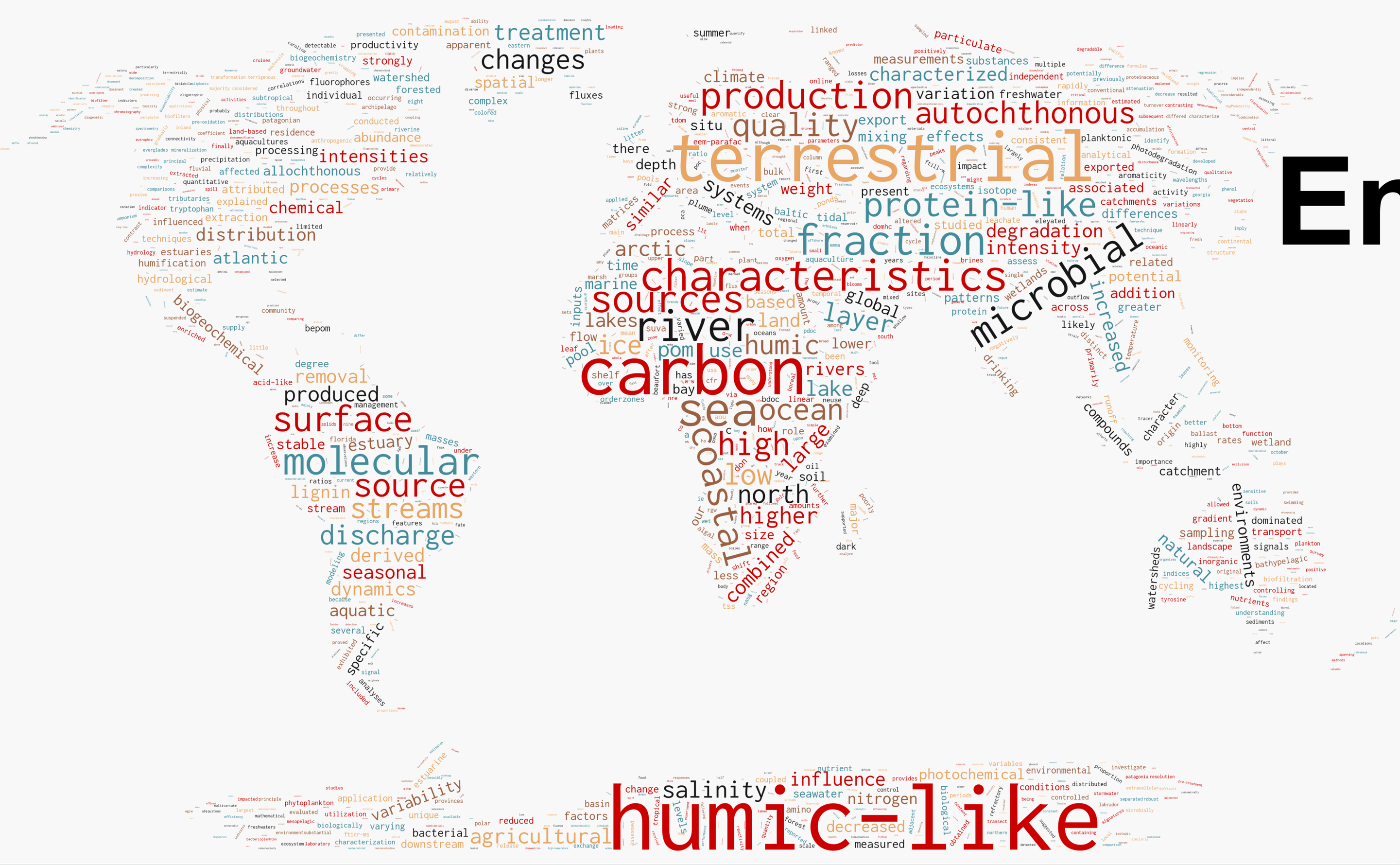
CHALMERS
UNIVERSITY OF TECHNOLOGY

Danmarks Tekniske Universitet
DTU

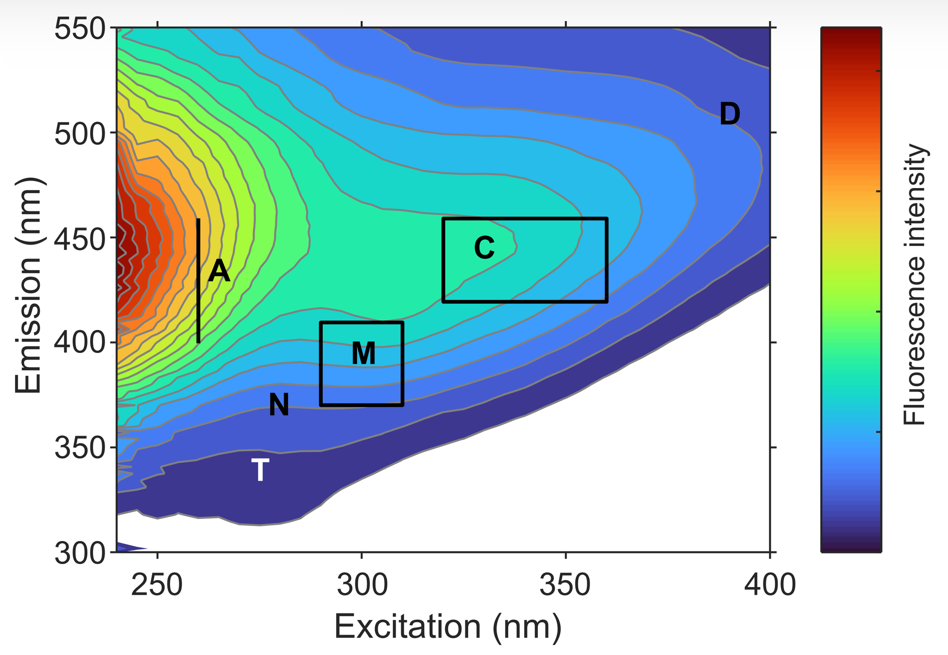


Emerging patterns in the global distribution of fluorescent dissolved organic matter

Urban J. Wünsch[1,2] Kathleen R. Murphy[2]

[1] Technical University of Denmark, Kgs. Lyngby, Denmark
[2]Chalmers University of Technology, Sweden

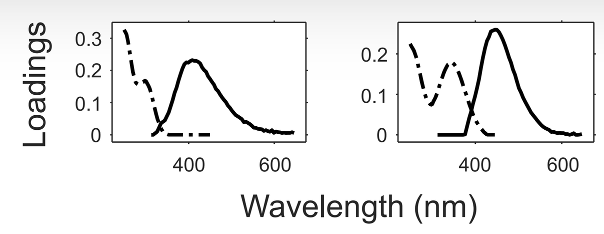
Background



Excitation-emission landscape of natural dissolved organic matter. Predefined peaks are superimposed for reference.

$$x_{ijk} = \sum a_{if} b_{jf} c_{kf} + e_{ijk}$$

Parallel factor analysis (PARAFAC)



Examples of PARAFAC component spectra. When multiplied with scores and summed across components, excitation loadings (dashed lines) and emission loadings (solid lines) yield the model representation of the raw fluorescnece EEM (left).

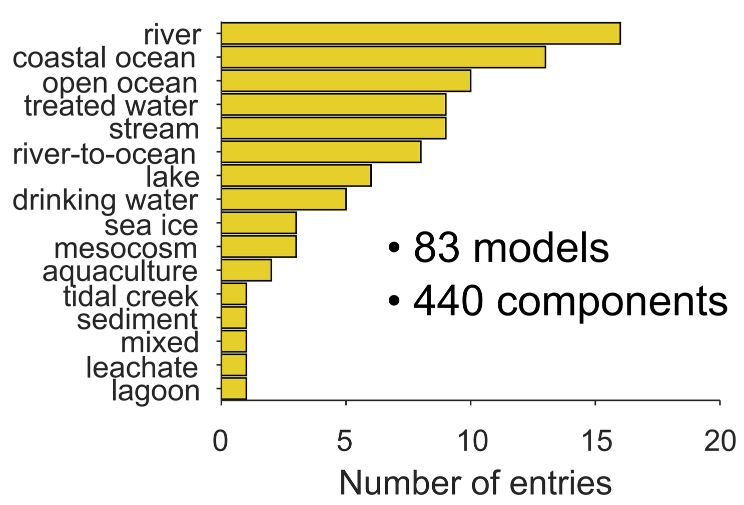
- Fluorescence is a non-destructive, semi-quantitative proxy for DOM quality in various applications
- Robust interpretation depends on inter-study comparability of analytical approach
- PARAFAC decomposition separates overlapping components & is a widely used analysis tool

But: Commonality of spectra / components (& interpretation) is not well constrained.

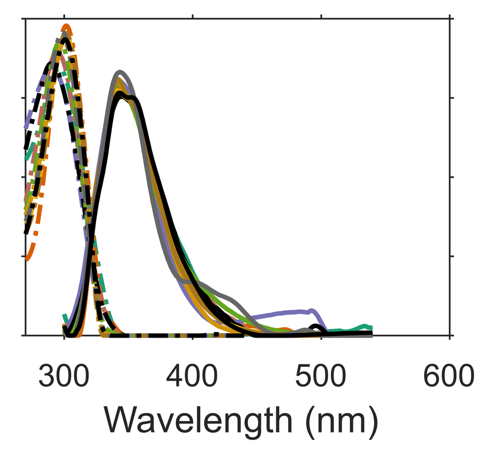
Aims

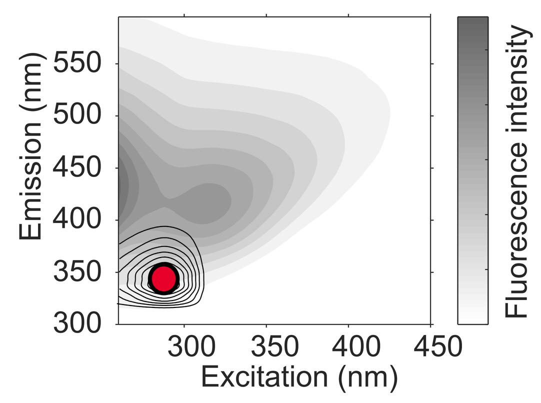
- Identify common fluorescence components across studies
- Compare location of common components with "picked peaks"
- Improve the biogeochemical / analytical interpretation of DOM fluorescence
- Simplify the description of DOM fluorescence with PARAFAC

Community approach: OpenFluor database



- 83 models
- 440 components

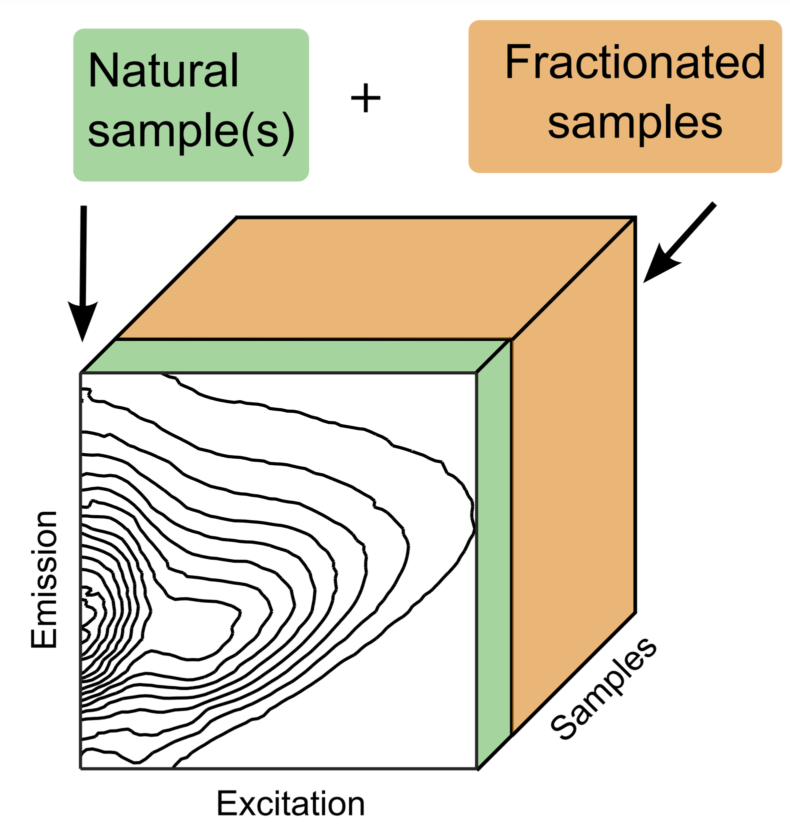




Approach:
- Physical / biogeo-chemical processes alter FDOM composition.
- PARAFAC identifies the common spectra.

Meta-analysis[1]:
- Retreival of data from openfluor.org
- Analysis of spectral similarity between all components
- Projection onto EEM space weighted by component frequency

Single sample approach: One-sample PARAFAC

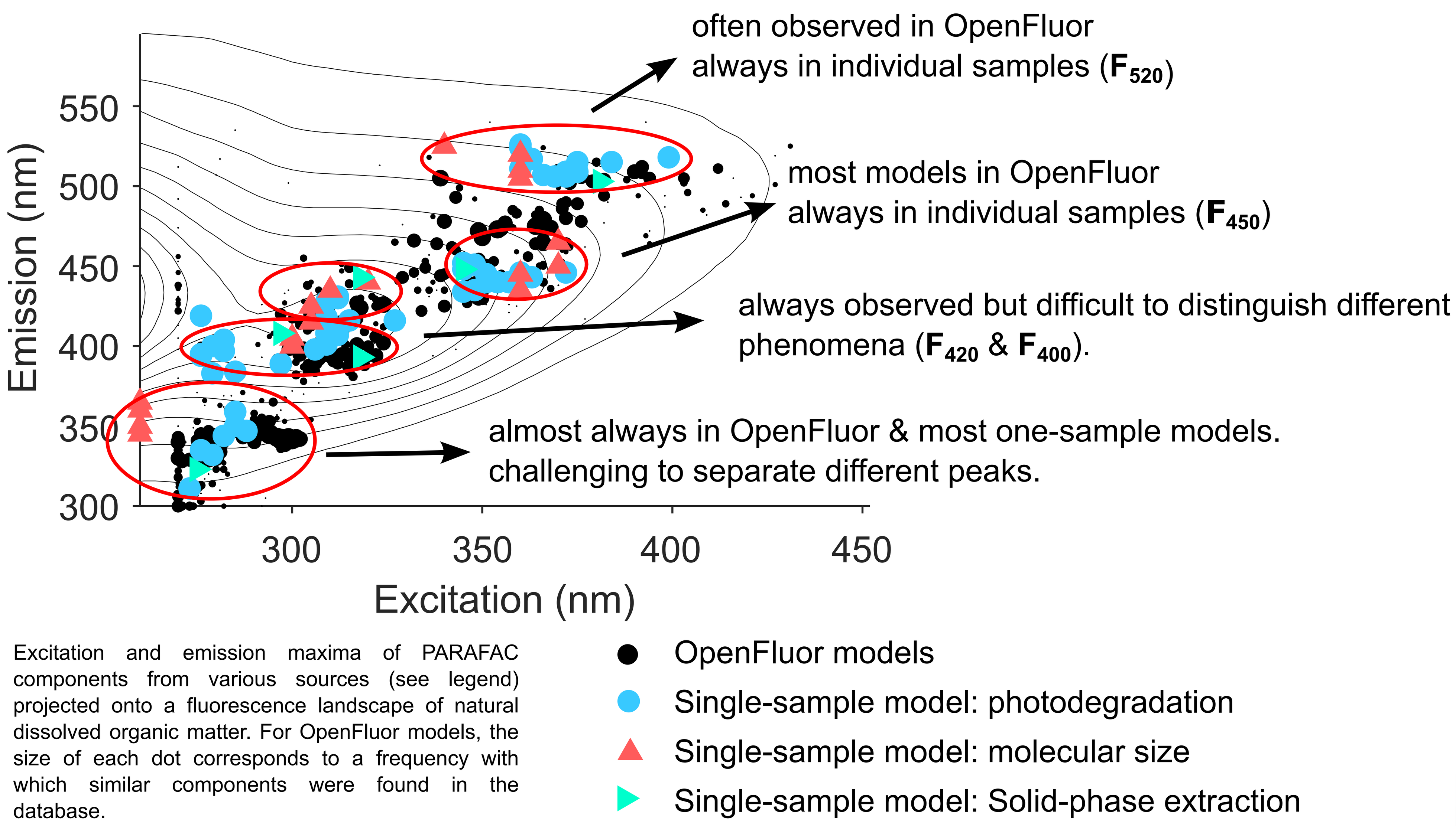


Approach:
- One sample is subjected to "stressor"
- Each DOM fraction responds differently
- Changes in fluorescence are recorded
- PARAFAC identifies the common spectra in *individual* samples

Options for fractionation:
- Molecular size[2]
- Photochemical degradation[3]
- Solid-phase extraction[4]

Samples characterized:
- 23 samples total
- Lakes, rivers, ocean
- Range of sources from autochthonous lakes to allochtonous rivers

Results



Excitation and emission maxima of PARAFAC components from various sources (see legend) projected onto a fluorescence landscape of natural dissolved organic matter. For OpenFluor models, the size of each dot corresponds to a frequency with which similar components were found in the database.

Take-away mesages

- Multivariate techniques no longer require large datasets
- FDOM fluorescence consists of at least four visible-emitting components
- Ubiquitous "humic-like" spectra
- Assuming too few components results in artefacts
- Often possible to get a better model by supplementing the dataset with fractioned samples
- Spectral shape and wavelength maxima do not reveal source of material

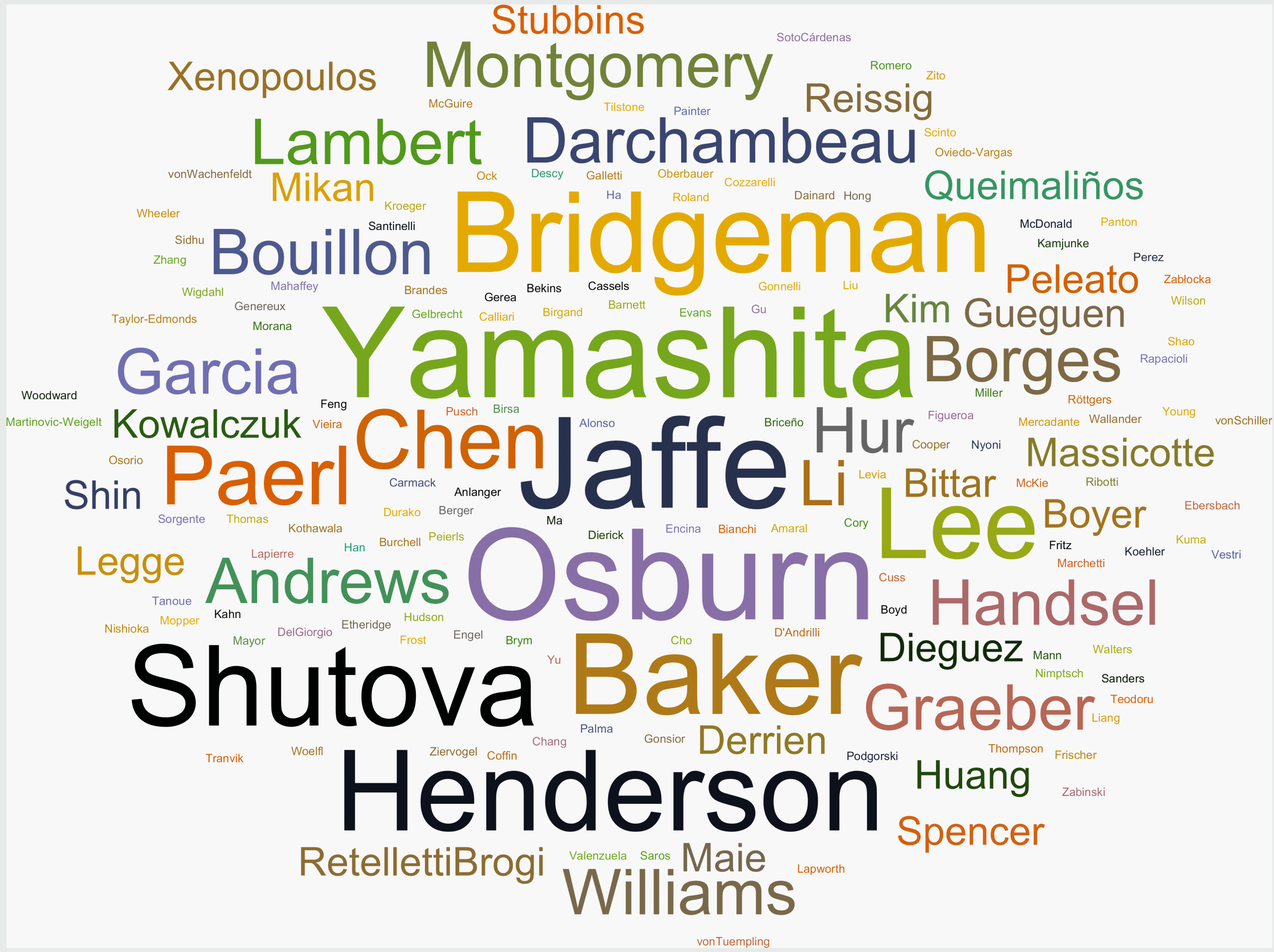
References

(1) Wünsch, U. J.; Bro, R.; Stedmon, C. A.; Wenig, P.; Murphy, K. R. Emerging Patterns in the Global Distribution of Dissolved Organic Matter Fluorescence. Analytical Methods 2019, 11 (7), 888–893. https://doi.org/10.1039/C8AY02422G.
(2) Wünsch, U. J.; Murphy, K. R.; Stedmon, C. A. The One-Sample PARAFAC Approach Reveals Molecular Size Distributions of Fluorescent Components in Dissolved Organic Matter. ES&T 2017, 51 (20), 11900–11908. https://doi.org/10.1021/acs.est.7b03260.
(3) Murphy, K. R.; Timko, S. A.; Gonsior, M.; Powers, L. C.; Wünsch, U. J.; Stedmon, C. A. Photochemistry Illuminates Ubiquitous Organic Matter Fluorescence Spectra. ES&T 2018, 52 (19), 11243–11250. https://doi.org/10.1021/acs.est.8b02648.
(4) Wünsch, U. J.; Murphy, K. A Simple Method to Isolate Fluorescence Spectra from Small Dissolved Organic Matter Datasets. Water Research 2021, 9. https://doi.org/10.1016/j.watres.2020.116730.

Acknowledgements: This study was in part funded by the Danish Council for Independent Research-Natural Sciences Grant DFF-1323-00336, Nordic5Tech collaborative funding (Technical University of Denmark), the Swedish Research Council (FORMAS 2017-00743 and 2013-1214).

Acknowledgements & contact info

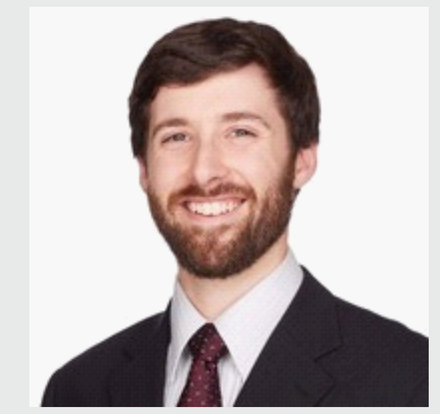
OpenFluor contributors



Photochemistry system and data collection

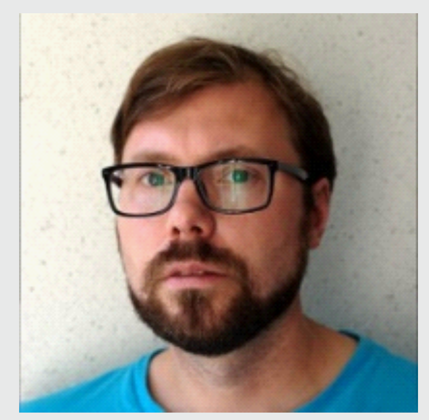
Michael Gonsior

Leanne Powers



Stephen Timko

OpenFluor & PARAFAC



Philip Wenig

Colin Stedmon

Rasmus Bro

Contact info

@UrbanWuensch ujwunsch.com urbw@dtu.dk

Opportunities

Postdoc in Fluorescent tracers of water quality and treatment. Contact Kathleen Murphy (murphyk@chalmers.se) for more information!