Spectroscopic analysis of DOM in waters – what is easy and what is not?

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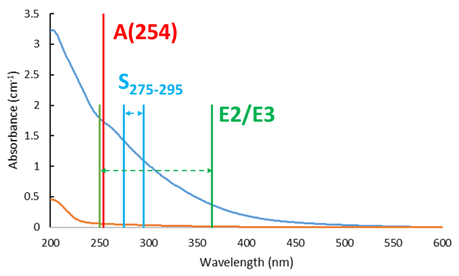
Background

For some years now, spectroscopic methods (**UV-visible spectroscopy**, **fluorescence spectroscopy**) have been widely used to characterize dissolved organic matter (DOM) in water samples (groundwater, surface water from rivers, lakes, etc.). Laboratory equipment (with minimal sample preparation) can be used, as well as portable or in-situ submersible probes. Descriptors can be computed to facilitate the exploitation of .the information contained in the spectra. However some precautions should be taken to make the full use of these techniques.

UV-visible spectroscopy

$$A = \varepsilon dc$$

According to the Beer-Lambert law with
A = absorbance
ε = molar attenuation coefficient or absorptivity of the attenuating species
d = optical path length
c = concentration of the attenuating species



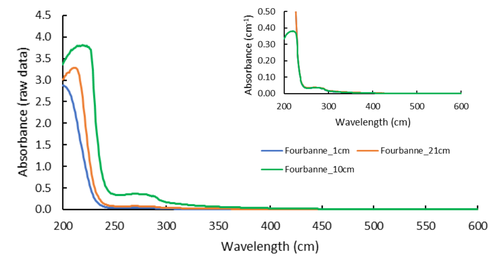
Some useful descriptors of DOM extracted from UV-vis spectra (Zhang et al. 2022 + incl. refs) are listed below:

Specific UV absorbance: $SUVA_\lambda = A(\lambda)/d/DOC$. $SUVA_{254}$ is often used
DOC = dissolved organic carbon

Spectral slope: $\alpha(\lambda) = \alpha(\lambda_0)\exp[S_{\lambda 0\text{-}\lambda}(\lambda_0\text{-}\lambda)]$ where $\alpha(\lambda)$ is the Naperian absorption coefficient ($\alpha(\lambda) = 2.303\ A(\lambda)/d$)
$S_{275\text{-}295}$ decreases when the molecular weight of DOM increases

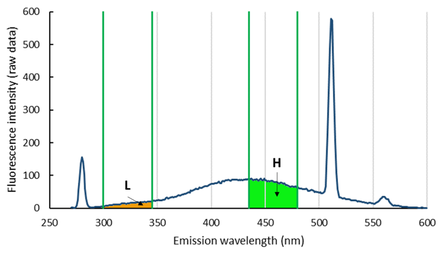
E2/E3 = A(250) / A (365) decreases when the molecular weight of DOM increases
E4/E5 = A(300) / A (400) (< 3.5 → mostly humic acid; > 3.5 → mostly fulvic acid

If the classical optical path length is 1 cm, it can be adapted to increase the sensitivity, especially for DOM- poor groundwater



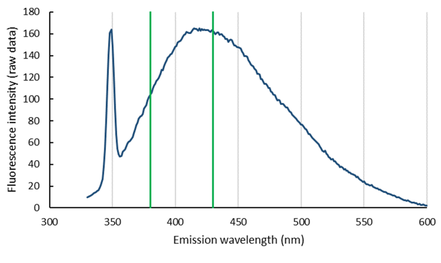
Fluorescence spectroscopy

Emission spectra (with excitation at fixed wavelength), synchronous fluorescence spectra (where the difference between excitation and emission is kept constant) and excitation-emission matrices are largely used to study DOM.



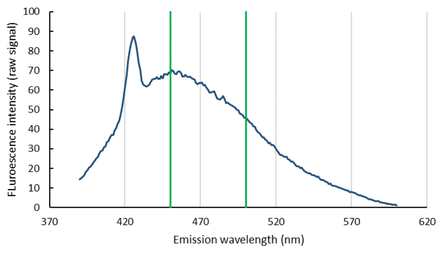
Humification index (HIX) with λ_{exc} = 254 nm (Zolnay, 2003)

$$HIX = \frac{H}{L} = \frac{\sum I_{\lambda em(435\ nm-480\ nm)}}{\sum I_{\lambda em(300\ nm-345\ nm)}}$$



Recent and authochthonous DOM: BIX with λ_{exc} = 310 nm (Huguet et al., 2009)

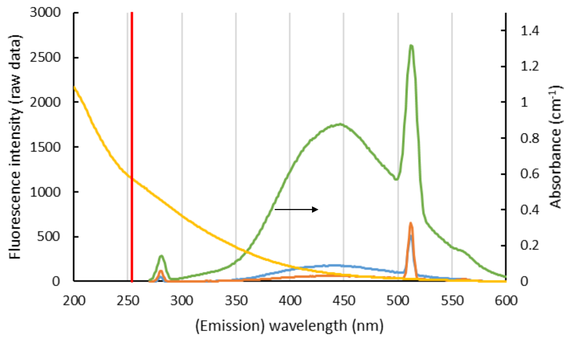
$$BIX = \frac{I_{\lambda em=380\ nm}}{I_{\lambda em=430\ nm}}$$



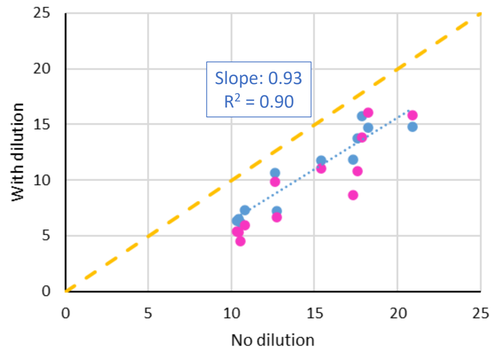
Origin of fulvic acids: FI with λ_{exc} = 370 nm (Mc Knight et al., 2001)

$$FI = \frac{I_{\lambda em=450\ nm}}{I_{\lambda em=500\ nm}}$$

The inner filter effect due to high sample absorbance (mostly at the lowest excitation wavelengths) is the main problem with fluorescence spectroscopy. In the laboratory, it is possible to dilute the sample, but it causes a global decrease of the signal.



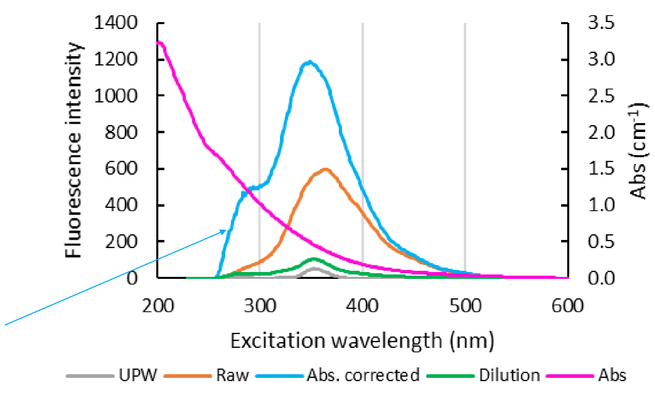
Raw signal, slits width = 2.5 nm
Dilution by 5, with UP water, slits width = 2.5 nm
Raw signal, slits width = 5 nm
Trout Beck sample



Effect of dilution by **UP water** and **Ringer solution** (150 µS/cm) on HIX (samples collected on the Wüstebach, Eifel, Germany)

Mathematical corrections of the inner filter effect have also been proposed. However, in the case of submersible probes, this correction may not be possible.

On synchronous fluorescence spectra, the correction based on the absorbance spectrum can be seen on the protein-like fluorescence.



Soil solution, Strengbach, Vosges, France

Conclusions

Optical methods are attractive for the monitoring of DOM at low-cost and with limited sample preparation. The inner filter effect due to absorbance should be recognized and clearly stated, especially with in-situ probes for which dilution is not possible. Effect of settings (slit width, i.e.) and manufacturers specifications should also be stated.

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