The fluorescence of dissolved organic matter in aquatic ecosystems
A spectral database for comparison with known compounds

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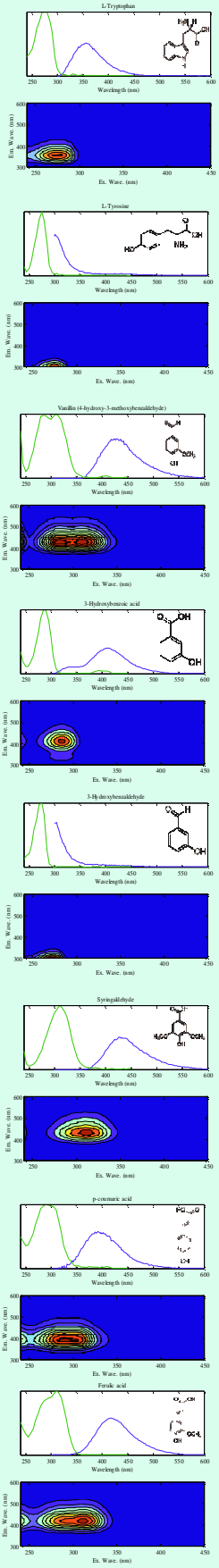


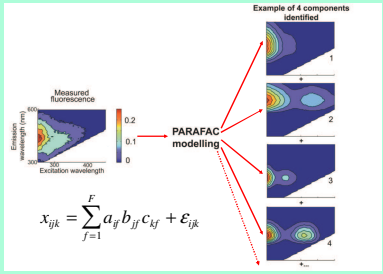
Abstract/Introduction

Fluorescence spectroscopy is used to trace and characterise dissolved organic matter (DOM) in aquatic ecosystems. DOM is a largely uncharacterised mixture of organic compounds originating from the degradation of terrestrial and aquatic plant material. The fluorescence spectra represent the overlapping spectra of all the fluorescent compounds present. Lately multi-way data analysis techniques such as parallel factor analysis (PARAFAC), are being applied to DOM fluorescence data and are able to isolate the signal from different independent fluorescent fractions. These identified fractions can then be used as a proxy to follow the internal dynamics/turnover of the DOM pool as a whole.

What is currently lacking is a better understanding of the chemical properties of the identified fluorescence fractions. Here a recently started web-based spectral database of organic fluorophores is presented. The database is freely available and the fluorescence data can be downloaded so that scientists can freely compare the fluorescence signals extracted from DOM with the fluorescence properties of known organic compounds.

PARAFAC – Mathematical Chromatography

PARAFAC is an alternating least squares regression procedure that splits the fluorescence signal into a series of tri-linear terms and a residual array.



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

When applied to fluorescence x_{ijk} is the fluorescence of sample *i* at emission wavelength *j* and excitation wavelength *k*. a_{if} is directly proportional to the concentration (e.g. µM C) of analyte *f* in sample *i*. b_{jf} is directly proportional to the quantum efficiency of fluorescence of analyte *f* at emission wavelength *j*. Likewise, c_{kf} is related to the specific absorption coefficient at excitation wavelength *k*. F is the number of components in the model and e_{ijk} is the residual matrix (unexplained signal). The model is fitted iteratively and the EEMs are separated into its underlying components, with no assumptions on the number of components or their spectral shape (Stedmon et al 2003).

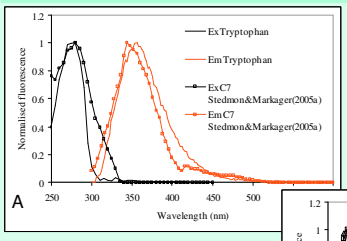
The Spectral Database

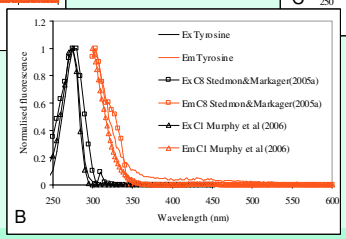
The database is hosted by the Chemometrics group of the Faculty of Life Sciences at the University of Copenhagen (formerly known as KVL-Royal Veterinary and Agricultural university) (www.models.life.ku.dk).

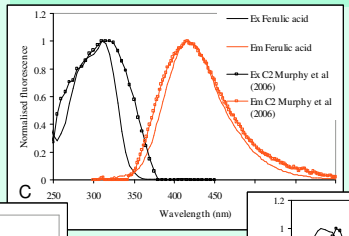
Initially two files are available;
- A summary document of the chemical and UV-Vis spectroscopic properties of each compound measured.
- An ASCII file with the excitation and emission spectra of each compound.

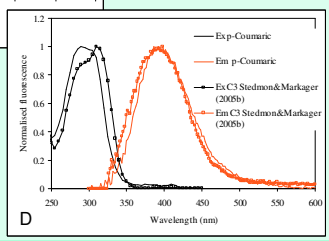
The database will soon be expanded to include;
- More compounds and IHSS humic standards.
- Guidelines for fluorescence spectral correction and calibration procedures.
- An ASCII file with currently published and available DOM PARAFAC components.
- An ASCII file with the carbon specific absorption spectra of the individual compounds.
- An ASCII file with the carbon specific fluorescence excitation-emission matrices (EEMs).
- Small datasets of DOM fluorescence for use in PARAFAC tutorials.

Please visit the site and offer feedback, such as additional compounds to include, or alternative suggestions to how the data are presented and made available in order to enhance the value of the site.









Comparison with published PARAFAC components

Initial comparisons with the limited initial database already reveal some interesting results. A range of the earlier published components have very similar fluorescence properties to the compounds in the database.

Four examples are shown.
Figure A: Component 7 in Stedmon & Markager (2005a) is similar to that of pure tryptophan.
Figure B: Both Stedmon & Markager (2005a) and Murphy et al (2006) identified DOM components which has very similar characteristics to tyrosine.
Figure C: The spectra for Ferulic acid is very similar to that of the humic fluorescence of Component 2 in Murphy et al (2006).
Figure D: p-Coumaric has very similar fluorescence properties to the humic fluorescence of Component 3 in Stedmon & Markager 2005b.

Acknowledgements

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References

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