APPLICATION OF SIZE-EXCLUSION CHROMATOGRAPHY FOR MONITORING OF WASTEWATER EFFLUENT POST-TREATMENT

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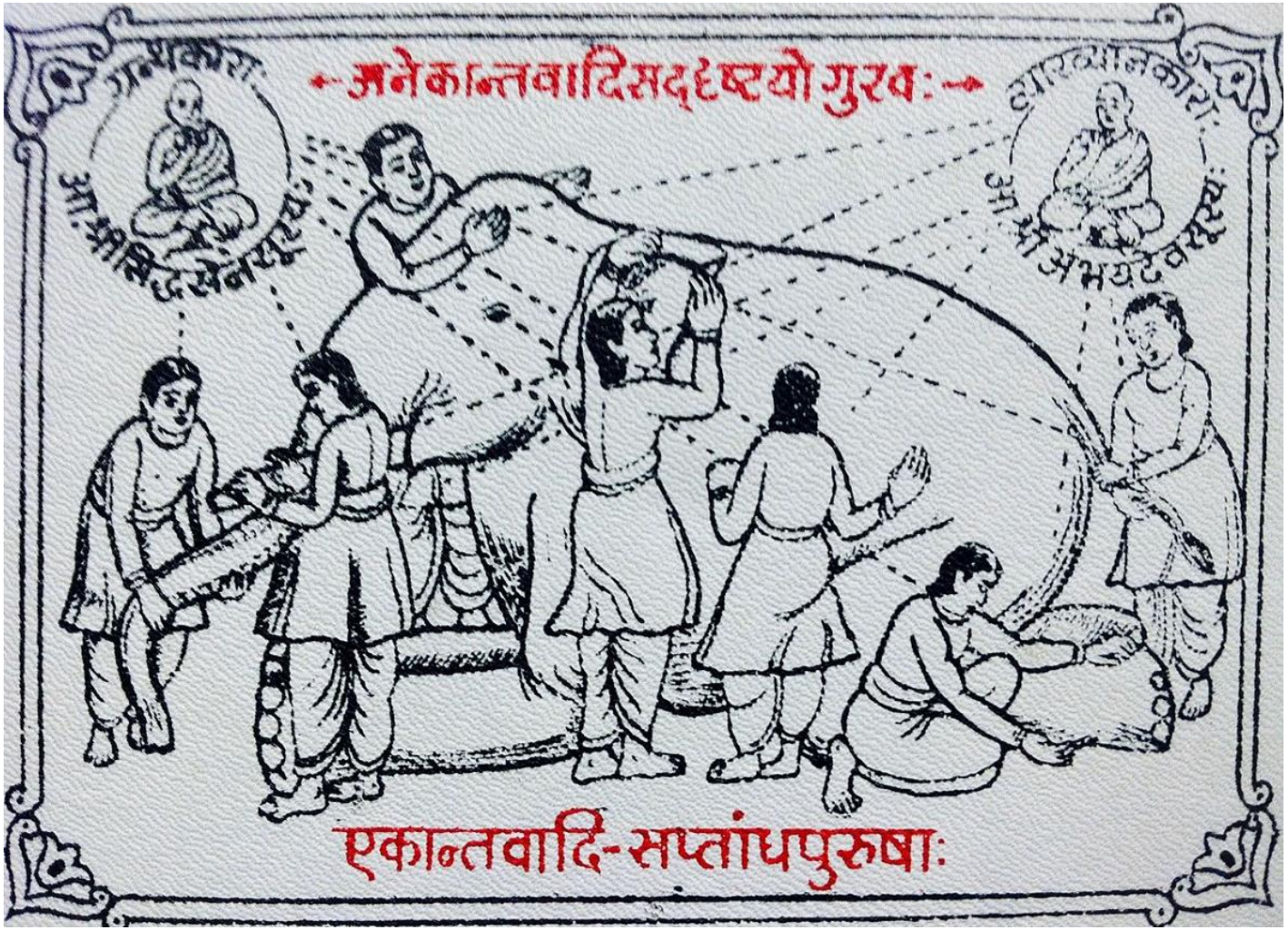
Content

- Measurement and Characterization of Organic Matter
- Materials and Methods
  - Nenäniemi WWTP and HPLC-SEC-UV/fluorescence
- Results
  - WWTP influent and effluent
  - WWTP purification performance
  - Recalcitrant COD
  - Enhancement of removal of organic matter

Background

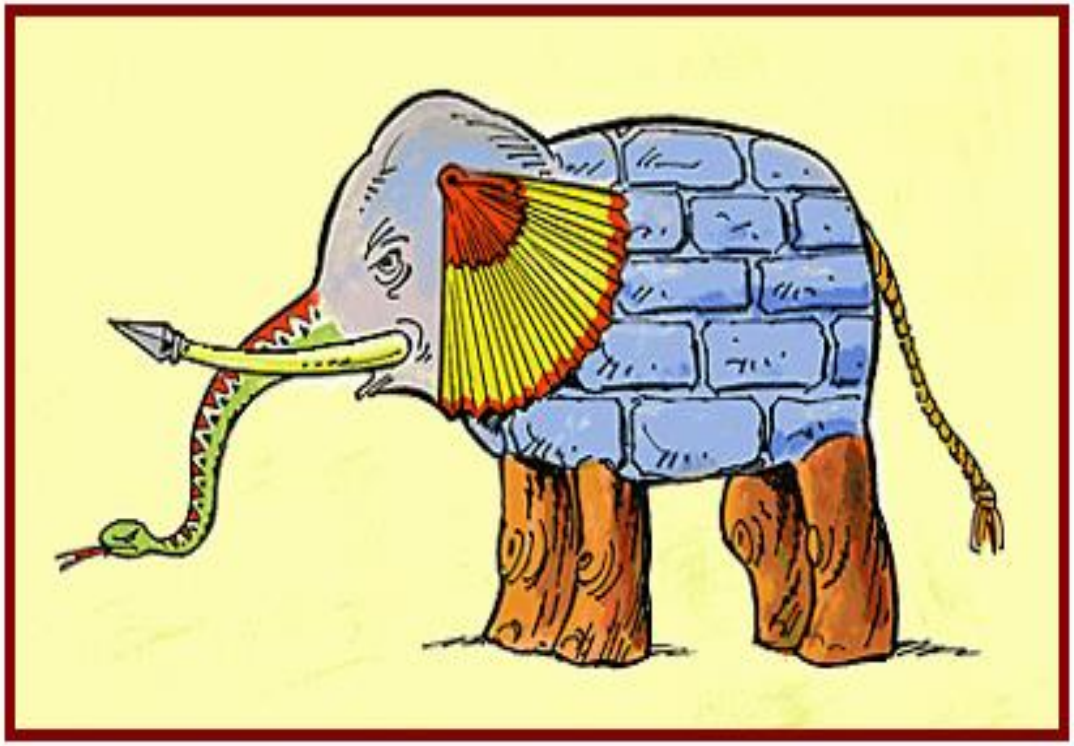
- Biological treatment incompletely removes recalcitrant fractions
- Contamination of recipient water
- Complex nature of influent and effluent
- BOD, COD, DOC, etc. provide limited information
- Advanced analytical tools are needed for optimization and monitoring of WWTP performance

Measurement and characterization of organic matter



https://en.wikipedia.org/wiki/Blind_men_and_an_elephant

Methods

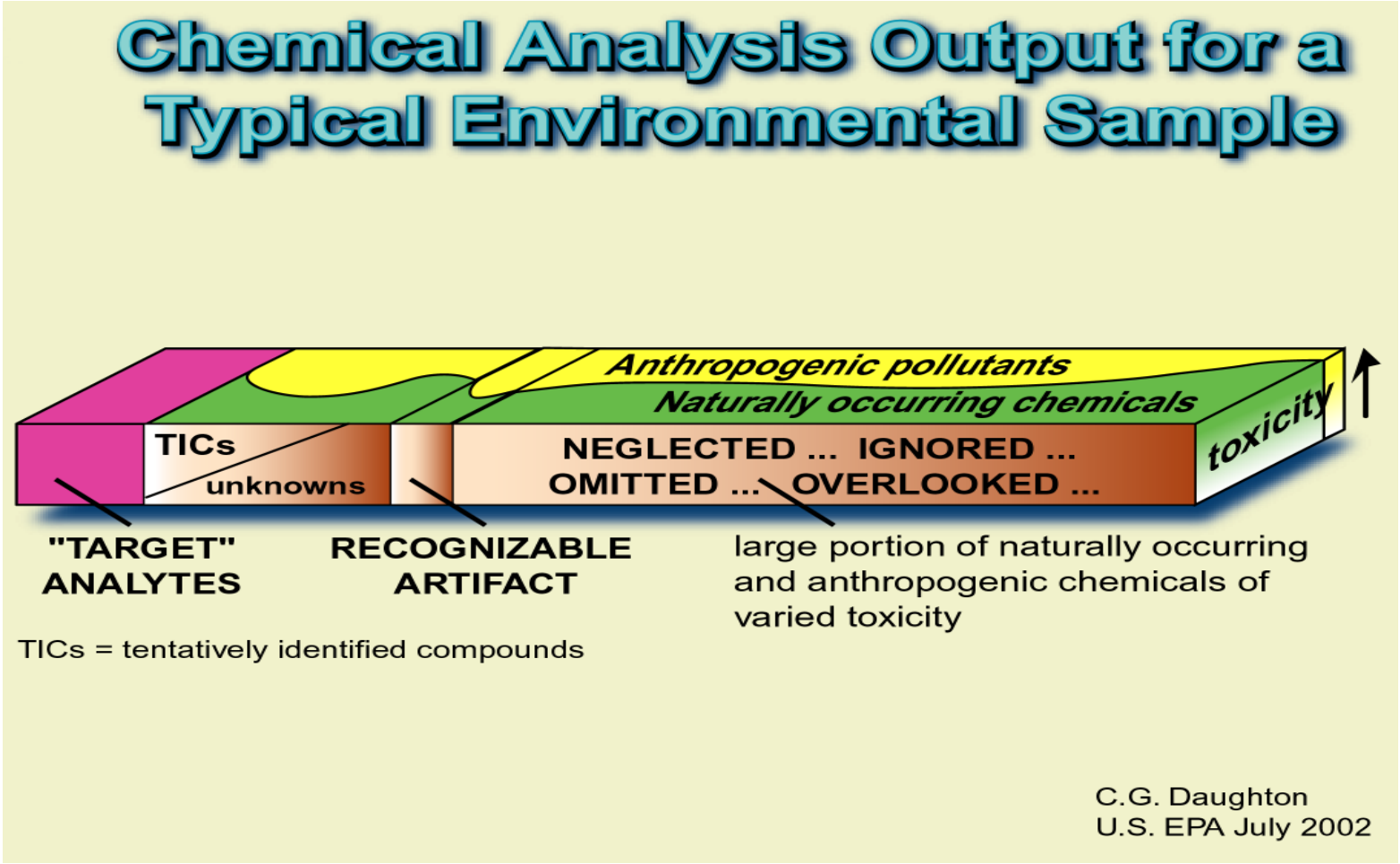


- BOD 5, 7 or 28 days
- COD Mn or Cr
- TOC/DOC
- AOX/POX/EOX
- SUVA
- Total fluorescence
- PARAFAC
- Targeted and non-targeted MS

NEED for operation monitoring, administration, assessment of environmental load

"One man's sample is another man's artefact"

Everyone appears to know what dissolved organic matter (DOM) is (Zsolnay / Geoderma 113 (2003) 187–209)



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HPLC-SEC: a new approach to characterise complex wastewater effluents

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Tampere, Finland; [c]Department of Biological and Environ
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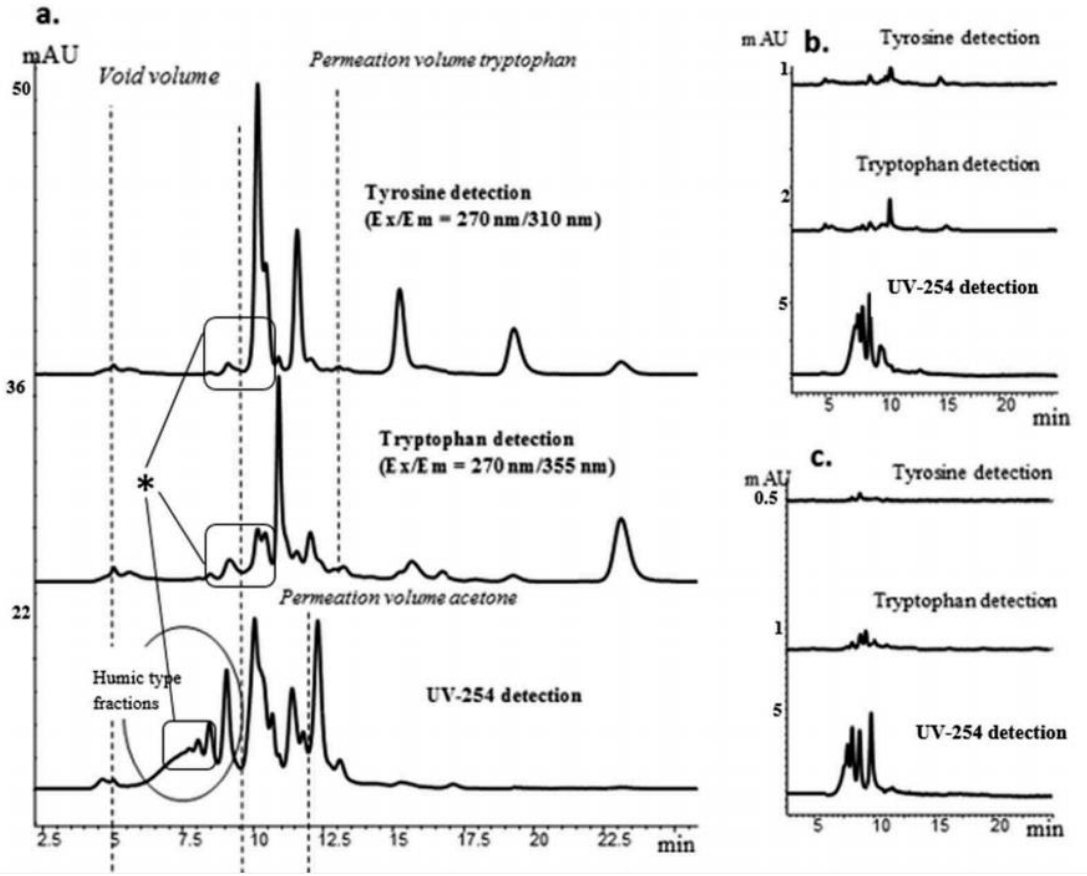
ABSTRACT

This work investigates the use of HPLC-SEC to
solved organic matter (DOM) of complex wastew
silica-based column, sodium acetate eluent and
tions were employed: UV-254 absorbance for
tryptophan-like (Ex/Em = 270/355) and ty
Em = 270/310) fluorescence for protein type cor
of eluent pH, eluent ionic strength and injec
separation efficiency were tested. Humic-type a
fractions were clearly differentiated and eluted w
calibration range. Eluent ionic strength had the g
on global resolution: the lowest eluent concent



dx.doi.org/10.1080/03067319.2016.1150463

Materials and Methods

- HPLC Shimadzu
- Column Phenomex Yarra 3000x
- Mobile phase: phosphate buffer

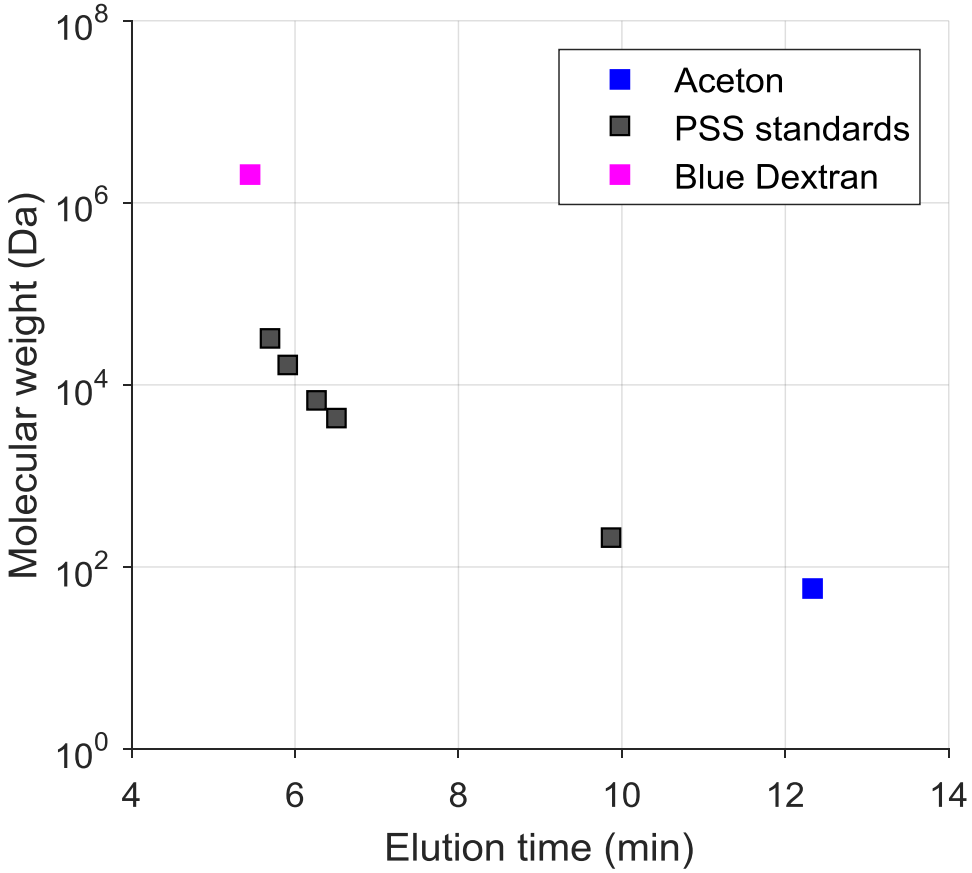
- UV detector (254 nm)

- Fluorescence detector
  - –Tyrosine (270/310 nm)
  - –Tryptophan (270/355 nm)
  - –Fulvic (330/425 nm)
  - –Humic (390/500 nm)

Wu et. Al (2003): 3687-3693

Her e. al Wat Research (2003): 4295-4303.

SEC calibration and MW estimation



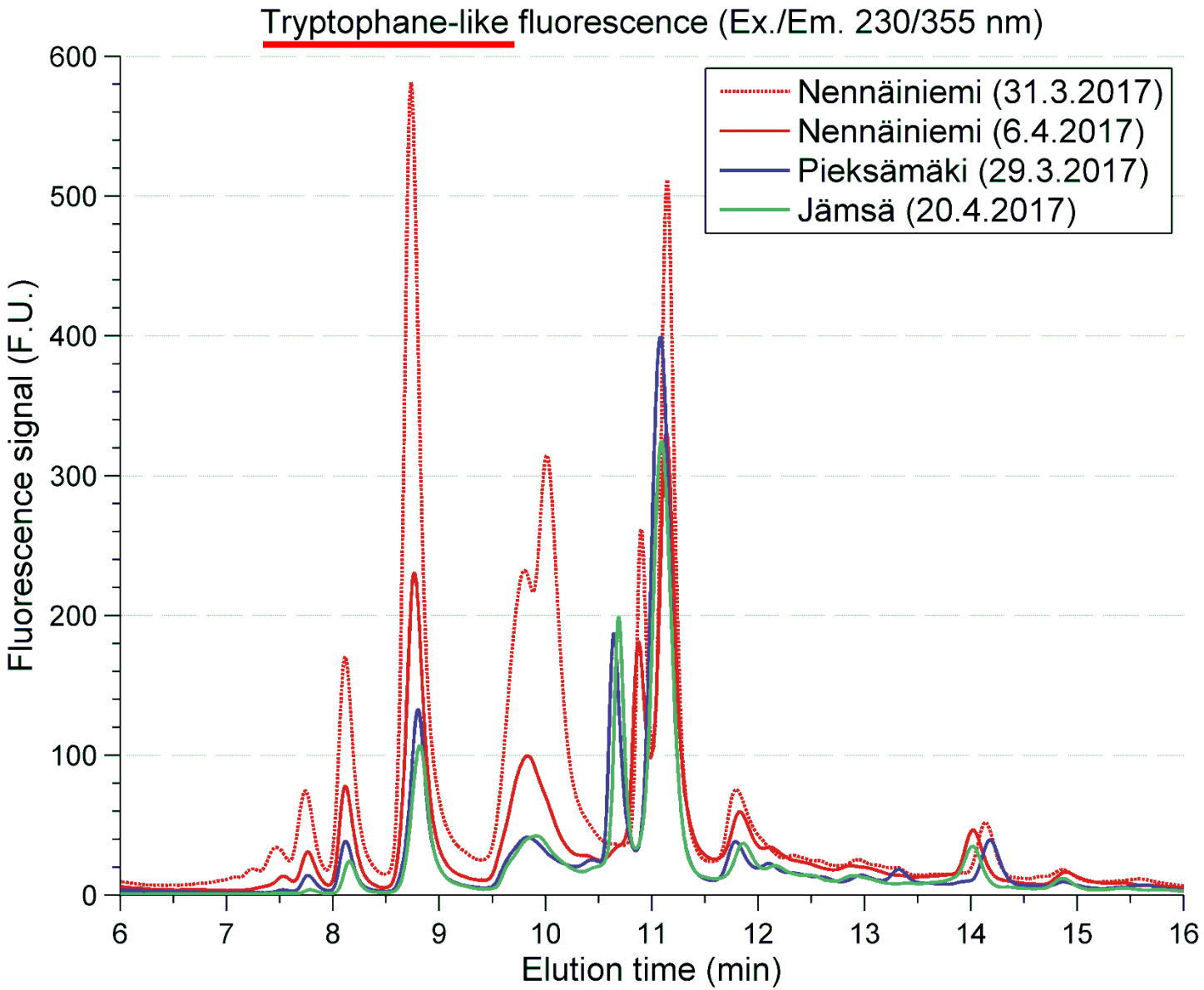
Fraction	Apparent MW (Da)
I	15 000 - 200 000
II	3 000 – 15 000
III	1 500 – 3 000
IV	900 – 1 500
V	400 - 900
VI	200 - 400
VII	58 - 200

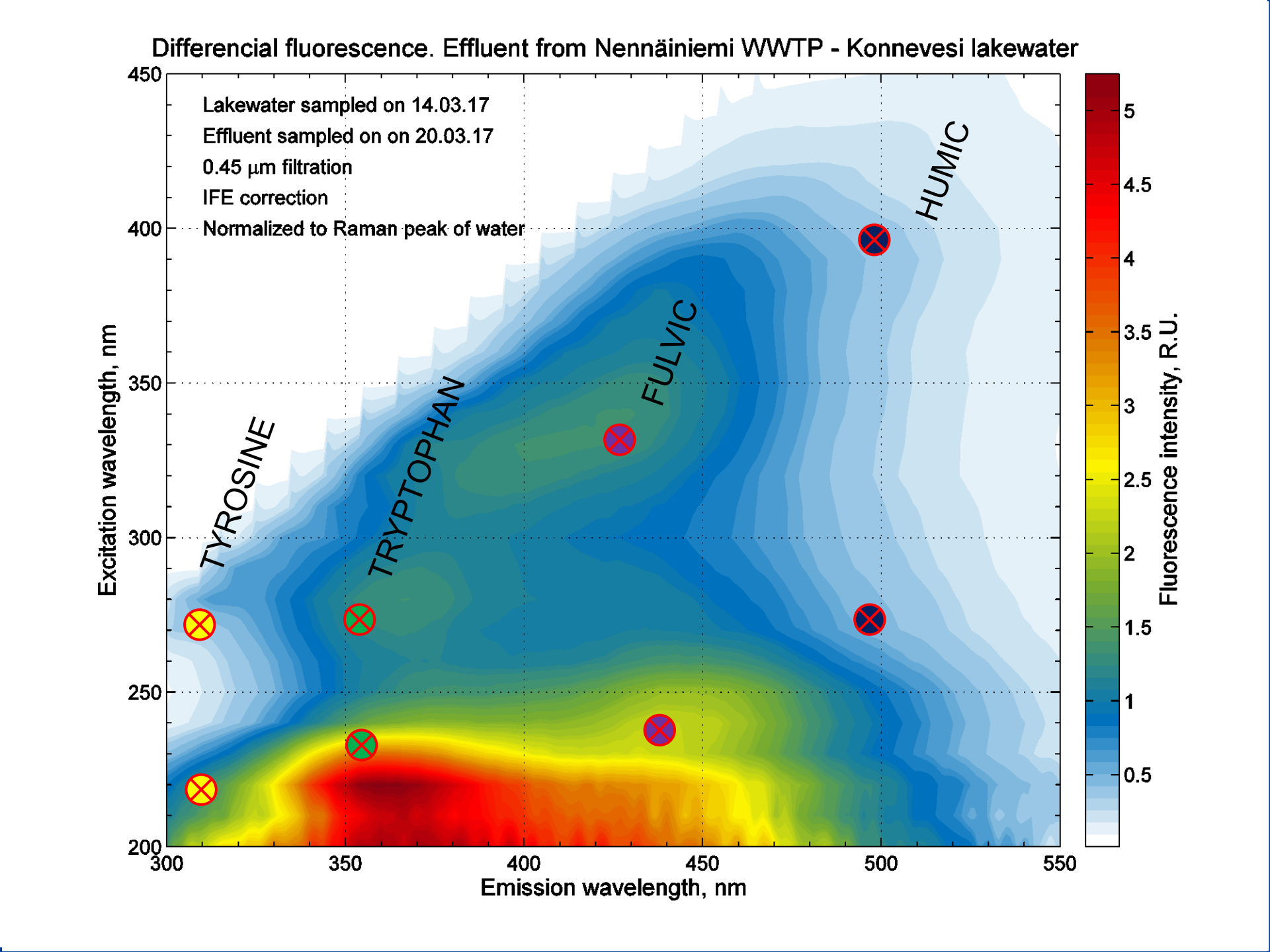
Nenäinniemi WWTP in Jyväskylä

- Screening
- Sand removal
- Primary clarifier
- Activated sludge basins
- Secondary clarifier
- (2018 nitrification + post treatment with ceramic filtration + UV treatment)

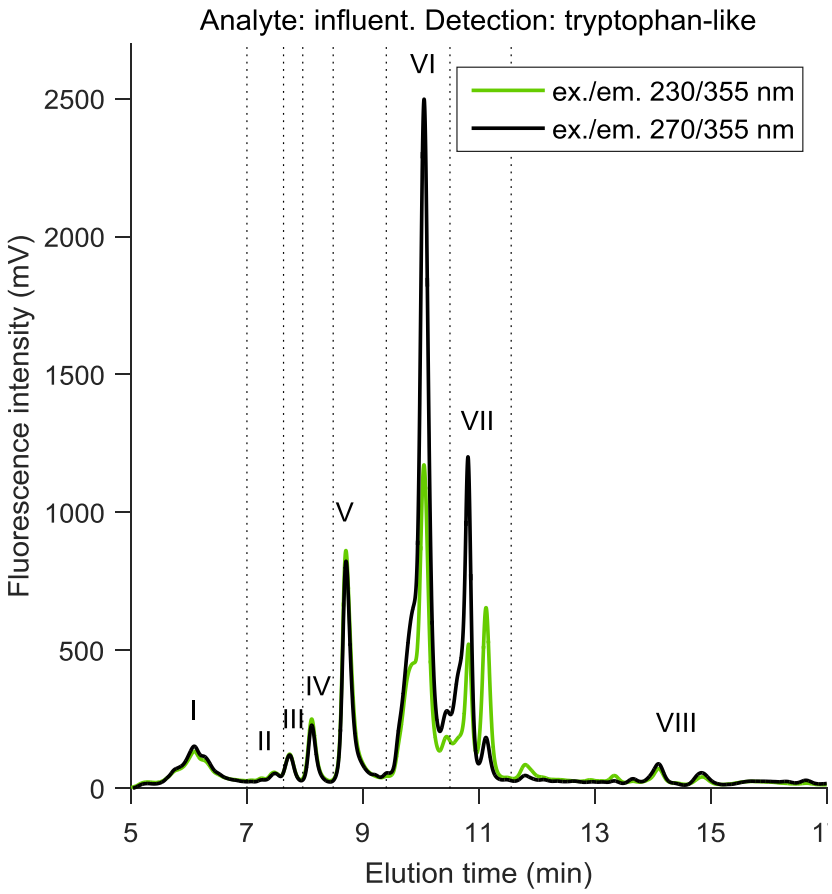
- 38 000 m^3/d, 188 000 inhabitants
- Purification efficiencies
  - BOD 96 → 95 % (85 %)
  - COC(Cr) 93 → 91 % (75 %)
  - P 95 → 92 % (60 %)

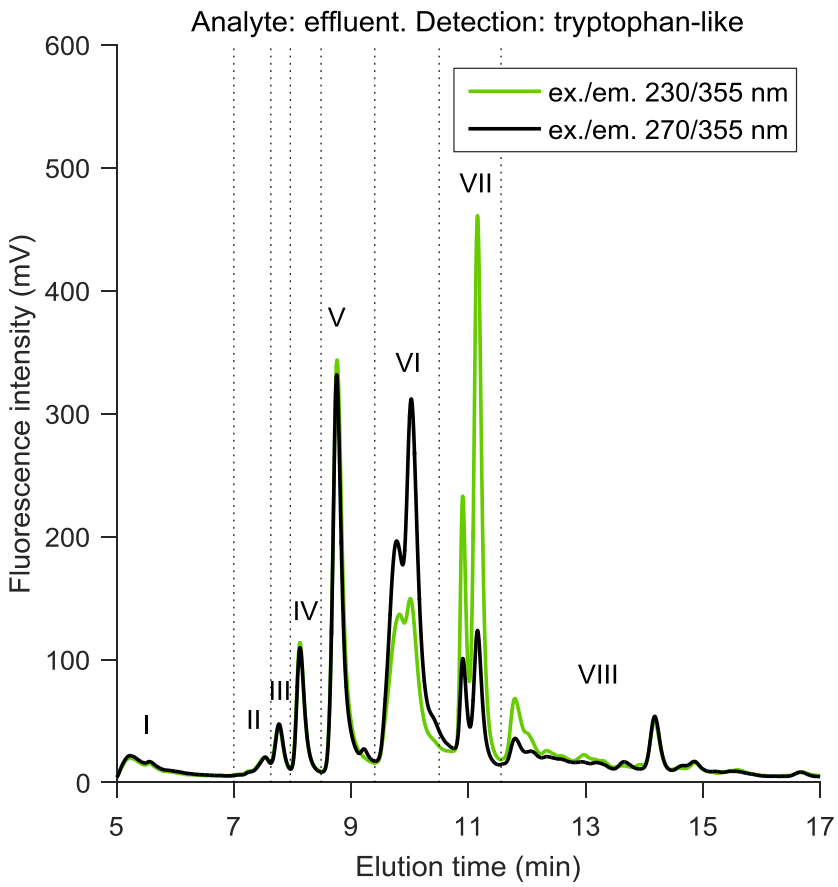
Comparison of different effluents of WWTPs



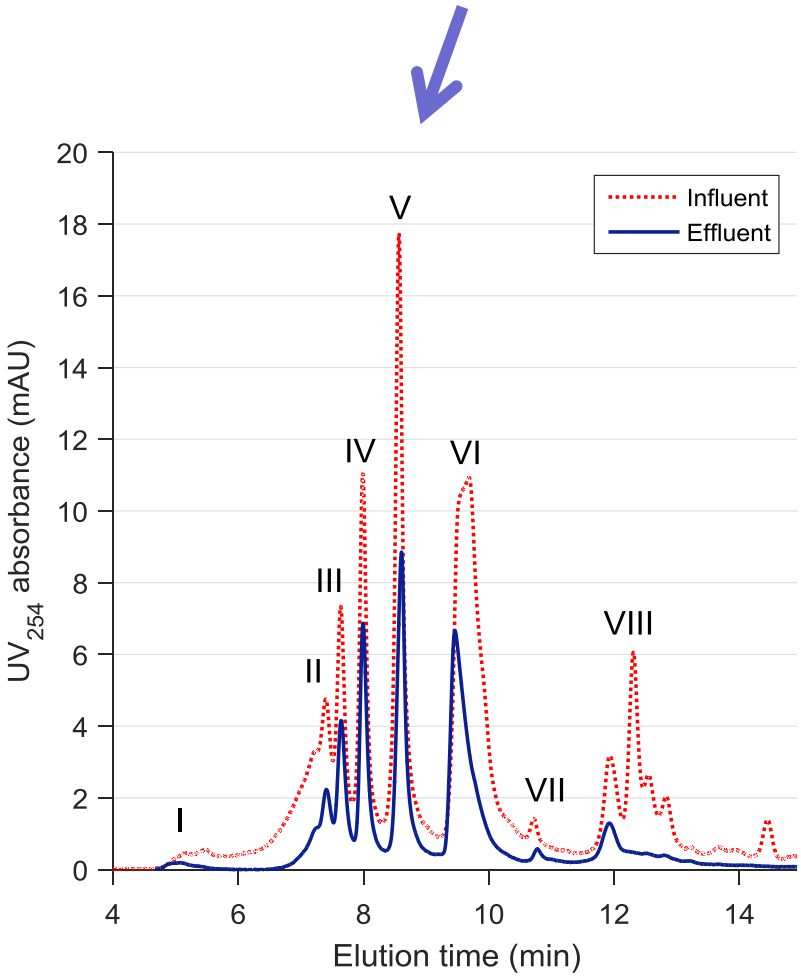

Differencial fluorescence. Effluent from Nennäiniemi WWTP - Konnevesi lakewater
Lakewater sampled on 14.03.17
Effluent sampled on on 20.03.17
0.45 μm filtration
IFE correction
Normalized to Raman peak of water
TYROSINE
TRYPTOPHAN
FULVIC
HUMIC
Excitation wavelength, nm
Emission wavelength, nm
Fluorescence intensity, R.U.
450
400
350
300
250
200
300
350
400
450
500
550
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5

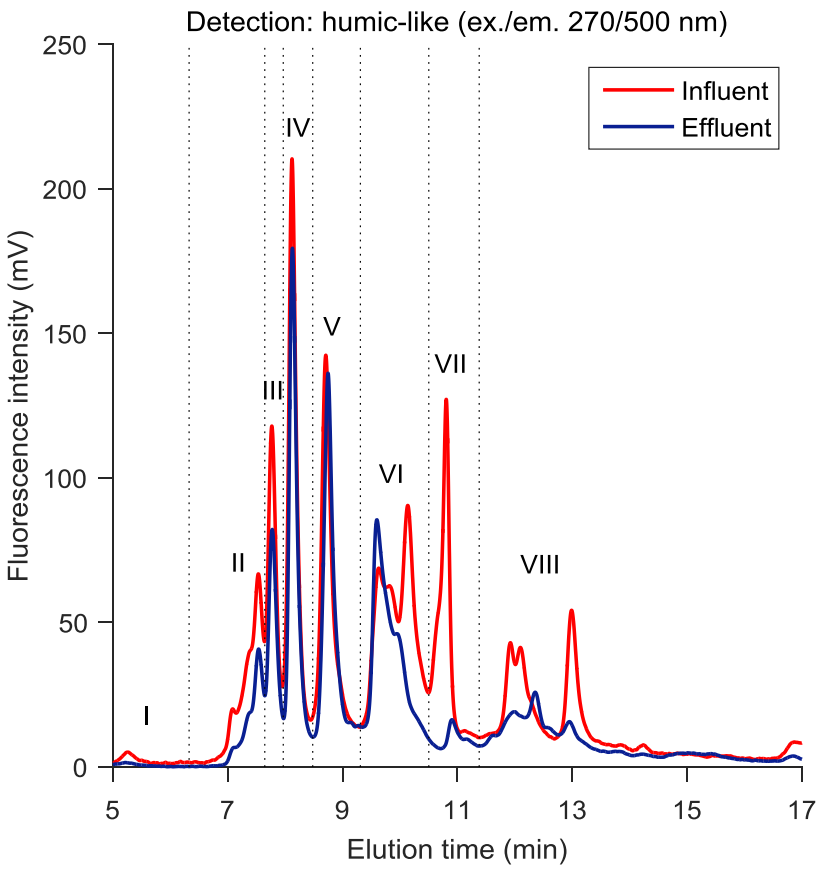
Examples of SEC chromatograms
Influent and effluent





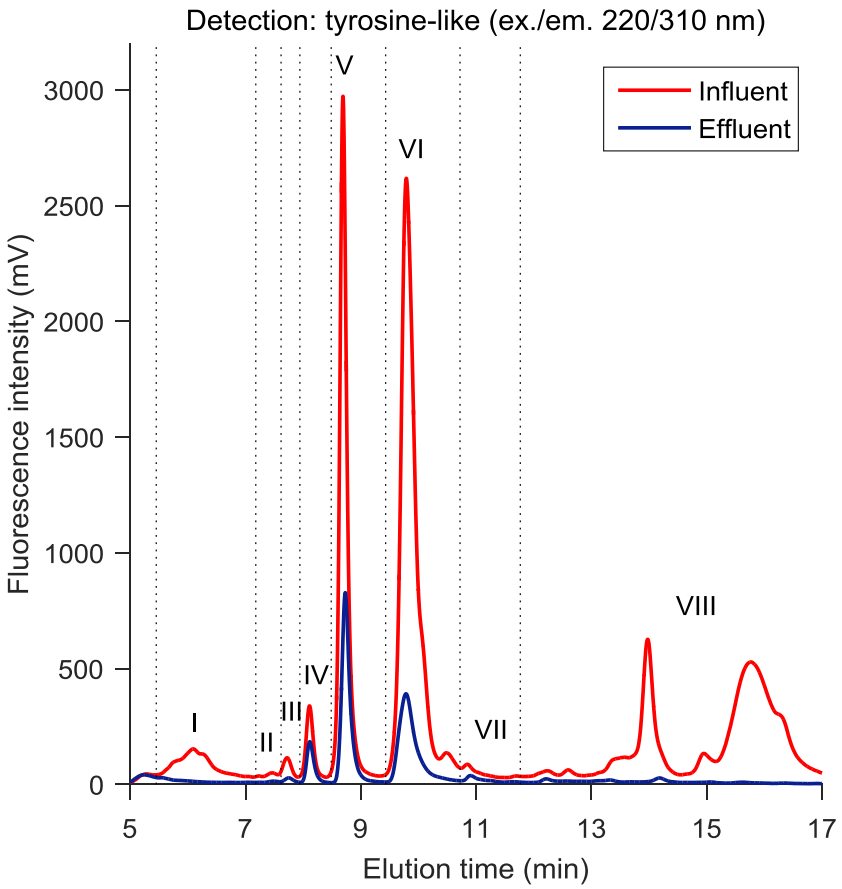
Removal of UVA_{254} and humic-like fluorescence

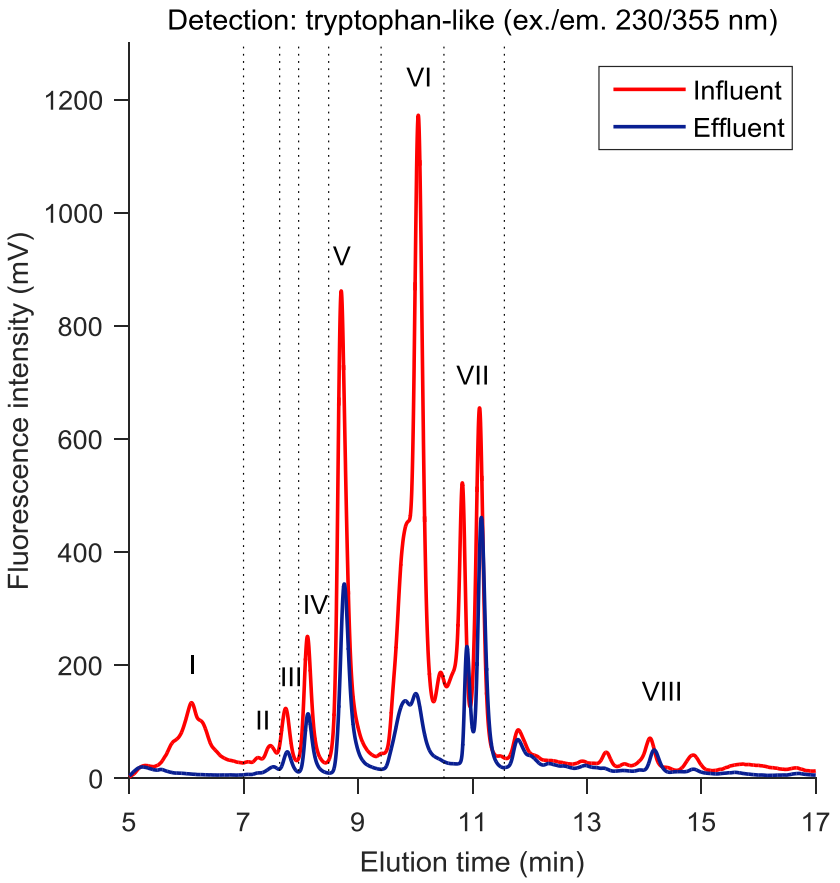




BOD_7 removal 94 %
COD_{Cr} removal 88 %

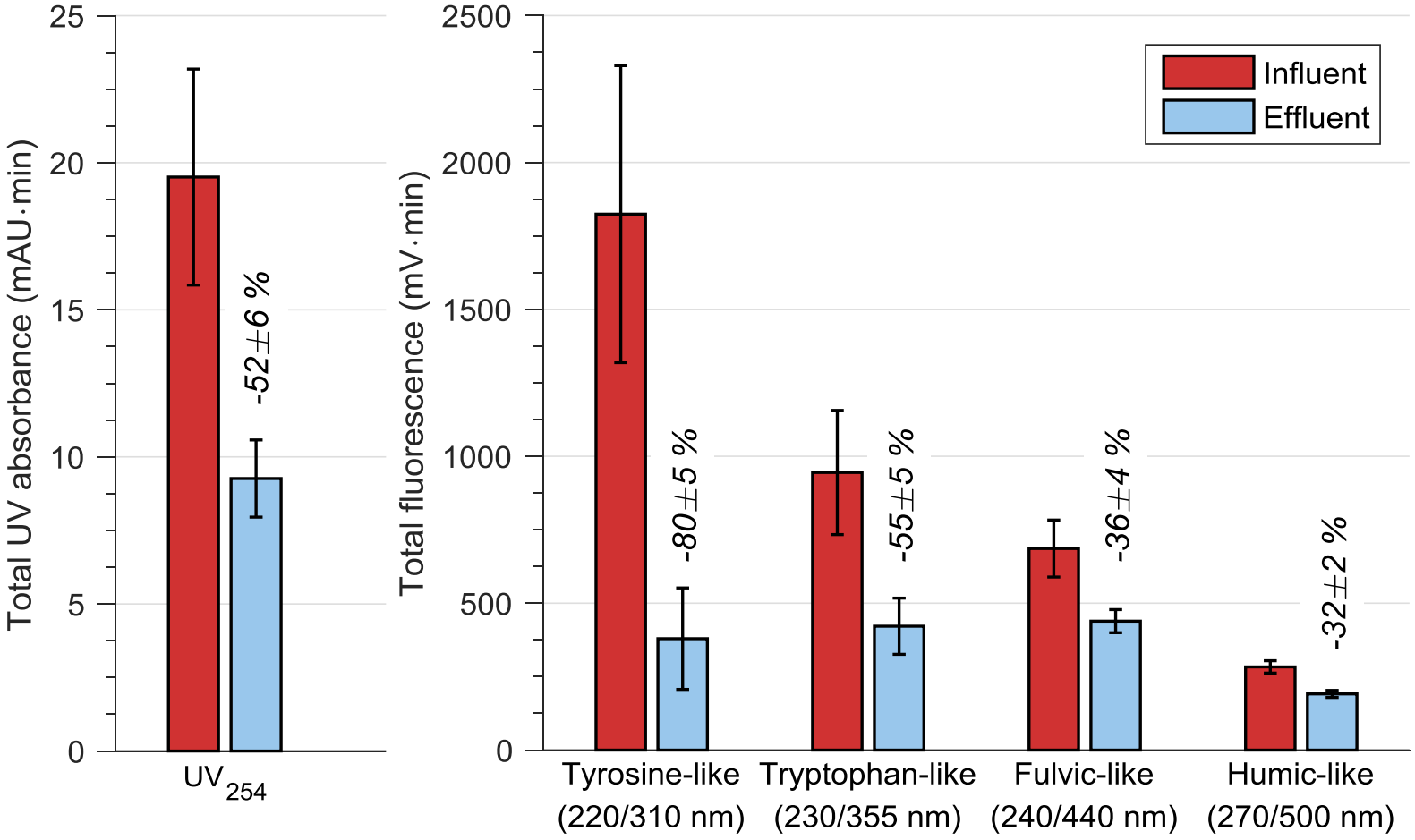
Removal of tyrosine- and tryptophan-like fluorescence



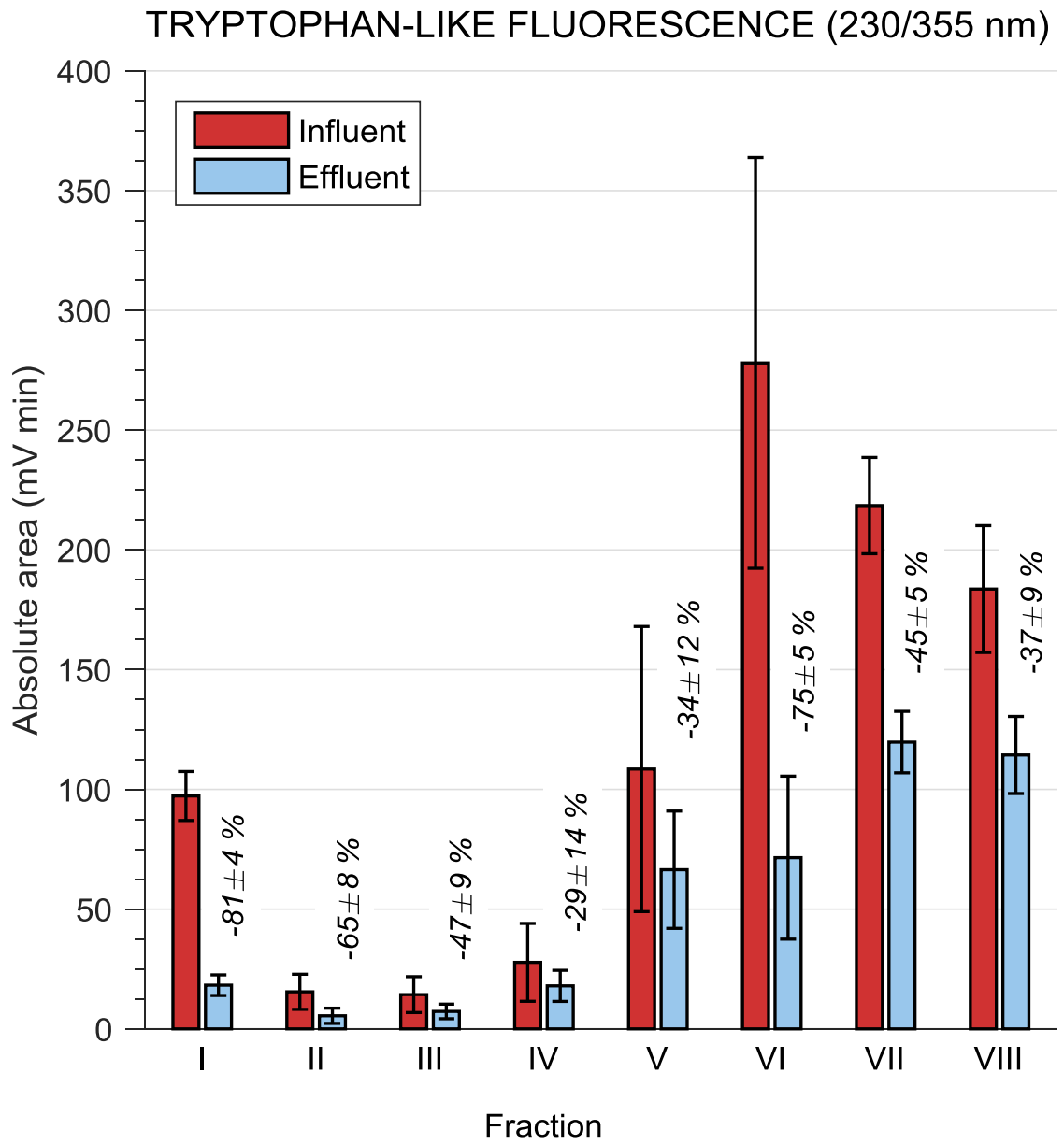


BOD_7 removal 94 %
COD_{Cr} removal 88 %

Removal of total UVA_{254} and total fluorescence

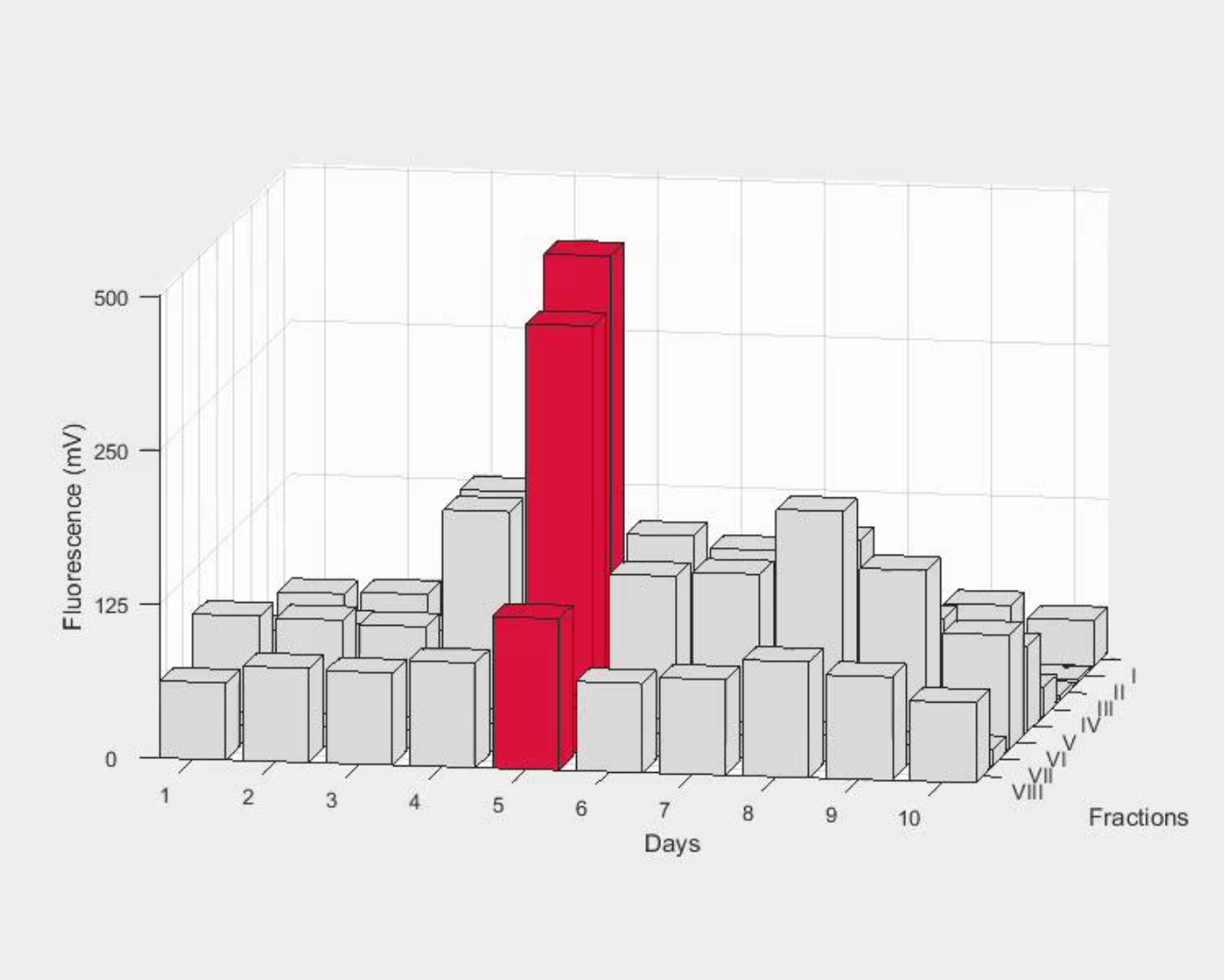


Removal of tryptophan-like fluorescence per fraction

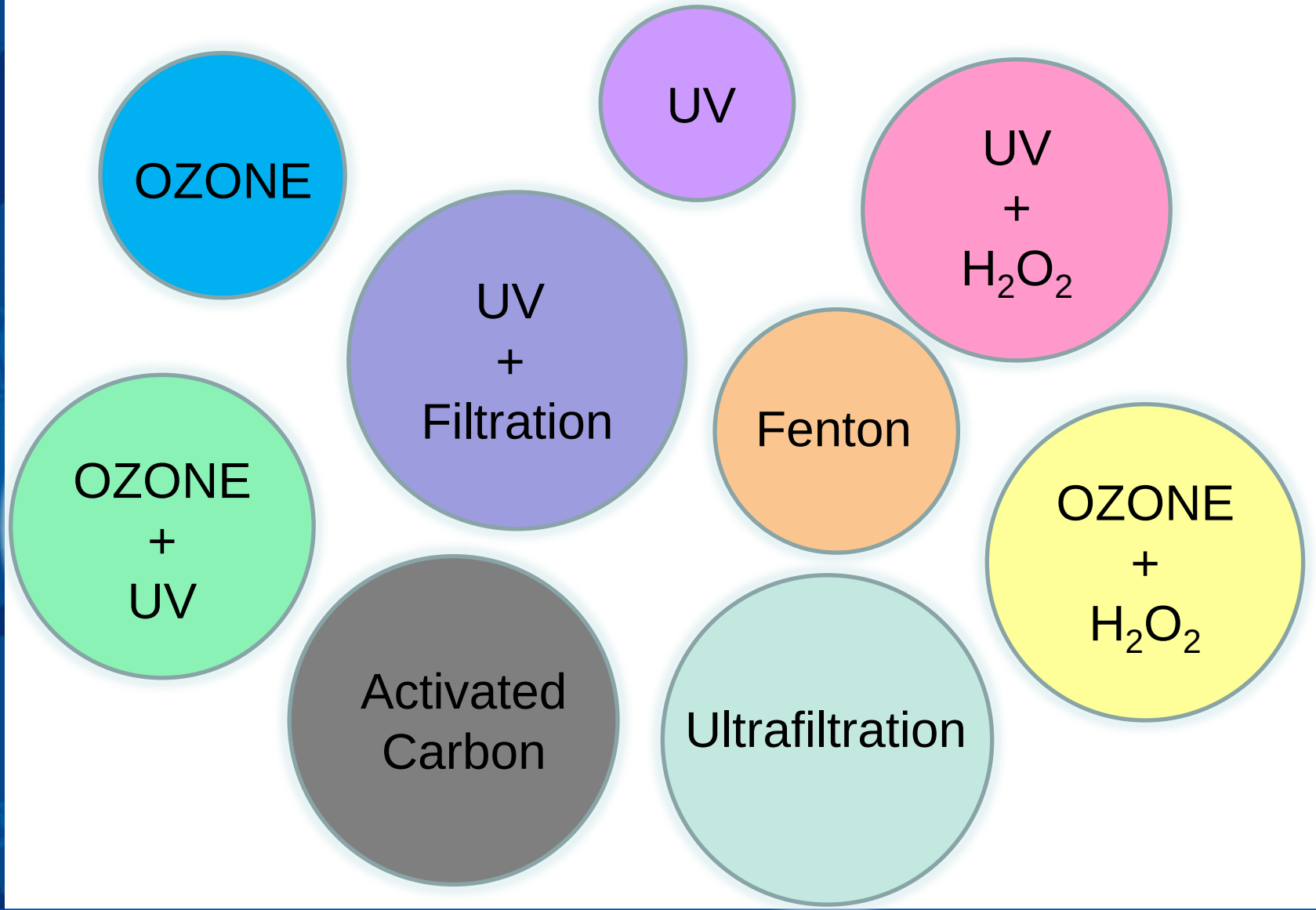


WWTP operation failure

Tryptophan-like fluorescence (10 days monitoring)



Post-treatment of municipal effluent



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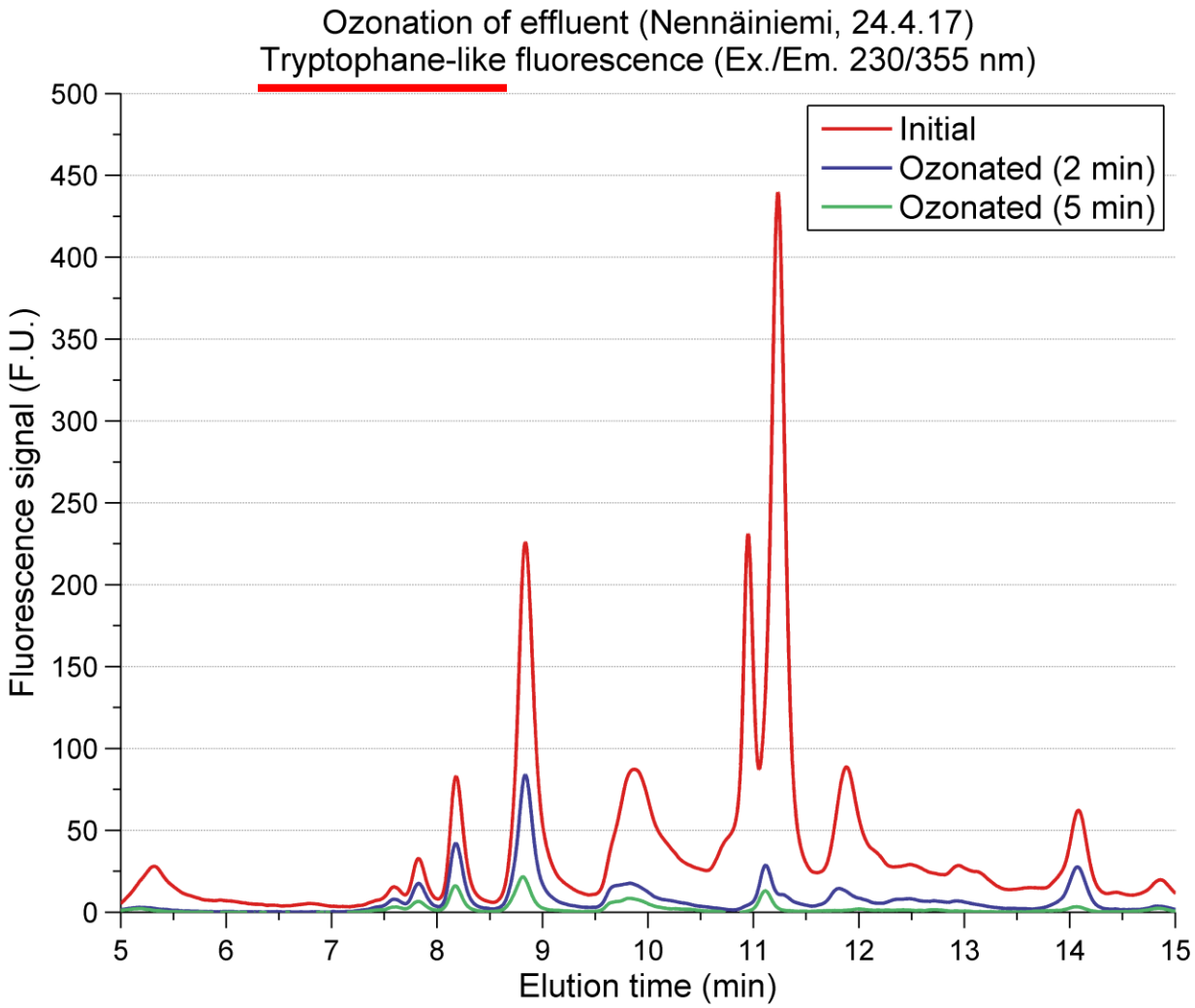
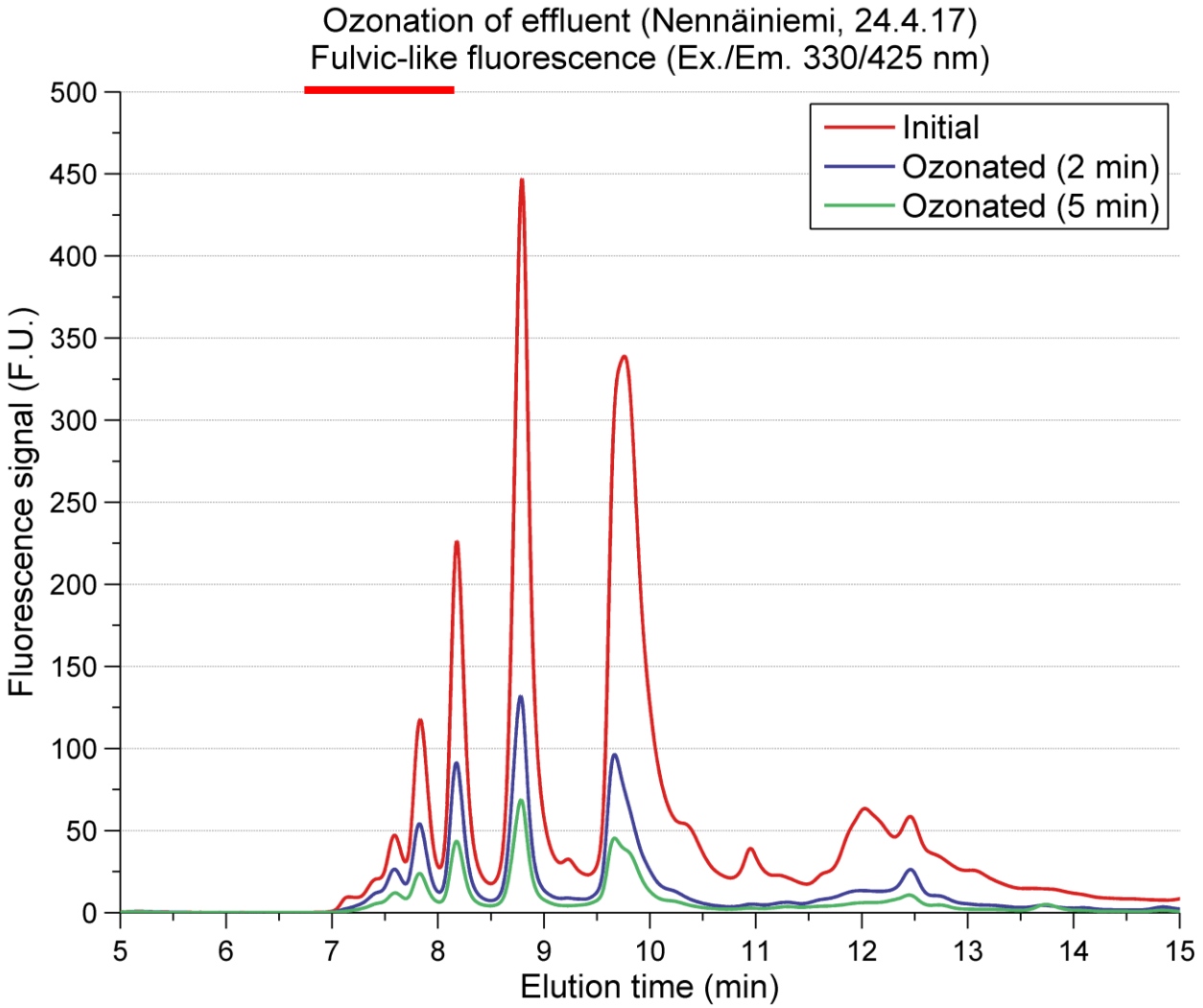


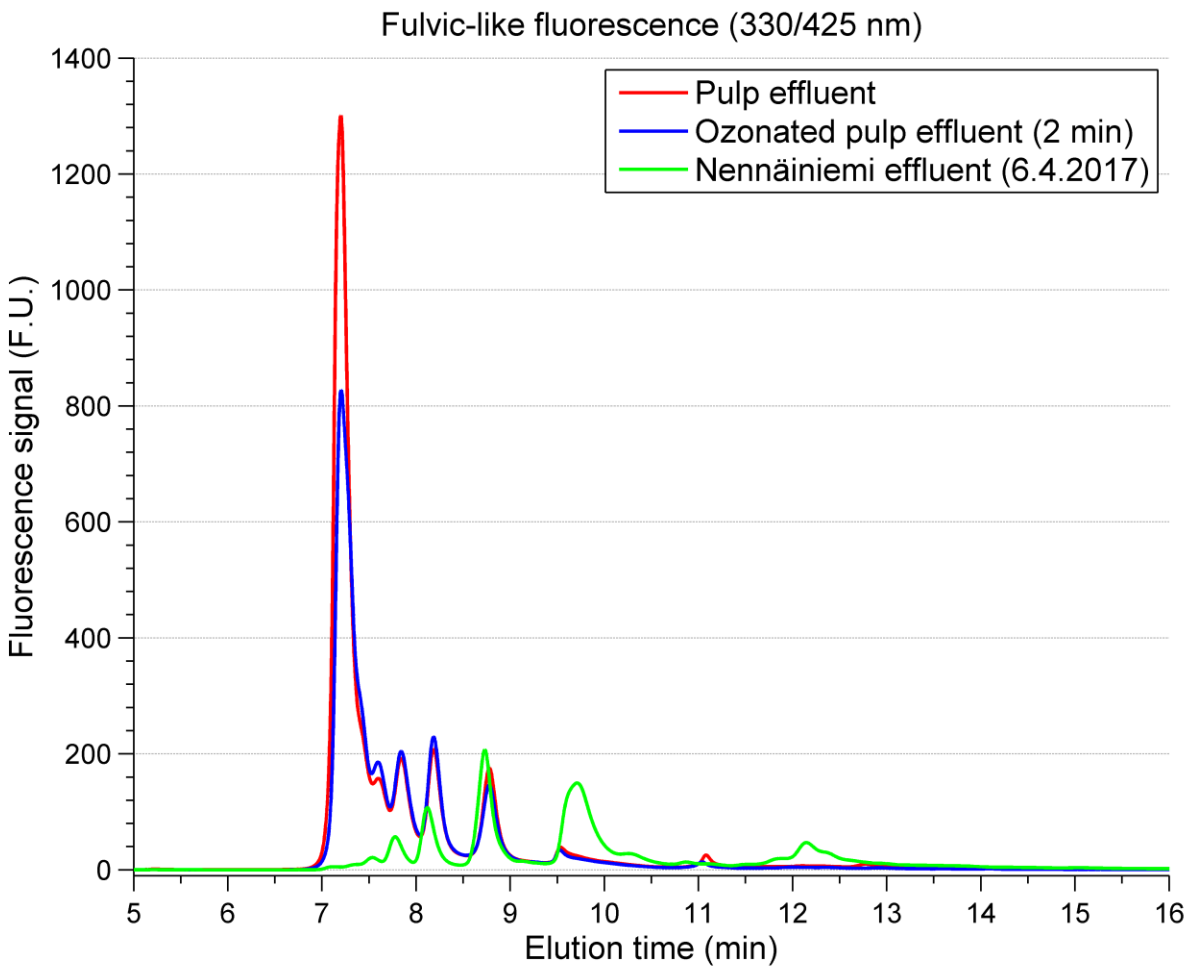
-80 % after 2 min

Post-treatment of municipal effluent



-70 % after 2 min

Post-treatment of industrial effluent (paper and pulp)



Conclusions

- HPSEC+UV+Fluorescence - very powerful combination
- Info of apparent molecular size of OM
- Multiple detectors and wavelengths simultaneously
- No inner filtering
- Minimal sample preparation
- Small sample volume (several mL)
- Fast (30 min/measurement)

Applications and further research

- Detailed characterization of organic matter from different sources
  - Municipal influents and effluents
  - Industrial wastewater
  - Landfill leachates
  - Origin of groundwater contamination
- Monitoring of treatment and post-treatment efficiency
- Source tracking (anaerobic digestion, etc.)
- Tracing of EfOM in natural waters
- A method to replace COD Cr / SUVA


Thank you!
Kiitoksia!
Tack!
Vielen Dank!
Спасибо!
Merci!