

From humic substances to carbon dots : fluorescence dependence on excitation wavelength



Dolenko Tatiana A. ¹, Kharcheva Anastasiia V. ¹, Khundzhua Daria A. ¹, Kuztetzov Artur I. ², Patsaeva Svetlana V. ¹, Vervalde Alexei M. ¹, Yuzhakov Viktor I. ¹

¹ Faculty of Physics, Lomonosov Moscow State University, Moscow, Russia; spatsaeva@mail.ru
² AS Ldiamon, Tartu Science Park, Riia 185, 51014, Tartu, Estonia; kuznetsov6a@gmail.com

Despite many years of spectroscopic investigations, the mechanism of light absorption and emission by humic substances is still unresolved and is a subject of active discussions. Their fluorescence spectra in visible region typically are broad and not well defined, giving so called "humic-type fluorescence", which leads them to be qualitative tools for organic matter characterization. To increase the amount of information to be extracted from the spectral analysis one can measure fluorescence emission spectra under various excitation wavelengths and to calculate fluorescence quantum yield. In this work we address the question whether the humic-type fluorescence of different samples is a collective property or it is originating from small individual emitters.

DISSOLVED ORGANIC MATTER

Chromophoric dissolved organic matter (CDOM) is present in all types of natural water in concentration varying from 0.5 to 50 mg/l, and represents a significant reservoir of organic carbon on Earth. The CDOM absorbs UV and visible light and is a major determinant of optical properties for both fresh and marine waters, directly affecting the spectral quality of the underwater light field.

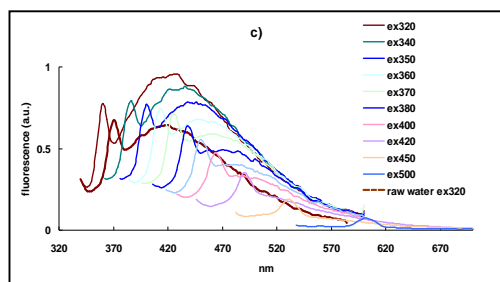


Fig.1. CDOM fluorescence spectra at different excitation wavelengths

HUMIC SUBSTANCES

Humic substances are major components of the natural organic matter in soil and water as well as in geological organic deposits such as lake sediments, peats, brown coals and shales. Humic substances contain a wide variety of molecular components representing a complex and poorly understood mixture of organic polymers that plays an influential role in terrestrial and aquatic ecosystems.

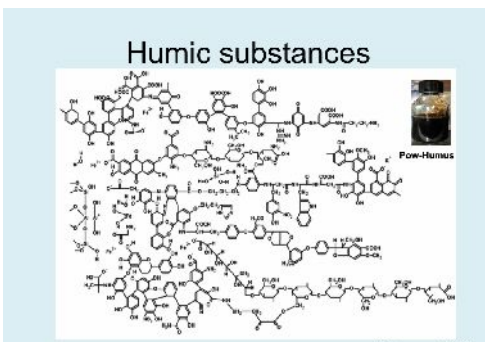


Fig.2. Klein hempel model for humic substances (1970)

CARBON DOTS

Carbon-based quantum dots (or carbon dots) represent assemblies of surface-passivated small carbon nanoparticles that are brightly fluorescent. Typically, carbon dots are less than 10 nm and have an sp² or amorphous carbon framework and a surface coated with oxygen-containing groups, polymers or other species.

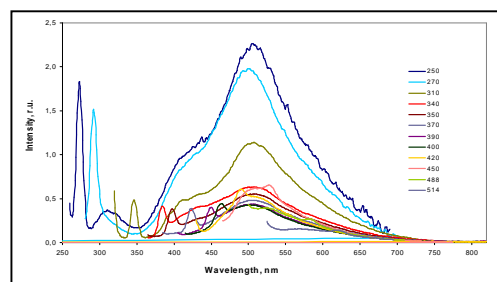


Fig.3. Fluorescence spectra for carbon dots in water at different excitation wavelengths

BIOFLUIDS

Fluorescence in biological fluids (serum, hemodialysate, hemofiltrate, urine) typically exhibits excitation/emission wavelengths 320±5/420±5 nm, and was enhanced in intensity for chronic kidney disease patients.

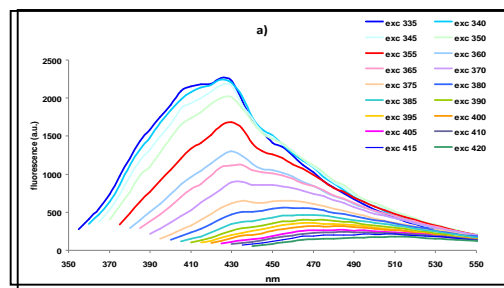


Fig.5. Fluorescence spectra at different excitation wavelengths for urine of chronic kidney disease patients

Fig.4. a) Fuchs's model for coal humic substance (W. Fuchs, Die Chemie der Kohle, 1931); b) model of luminescent oxidized graphene (D. Pan et al., Adv Mater, 2010)

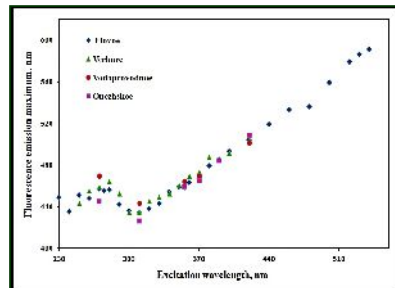
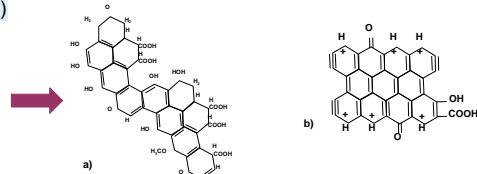
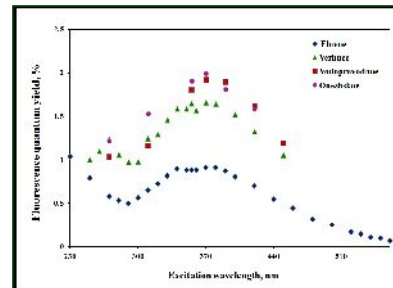


Fig.6. Emission wavelength (left) and fluorescence quantum yield (right) as a function of excitation wavelength for CDOM in different lakes



EMISSION WAVELENGTH: BLUE SHIFT AND RED SHIFT

For natural aquatic and soil HS samples the effect of emission "blue shift" was observed when emission maximum shifted to shorter wavelengths with excitation rising from 270 to 310 nm. Under excitation beyond 310 nm natural aquatic and soil HS samples demonstrated shift of fluorescence to longer wavelengths in parallel to increase of excitation wavelength. Other samples like commercial HS products (fulvic and humic acids), carbon dots and biofluids showed constancy of emission wavelength under UV excitation till certain wavelength, and the "red shift" of emission maximum at longer excitation wavelengths.

CONCLUSIONS

The phenomenon of humic-type fluorescence manifests itself in the variety of different samples (CDOM in natural water, HS of different origin, biological fluids, and carbon dots) as a rather universal excitation-wavelength dependent fluorescence.

The phenomenon can be interpreted as a manifestation of self-assembling of small fluorophores into larger nanoparticles. The fluorophores of natural CDOM and HS are more diverse than carbon dot emitters because of their genesis and biogeochemical nature.