Dissolved humic substances and fungal metabolites can exhibit similar fluorescence properties

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Introduction. The fluorescence spectroscopy (FS) is commonly used to characterize humic substances (HS), the main components of natural organic matter (NOM) (Coble et al., 1996; Shubina et al., 2010). FS can be used as well to discriminate microbial cells and biochemical processes (Pan, 2015; Assawajaruwan et al., 2017). The release of colored dissolved organic matter (CDOM) by different groups of microorganisms (different phytoplankton and cyanobacteria) was studied earlier (Castillo et al., 2010; Zhao et al., 2017). It is promising to continue studying the possibilities of filamentous fungi for the production of FDOM, similar to that found in water and soil environments.

This study was aimed to assess fluorescence properties of fungal cultural liquids and to reveal their similarity with fluorescence properties of aquatic CDOM and that of humic product.

Material and methods.

We investigated fluorescence properties of cultural liquids of four fungal strains *Alternaria alternata, Cladosporium cladosporioides,* and *Trichoderma harzianum*, and compared them with fluorescence properties of humic product (humic acid from coal - HAcoal) and aquatic CDOM. Fluorescence spectra were measured using a luminescence spectrometer Solar CM2203 at wavelengths of the exciting radiation ranging from 250 to 500 nm.

The fluorescence properties of molecules were described by such parameters as dependence of emission wavelength λem on excitation wavelength λex, and the value of fluorescence quantum yield (QY) (number of fluorescent photons per photons absorbed).

Table 1. Emission maxima, "blue shift" and QY values

Samples	max			Blue shift		QY, %		
	λex= 270	λex= 310	λex= 355	Δ1	Δ2	λex= 270	λex= 310	λex= 355
A.alternata	423	411	421	12	10	2.86	0.84	5.39
C.cladosporioides	420	408	429	12	21	2.85	0.86	2.03
T.harzianum	446	447	455	-	8	1.16	0.67	0.75
HAcoal	446	431	464	15	33	1.48	1.95	1.48
Aquatic DOM	455	435	456	20	21	1.4	1.8	2.7

Δ2=λmax(355) - λmax(310); Δ1=λmax(270) - λmax(310)

No "blue shift" means the presence of NAD(P)H and absence of melanins

Results

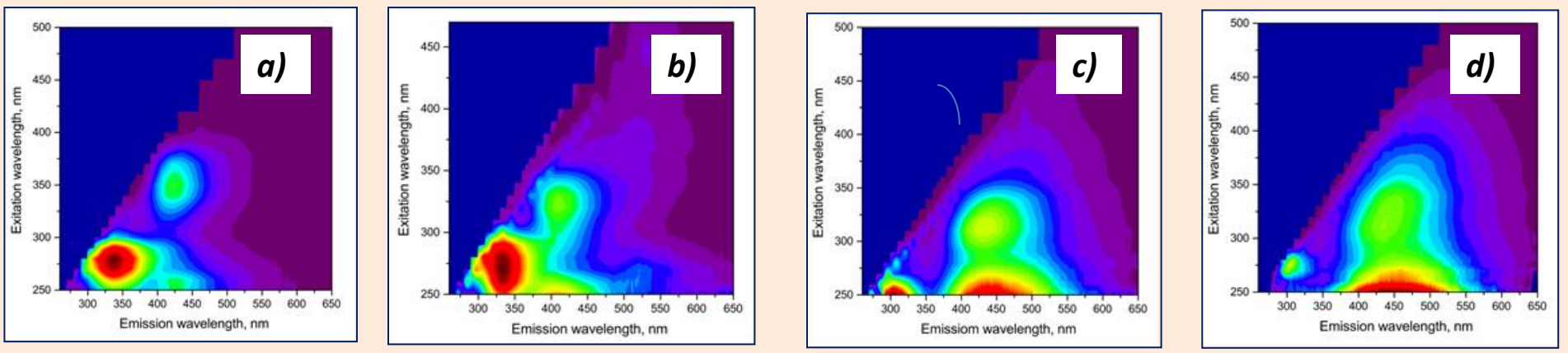

Fig. 1. Excitation-emission matrix (EEM) of the fungal samples: a) A. alternata, b) C. cladosporioides, c) HAcoal, d) aquatic DOM

The fluorescence of fungal cultural liquids, aquatic CDOM and HA coal is caused by **two main groups of fluorophores:**

- **"protein-like"** with excitation and emission maxima below 305 and 380 nm, respectively,
- **"humic-like"** with emission maximum located within 380–470 nm under excitation within the wavelength range 220–360 nm.

Fluorescent CDOM released from some fungal cultures (especially *C.cladosporioides*) also showed comparable apparent fluorescent QY, blue shift of emission spectra, and a very close match of ultraviolet–visible absorbance. Given the importance of filamentous fungi in the global carbon cycle our results indicate that filamentous fungi are likely to be important sources of aquatic and soil fluorescent CDOM.