# UV-Vis spectroscopic study of coloured dissolved organic matter (CDOM) in the pristine Krka River estuary (Croatia)

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## Introduction

Natural organic matter (NOM) is one of the major components of aquatic ecosystems which controls functioning of ecological processes and biogeochemical cycles. Coloured dissolved organic matter (CDOM), as an important part of the NOM, is responsible for the light absorption. For many estuarine systems, riverine discharge is considered as the main source of DOM. However, freshwater systems from karst regions without notable anthropogenic influence, could deviate from this common pattern (Cindrić et al., 2015). The Krka River (and its estuary) is the typical example: the concentration of dissolved organic carbon (DOC) is at the same level (winter) or only slightly above the level of clean seawater (summer).

## Study site and methodology

The Krka River estuary is a typical, highly stratified estuary. Its vertical gradient is characterized by three layers: (1) surface fresh/brackish layer (FWL), (2) freshwater-seawater interface (FSI) and (3) seawater layer (SWL). Halocline is usually positioned between 1.5 and 3 m, and its "thickness" varies between few cm only to 1 m. Samples were collected at 16 locations during two contrasting periods: in winter (high Krka River flow) and summer (low Krka River flow). For summer sampling, both FWL and SWL samples were collected, whereas for winter campaign only FWL was sampled. For both periods, samples of vertical profiles (6 depths) were also taken at more downstream site ($20^{th}$ km). Samples collected using van Dorn type horizontal sampler (alfa or beta, Wildco) were on-board filtered using precleaned (MQ +sample) syringe 0.22 μm CA filters (Sartorius). UV-Vis spectra were measured on Perkin Elmer Lambda 45 spectrometer using 1cm and/or 10 cm quartz (Suprasil) cuvettes. UV-Vis spectra were treated using newly purpose-developed software package, ASFIt.

## Results and discussion

As expected, concentration of DOC in the estuary is in average higher in the summer than in the winter period, as a consequence of higher biological activity. While in winter period concentration of DOC in the Krka River (0 km) is lower than in the open coastal location, in the summer period ~60% higher DOC is registered in the river and in majority of estuarine region, but with unchanged concentration at the position of open coastal location.

Typical spectral characteristics, spectral slope $S_{275\text{-}295}$ and absorption coefficient at 254 nm ($a_{254}$), obtained for both periods are presented in Figures 1A and 1B. Lower spectral slope was found in freshwater compared to seawater, which is very common for estuarine regions. Increase of $S_{275}$ with the salinity indicates decrease in the humic acids as a terrestrial component with higher molecular weight and the aromaticity (Helms et al., 2008). This trend is more obvious for the winter, than for the summer campaign, with evidently higher average spectral slope obtained in summer samples. Similar trends were found for absorption coefficient at 254 nm for both periods, despite evident differences in DOC concentrations (Fig 1B).

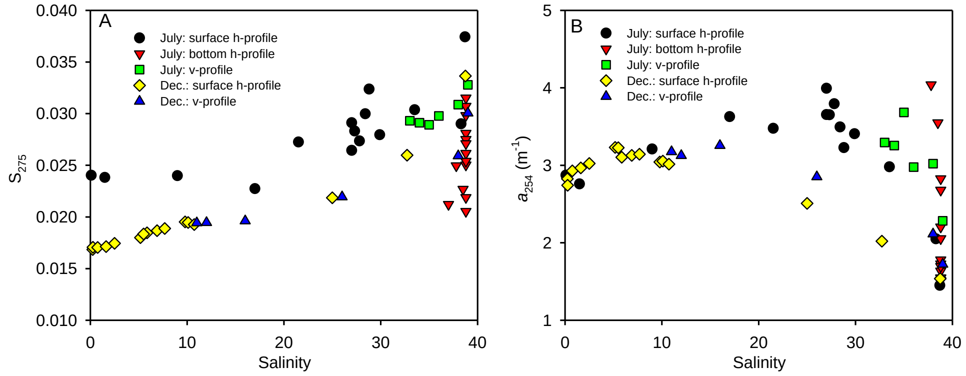


**Figure 1**. (A) Relationship of spectral slope ($S_{275}$) and (B) absorption coefficient ($a_{254}$) with the salinity.

Increase of DOC is expected to be reflected also on the intensity of $a_{254}$, however different trends were observed for summer and winter period, avoiding use of this parameter for simple estimation of DOC concentration. Several other relationships and fitting equations were reviewed in order to find the optimal way of relating absorbance and DOC concentration. If results for each campaign and profile are treated separately, a much better relationship between measured and estimated DOC concentration could be obtained based on the log-linearized equation proposed by Fichot and Benner (2011) (Fig. 2A):

$$\ln[\text{DOC}] = \alpha + \beta \times \ln[a(275)] + \gamma \times \ln[a(295)]. \qquad \text{(eq 1)}$$

As noted within the Fig 2A, parameters of equation (1) differ among season and profile showing specificity of this relationship. If all results were fitted, most of the results fall within the ±20% from the measured value, and thus could be used for screening purposes (Fig 2B). These estimates were obtained using very limited number of data, covering only one winter and summer season, and thus should be further updated and confirmed (or rejected) with new sets of data in order to be applicable for general DOC estimation for this estuarine system.

UV-Vis spectra were additionally treated by using Gaussian decomposition method (combination of exponential and n-gaussian functions), recently suggested by Massicotte and Markager (2016).

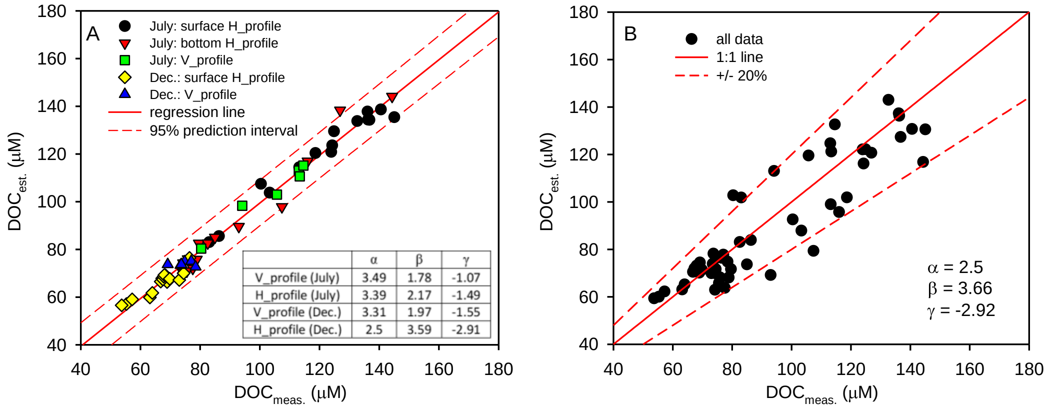


**Figure 2**. (A) estimated (eq 1) versus measured DOC concentration using separate data as noted in the table (H_profile July includes bottom and surface samples) and (B) same as (A) with all results used for fitting. (H - horizontal or V-vertical profile).

## References

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