



Linking of EEM spectra with FTICRMS data via van Krevelen diagrams and rank correlation

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DOM plays an important role in both natural and engineered water systems. Due to its sensitivity and non-destruction of samples EEM is widespread used for comprehension of CDOM. EEM provides sensitive bulk optical parameters with low structural resolution concerning DOM quality even when spectra are modelled by PARAFAC or EEM is coupled to chromatography. Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) is a high-resolution analytical tool to determine the elemental compositions of thousands of DOM components directly out of mixtures. Lacking the ability for identification of distinct chemical substances (isomers), the elemental compositions can nevertheless be allocated to biogeochemical pools by means of van Krevelen diagrams.

The spearman rank correlation was applied to link the EEM intensities (humic like fluorescence) with exact molecular formulas and their corresponding relative mass peak abundances. The initiative for this study to find out what is humic like fluorescence was the environmental problem of increasing levels of organic carbon in fresh waters as a great challenge for processing and commercial supply of drinking water.

In the southern Saxony region, Germany, raw drinking water is mainly received from reservoirs situated in the ore mountains (Erzgebirge). Most of these reservoirs are affected by high concentrations of humic substances detected by the drinking water administration via measurement of the dissolved organic carbon (DOC) and the spectral absorption coefficient at 254 nm (SAC254). To get a better insight into the DOM composition, the seasonal variability of DOM quality was determined using EEM and FTICRMS and coupling these two methods in the catchment area of the reservoir Muldenberg. Thereby, humic-like fluorescence could be allocated to the pool of oxygen-rich and relatively unsaturated components with stoichiometries similar to those of tannic acids [1].

[1] Herzprung, P., von Tümpeling, W., Hertkorn, N., Harir, M., Büttner, O., Bravidor, J., Friese, K., Schmitt-Kopplin, P. Variations of DOM quality in inflows of a drinking water reservoir: Linking of van Krevelen diagrams with EEMF spectra by rank correlation. *Environ. Sci. Technol.* 46, 5511-5518 (2012).