

—■ C1 —■ C2 —■ C3 —■ C4 —■ C5 —■ C6 —■ C7 —■ C8 —■ C9 —■ C10 — Flow DOC

A Low flow (June-November 2015)

B High flow (May-June 2016)



Chronic of fluorescence intensity, DOC concentration and measured flow in the Seine River, upstream of Parisian conurbation

➤ Low flow :

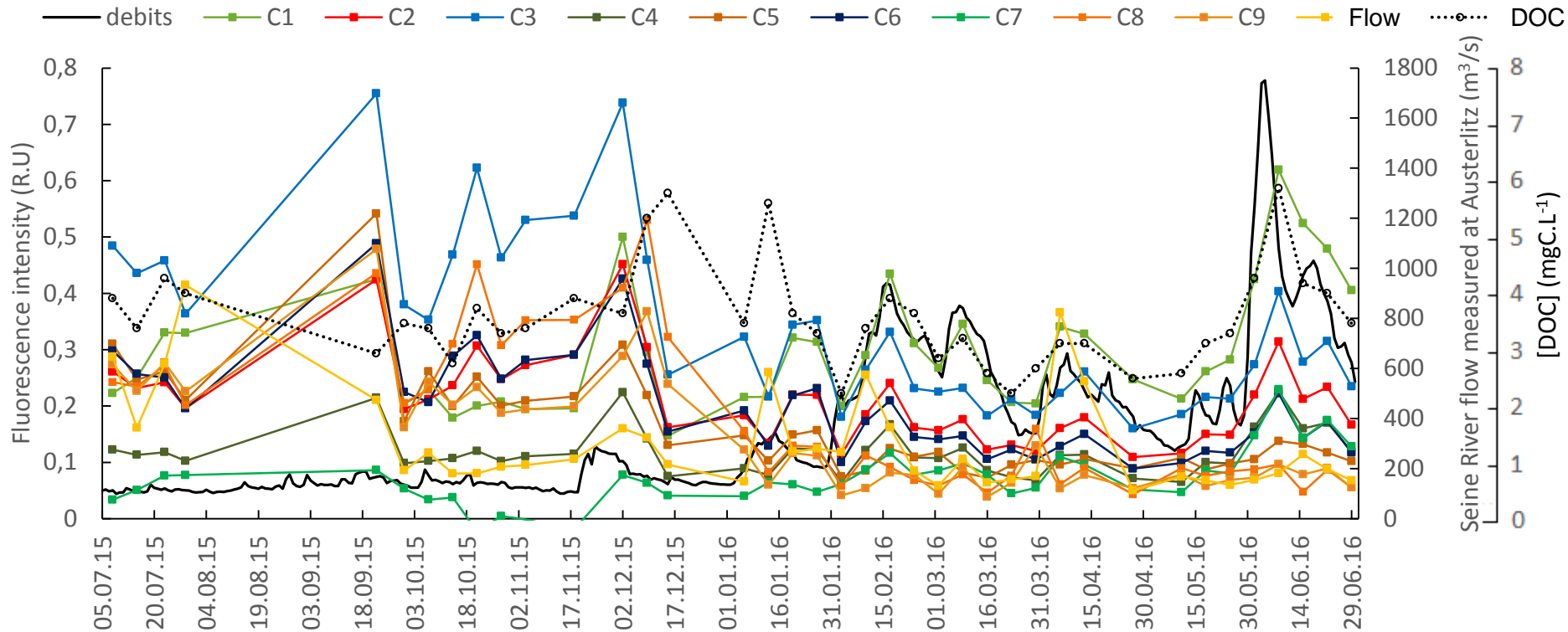
- Acid fulvic-like (C1)
- Biological humic-like substances (C3)
- Protein-like (C5 + C10)

➤ High flow :

- Acid fulvic-like (C1)
- Biological Humic-like substances (C3) + Humic-like substances (C2)

✓ EEM Fluorescence Spectroscopy is able to following change of DOM quality

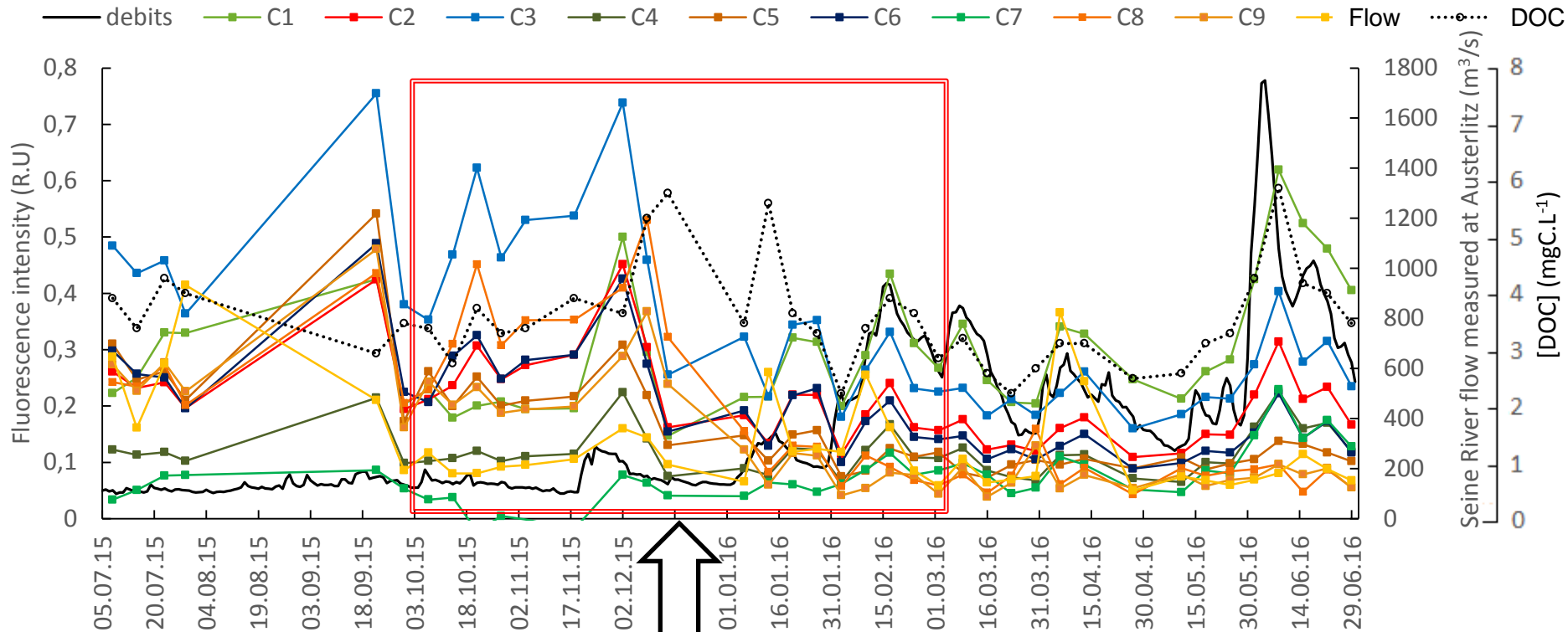
Downstream of Parisian conurbation (Conflans-Sainte-Honorine)



Chronic of fluorescence intensity, DOC concentration and measured flow in the Seine River at Conflans-Sainte-Honorine (Downstream) from July 2015 to June 2016

➤ Variations of fluorescence intensity in the Seine River impacted by flow variation, but....

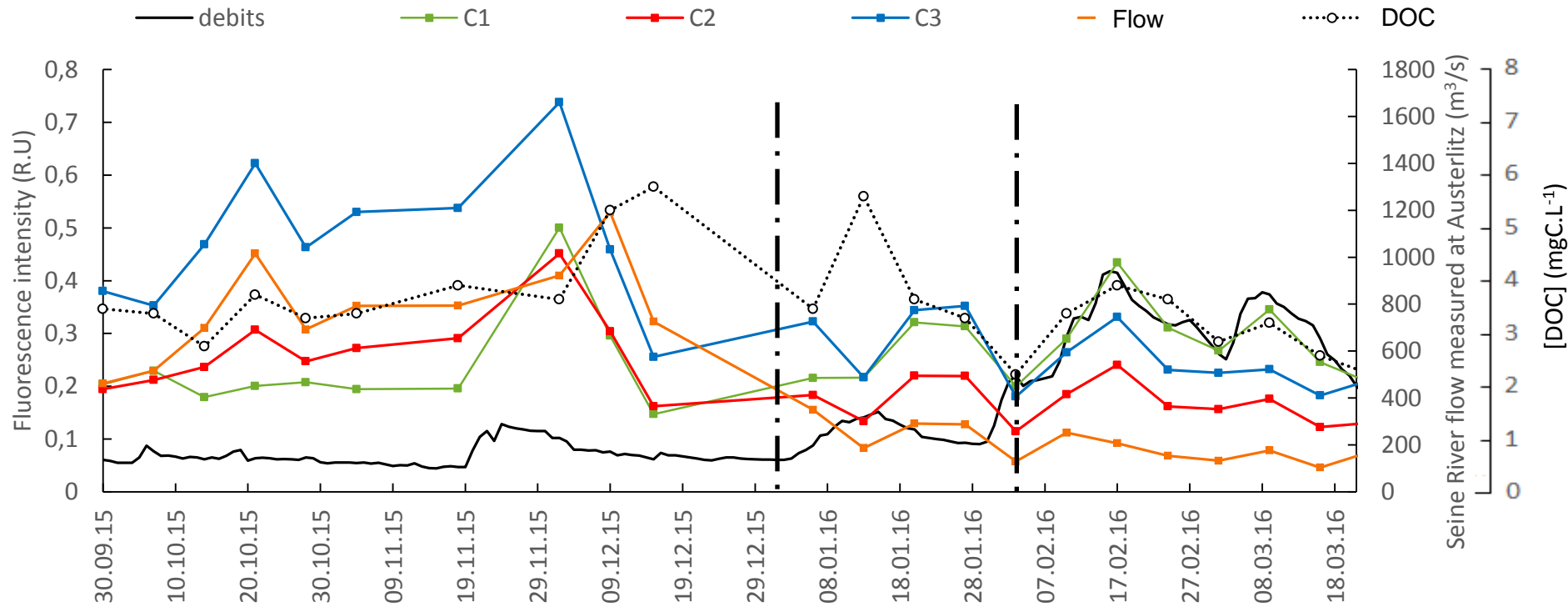
One year of DOM fluorescence monitoring : Downstream of Parisian conurbation (Conflans-Sainte-Honorine)



Chronic of fluorescence intensity, DOC concentration and measured flow in the Seine River at Conflans-Sainte-Honorine (Downstream) from July 2015 to June 2016



One year of DOM fluorescence monitoring : Downstream of Parisian conurbation (Conflans-Sainte-Honorine)



Chronic of fluorescence intensity, DOC concentration and measured flow in the Seine River at Conflans-Sainte-Honorine (Downstream) from September 2015 to March 2016

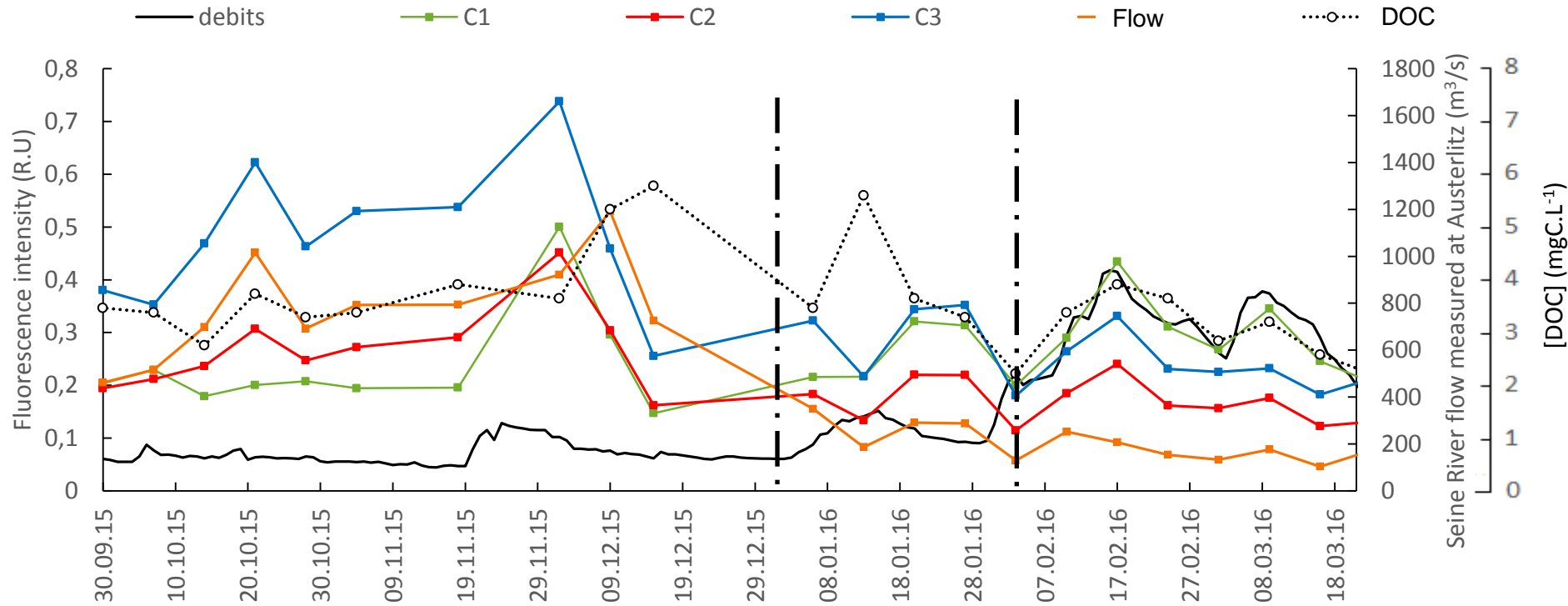
➤ From 07/10/15 to 06/01/16

MOD Biological humic like (C3) + protein-like (C8)

➤ From 06/01/16 to 16/03/16 :

- Acid fulvic-like (C1)
- Biological Humic-like substances (C3)
- + Humic-like substances (C2)

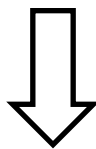
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➤ From 07/10/15 to 06/01/16

MOD Biological humic like (C3) + protein-like (C8)



Maintenance of WWTP = Impact of WWTP effluent

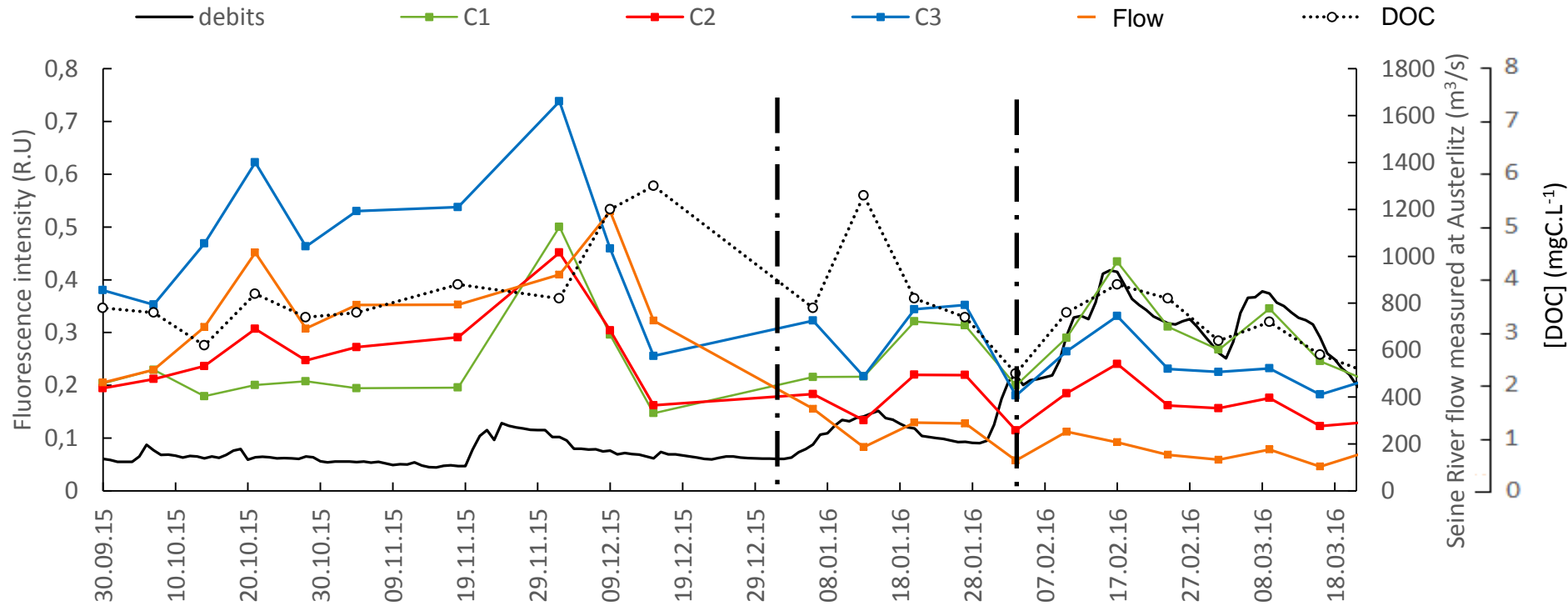
➤ From 06/01/16 to 16/03/16 :

- Acid fulvic-like (C1)
- Biological Humic-like substances (C3)
- + Humic-like substances (C2)



End of WWTP malfunctioning + flow increase

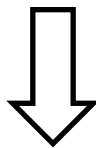
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MOD Biological humic like (C3) + protein-like (C8)



✓ **3D EEM Fluorescence spectroscopy highlight WWTP impact on receiving water**

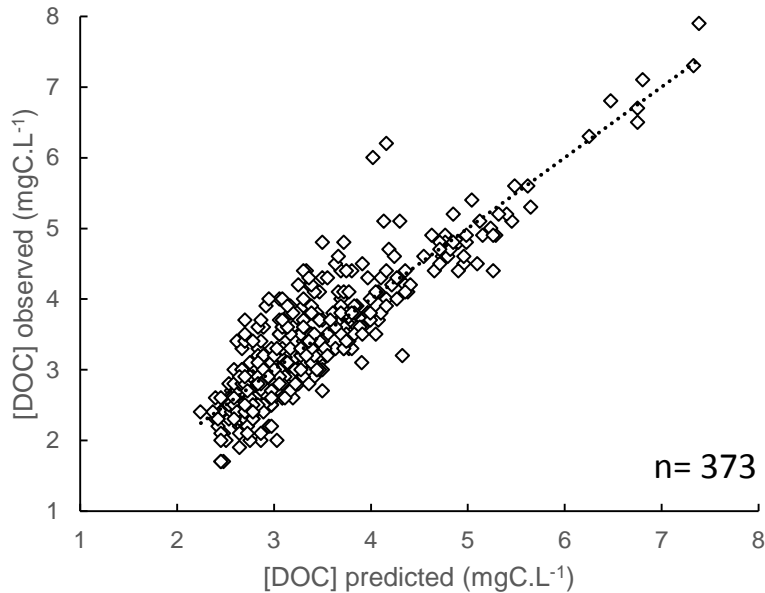
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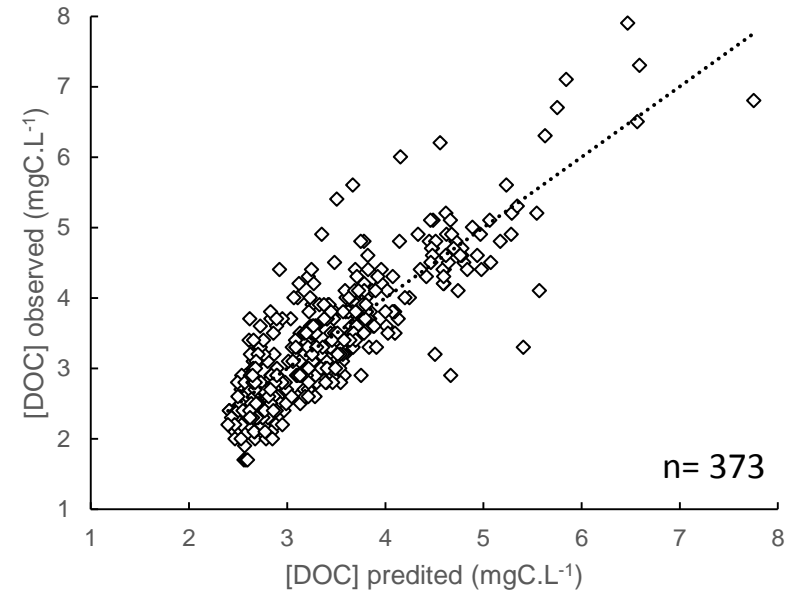
DOC prediction (all sampling sites): Absorbance 254 nm vs Fluorescence

[DOC] (mgC.L⁻¹) predicted by **Abs 254 nm**
 $r^2 = 0,790$ $p < 0,0001$



Correlation between [DOC] predicted with simple linear regression and [DOC] observed values in all sampling sites (Seine-Oise-Marne Rivers)

[DOC] (mgC.L⁻¹) predicted by **C4 (Humic-like fluorescence)**
 $r^2 = 0,718$ $p < 0,0001$

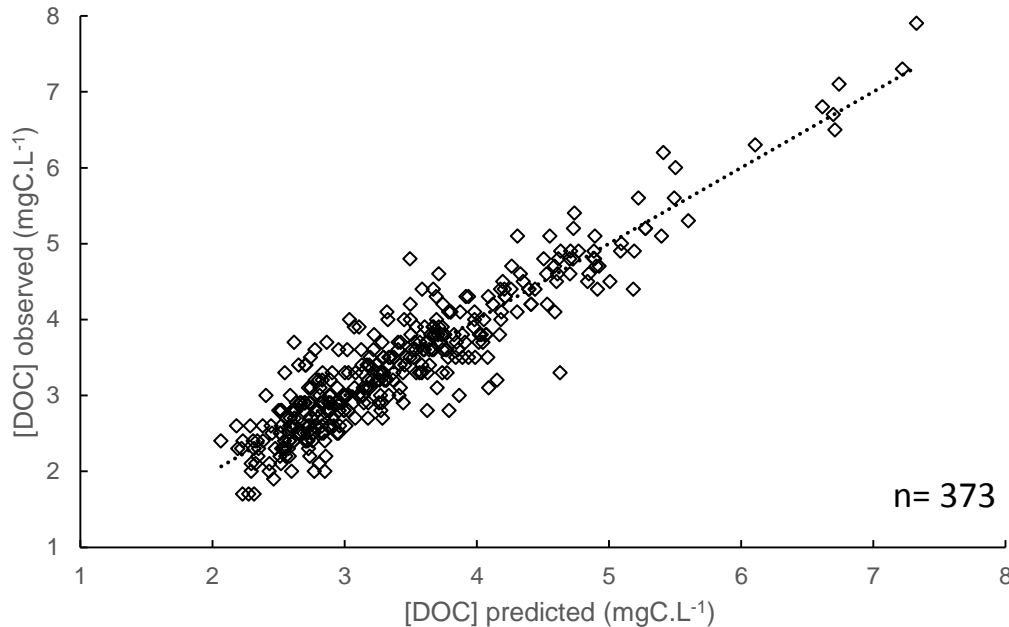


Correlation between [DOC] predicted with simple linear regression and [DOC] observed values in all sampling sites (Seine-Oise-Marne Rivers)

- Good [DOC] prediction with Absorbance 254 nm
- Fluorescence of Humic-like component is also correlated with [DOC]

DOC prediction (all sampling sites)

[DOC] ($\text{mgC}\cdot\text{L}^{-1}$) by fluorescence (C8, C10) and Abs 254 nm
 $r^2=0,860$ $r^2_{\text{ajusted}}=0,858$ $p<0,0001$



Correlation between [DOC] predicted with multiple linear regression and [DOC] observed values in all sampling sites (Seine-Oise-Marne Rivers)

- Amelioration of [DOC] prediction by Abs 254 nm with Protein-like fluorescence (C10 tyrosine + C8 tryptophan)

Conclusions

- Fine approach of DOM fluorescence by EEM-Fluorescence Spectroscopy
=> 10 PARAFAC components
- 3D EEM-Fluorescence Spectroscopy allow to follow spatio-temporal variation of DOM quality/quantity in the Seine River
 - Fluorescence intensity variations from downstream to upstream + Seasonal variations
 - Highlight of protein-like component « effluent WWTP finger-print »
- Better prediction of DOC by EEM-Fluorescence Spectroscopy combined with Uv-visible Spectroscopy at 254 nm.

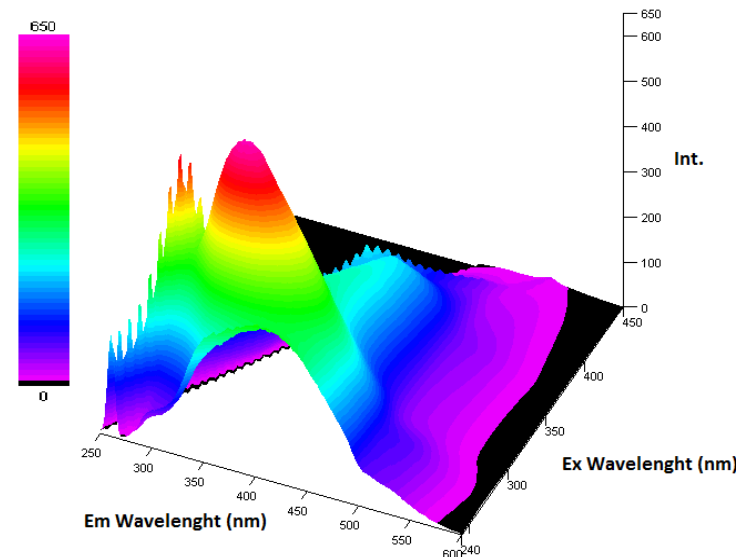
EEM-Fluorescence Spectroscopy = great application potential:
DOM treatability potential (Drinking Water treatments)
Information on receiving water biochemistry

Thanks for your attention

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



Angélique Goffin: goffin.angel@gmail.com



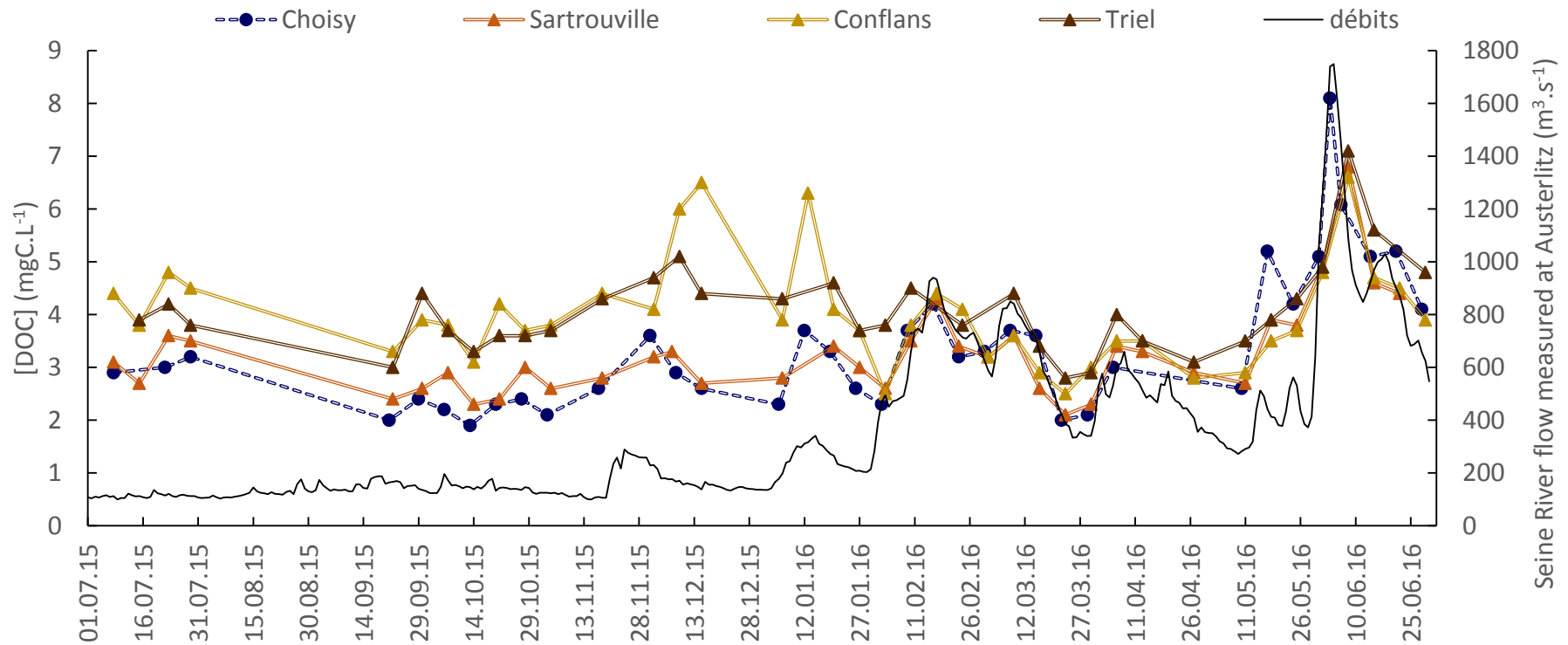
Acknowledgments:

French ministry

Elise Alibert & SIAAP Laboratory.



DOC variation in the Seine River



*Chronicle of DOC concentration and measured flow in the Seine River
For upstream (dotted line) and downstream (full line) of Paris between July 2015 and June 2016*