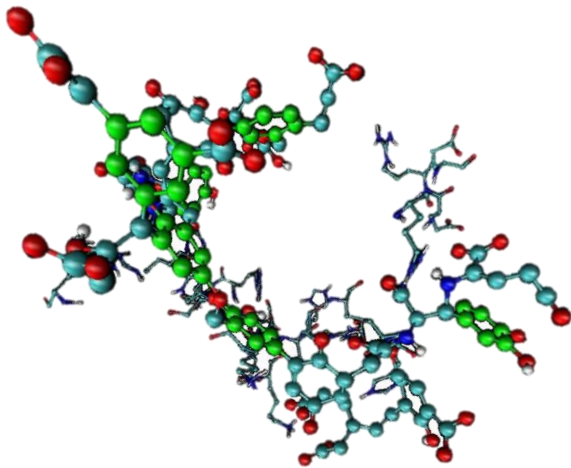




Natural organic matter: genesis and optical properties

Olga Yakimenko



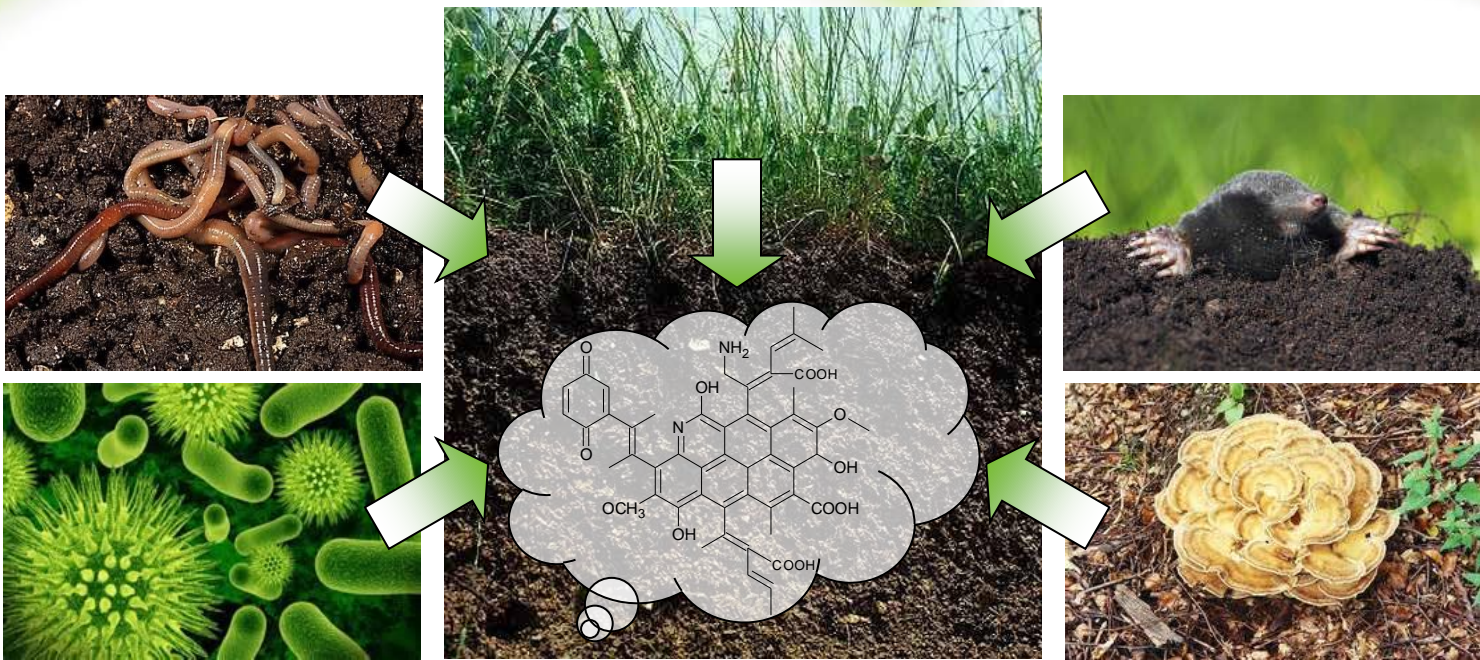
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Overview

- Natural organic matter: what it is?
- Optical and luminescent properties of NOM
- Case study: Absorption and Fluorescence Proxies to Characterize Source Organic Matter of Humic Products

Natural organic matter (NOM)



NOM is a product of plant and animal tissue decay, and is of pivotal importance in the environmental status of an ecosystem.

NOM



Soils:

Podzols 3%
Cambisols 6%
Chernozems 12%



Sediments:

Lignite 90%
Peat 60%
Peloids 70%

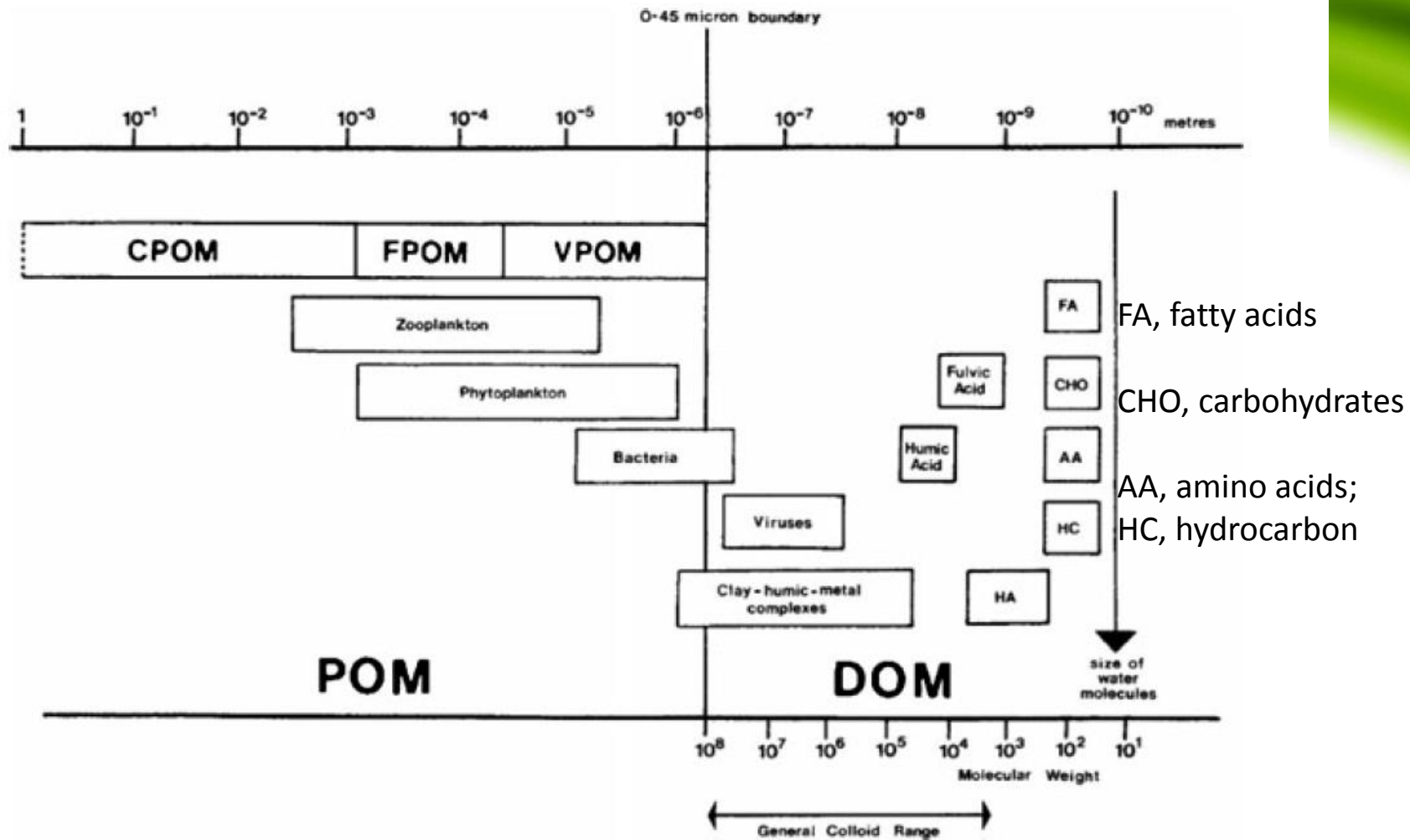


Natural waters:

Sea waters $0,3 \times 10^{-3}\%$
River waters $2 \times 10^{-3}\%$
Bog waters $2 \times 10^{-2}\%$

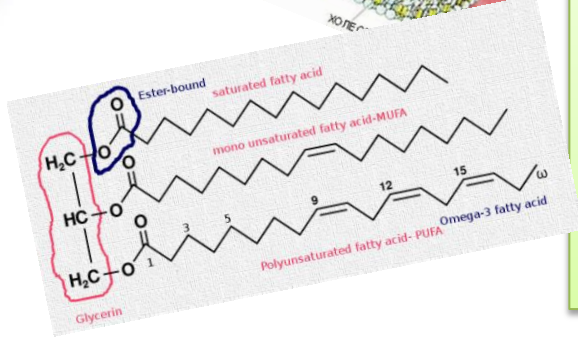
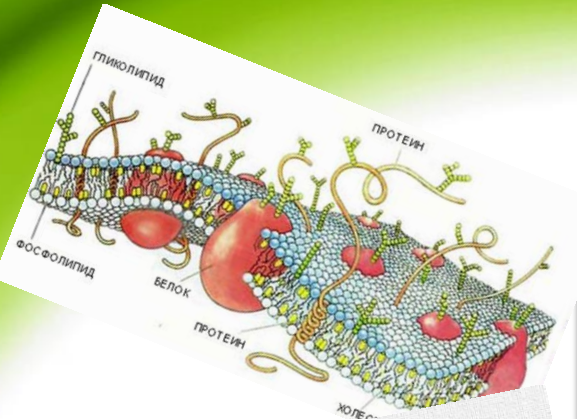
NOM is found in soil, sediments, and natural water and consists of HUMIC SUBSTANCES and individual organic components

Dissolved OM and Particulate OM

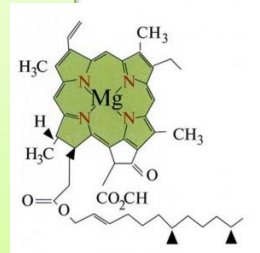
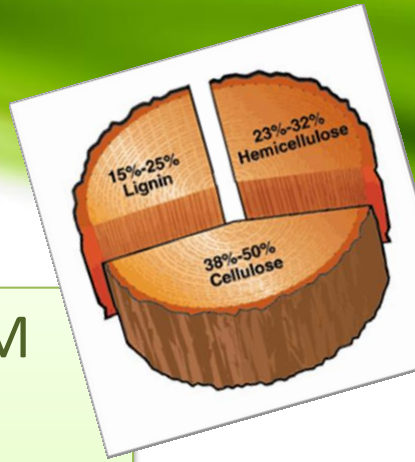


Size range of particulate (POM) and dissolved organic matter (DOM) and organic compounds in natural waters (Thurman, 1985)

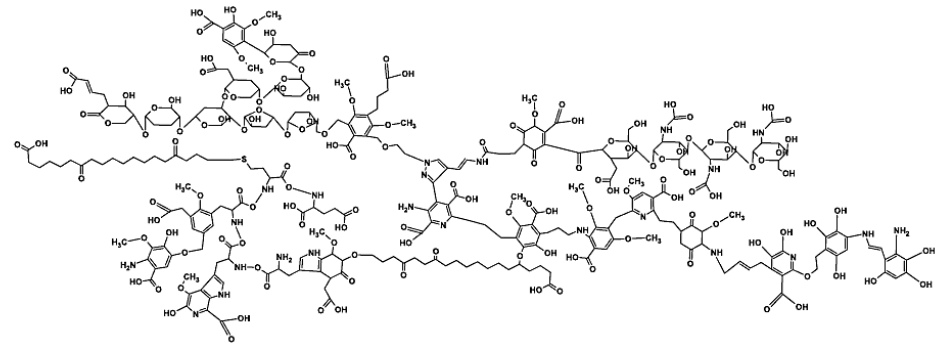
Molecular components of NOM



- Lignin – tracer for terrestrial OM
- Carbohydrates
- Proteins and Amino Acids
- Hydrocarbons and Fatty Acids
- Pigments



Humic substances



Нефракционированное природное ОВ содержит ГВ (ГК+ФК) и НОС
 NOM contains *individual organic compounds* and *humic substances*

GENESIS of NOM

Terrestrial

result of biological degradation and progressive concentration of organic compounds particularly resistant to degradation. Degradation of vascular plants furnishes DOM containing approximately 10 % proteins, 30–50 % carbohydrates (mainly cellulose), some lipids concentrated in the roots and leaf cuticles, 15–25 % lignin , and other biomacromolecules

Geological

Most stable organic compounds, mostly HA

Aquatic

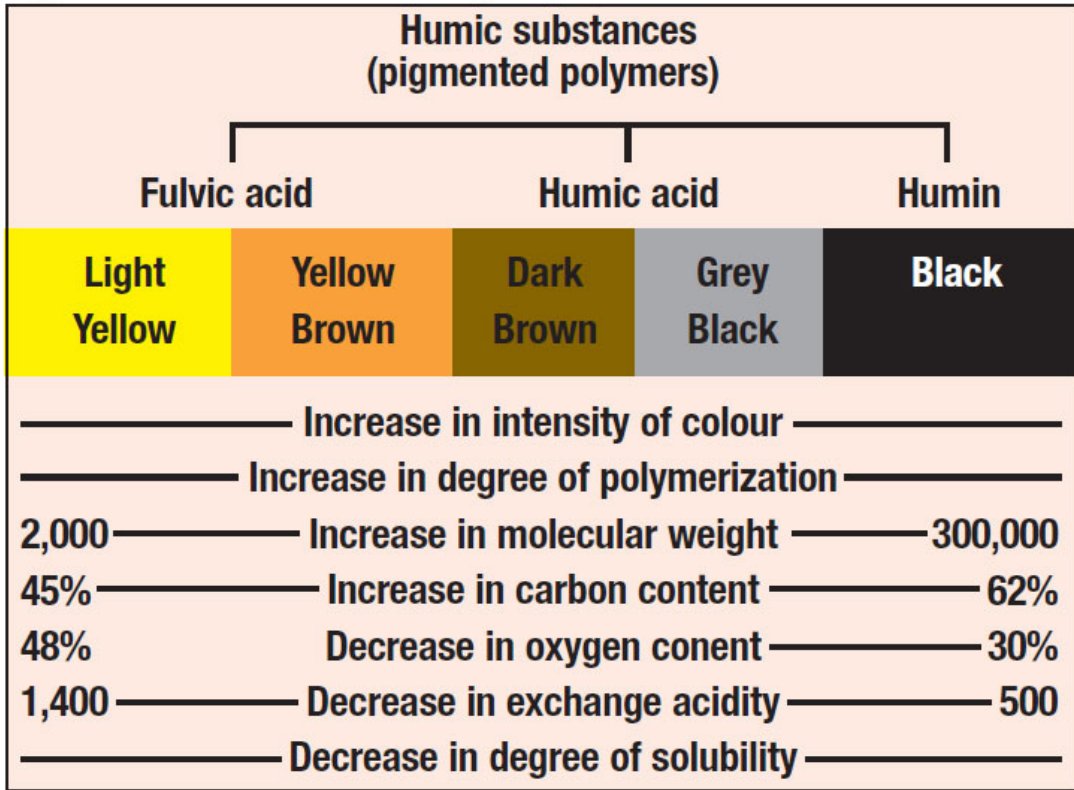
Formed as a product of the biochemistry of life forms, for example diatoms, bacteria, algae, or microfauna. These may either actively release organic matter or undergo natural decay after cell death; their metabolic diversity is one of the factors resulting in the heterogeneity of DOM.

Marine DOM is subjected to much faster dynamics because it is dissolved in a water mass. DOM is therefore transferred in larger amounts than SOM, and its availability for enzyme activity, oxidation, or metal complexation is significantly larger than that of SOM.



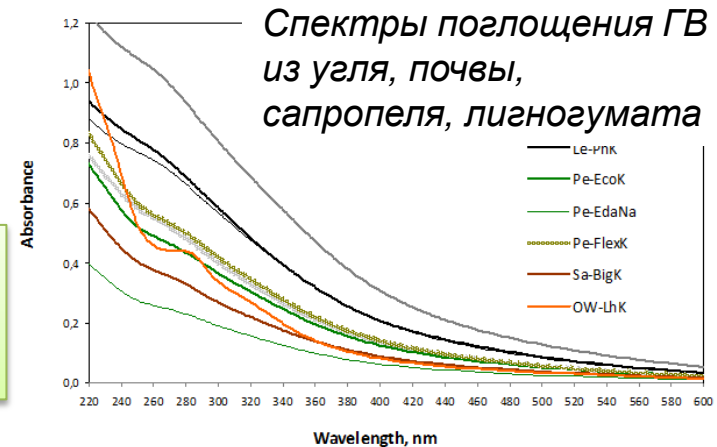
Chromophoric DOM

Figure 1 : Postulated relationships between different humic substances



Chemical properties of humic substances (Stevenson 1982)

For DOM to have chromophoric properties it must contain unsaturated and conjugated groups, for example aromatic or quinoid structures.



Some UV-vis indices for HS characterization

Показатель	Способ определения или расчета	Пояснение
Специфическая адсорбция	Поглощение при 240, 254, 267, 270, 280, 400, 465, 472, 600, 650 и 665 нм, нормализованное по содержанию ГК в растворе, мг/л	Общие характеристики
$SUVA_{254}$	Поглощение на 254 нм, нормализованное по содержанию С в растворе, мг С/л (A_{254}/DOC)	Показатель степени ароматичности РОВ
$E_2:E_3$	Отношение величин поглощения при 250 и 365 нм, (A_{250}/A_{365})	Коррелирует с молекулярной массой и ароматичностью ГВ
$E_4:E_6$	Отношение величин поглощения при 465 и 665 нм (A_{465}/A_{665})	Коррелирует с возрастом и степенью ароматичности ГК и ОВ; используется как показатель гумификации
$E_{270/400}$	Отношение величин поглощения в UV-Vis области для соответствующих длин волн	Характеризует деградацию фенольного/хинонного ядра ГК до простых фенол-карбоновых структур
$E_{280/472}$	Отношение величин поглощения в UV-Vis области для соответствующих длин волн	Отражает соотношение между лигнинами и другими материалами начальной стадии гумификации
$E_{280/665}$	Отношение величин поглощения в UV-Vis области для соответствующих длин волн	Показывает соотношение между негумифицированным и гумифицированным материалом
$\Delta \log K$	$\Delta \log K = \log A_{400} - \log A_{600}$	Показывает наклон спектральной кривой в определенном интервале. Связывают со степенью гумификации ОВ
Наклон спектральной кривой, S_r	Безразмерное отношение наклонов в коротковолновой (275-295 нм), и длинноволновой (350-400 нм) областях	Описывает форму спектральной кривой; не зависит от концентрации РОВ, трактуется как показатель источника, качества и диагенеза РОВ
$FDR_{240/280}$	Отношение амплитуд при 280 и 240 нм в спектре производной первого порядка. Аналог S_r , но вычислен в более узких спектральных интервалах	Характеризует изменение наклона в спектрах поглощения при определенных длинах волн, выбранных в качестве плеч в производной спектра первого порядка.
$SDR_{267/280}$	Отношение амплитуд на 267 и 280 нм в спектре производной второго порядка	Производная второго порядка используется для разрешения перекрывающихся пиков в виде плеча в исходных спектрах поглощения.

Case study

- Objective

to determine indicators using absorption and fluorescence spectra in combination with derivative spectroscopy that might serve as tools to compare HPs from various environments

- Materials

Humic products from:

- coalified materials (brown coal and leonardite): 4 samples



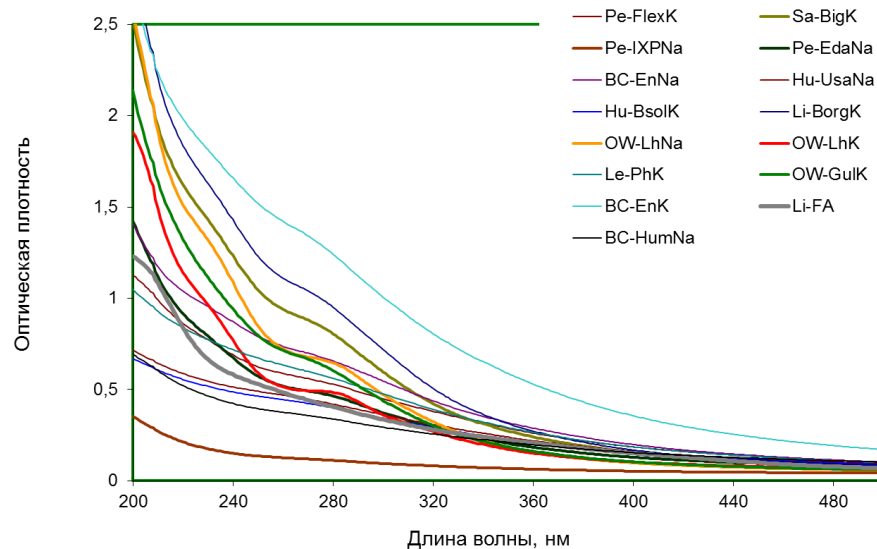
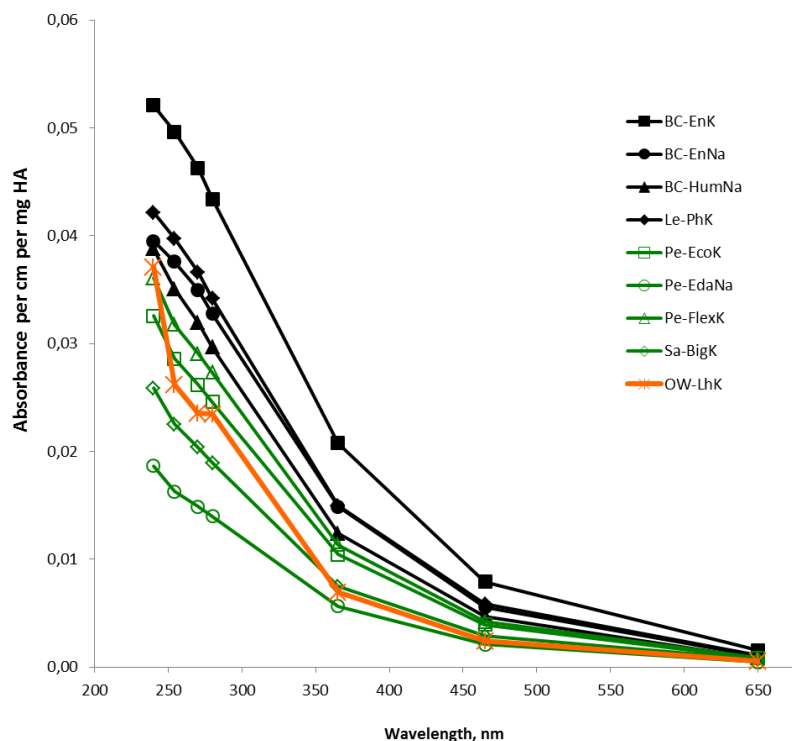
- Peat (3 samples) , lake bottom sediment (1 sample)



- organic waste material (lignosulphonate)

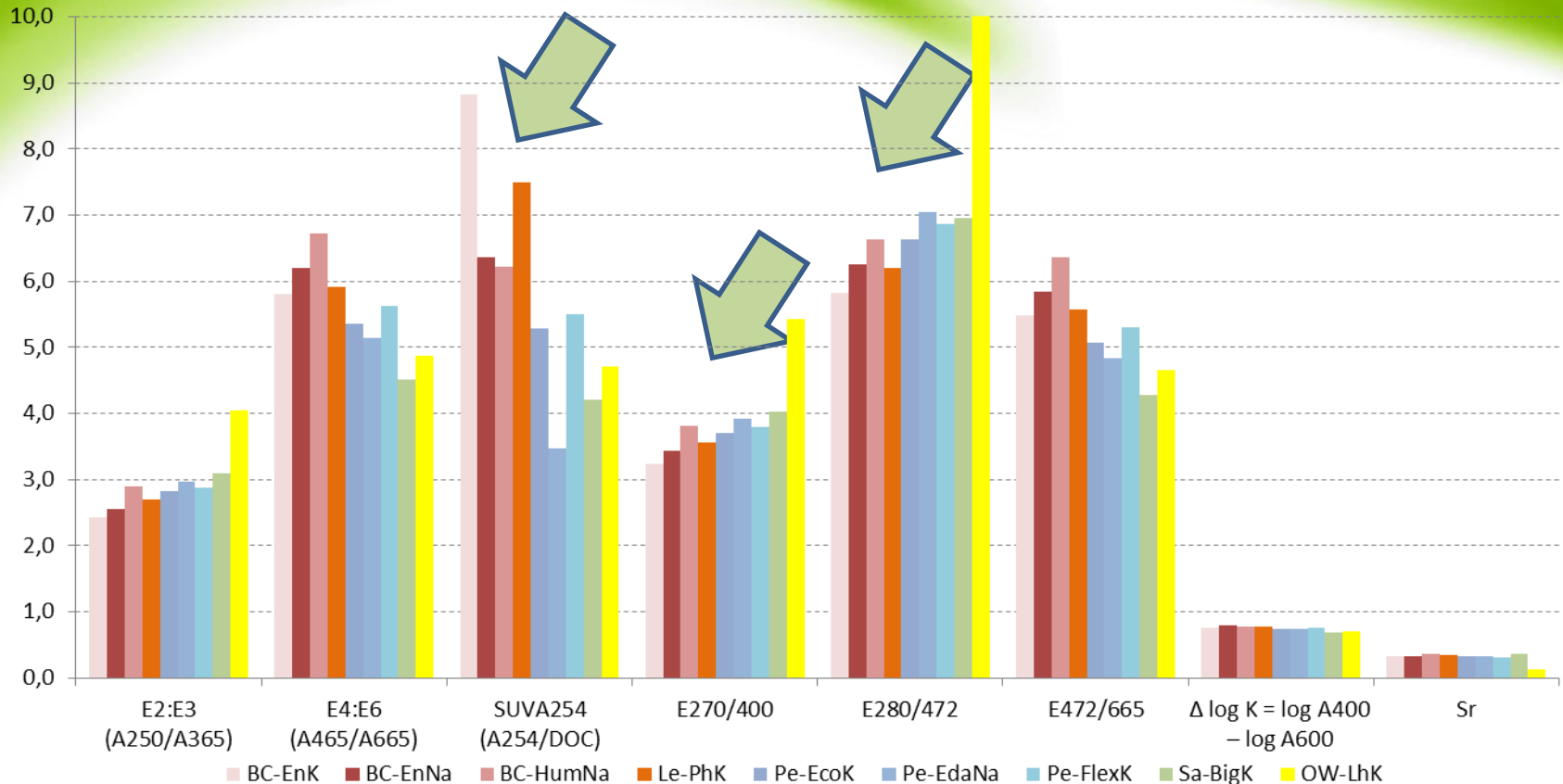


Specific absorbance of HA isolated from humic products in UV-vis spectral range (absorbance normalized by the content of HA in solution, mg L^{-1})



Absorbances normalized by sample weight are the highest for HA from coal-derived HPs and about 2-2.5 times lower for HA from other HPs over all the spectral range

Descriptive ability of UV-vis indices

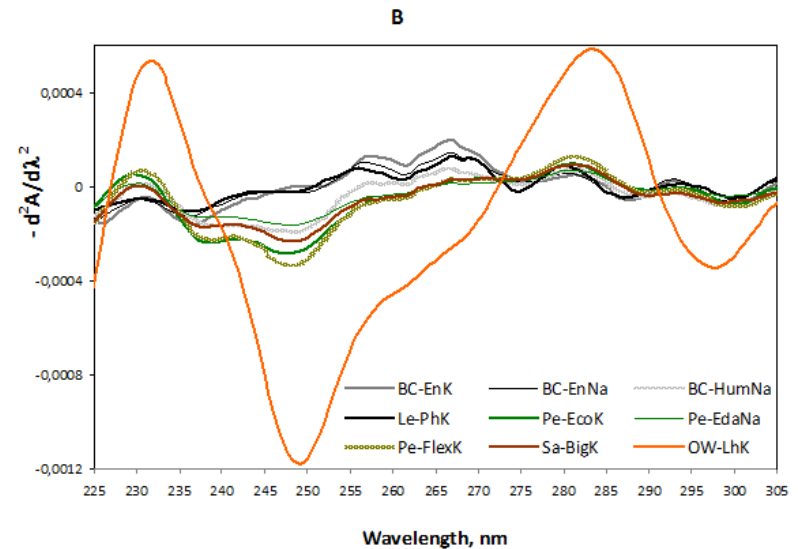
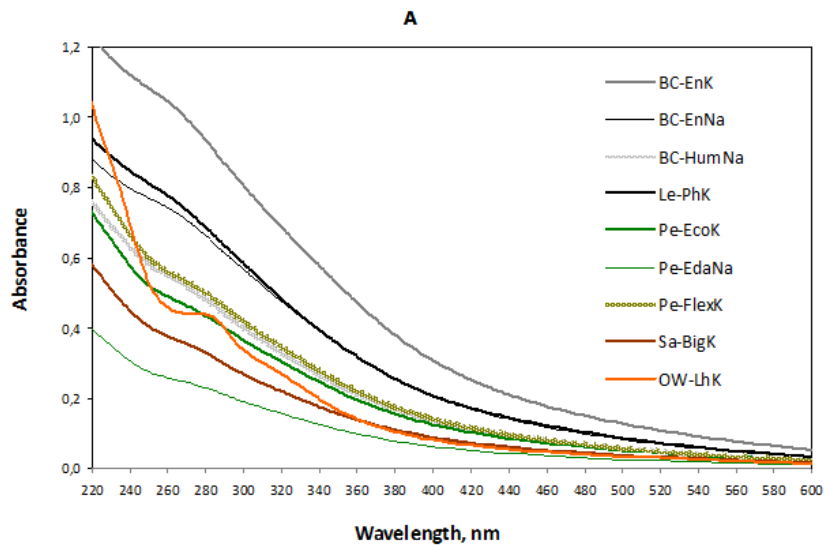


$E_{280/665}$, $E_2:E_3$, $E_4:E_6$, $\Delta \log K$ and Sr have close magnitudes for studied HA derived from HPs from fossils, peat and sapropel and may not be used for the discrimination of peat from fossils HPs.

$SUVA$, $E_{270/400}$, $E_{280/472}$ showed a higher descriptive ability for identification of OM-source of HPs.

Absorption spectra of some HA isolated from coal-, peat-, sapropel- and lignosulphonate-derived humic products

Second-order derivative of those spectra in the UV spectral range

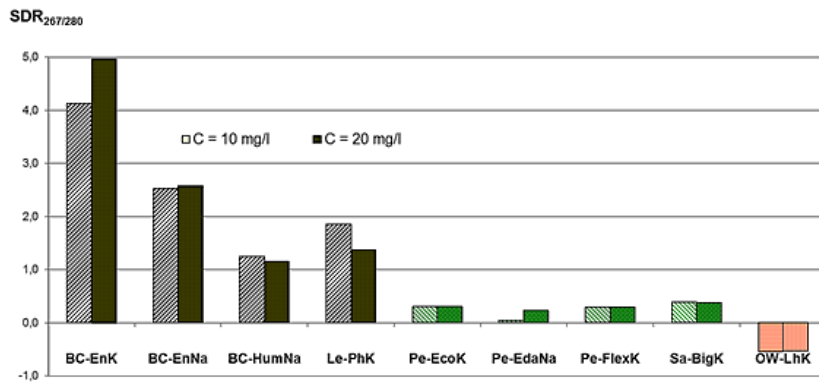


In UV-region spectra of some HA give weak maxima or shoulder around 230 and 280 nm, which can be seen much more distinct as extrema in the second-order derivative of the optical density. The most distinct maxima are observed for the HA from lignosulphonate-derived HP at 230 and 285 nm. The reason is presence of low molecular weight phenolic compounds.

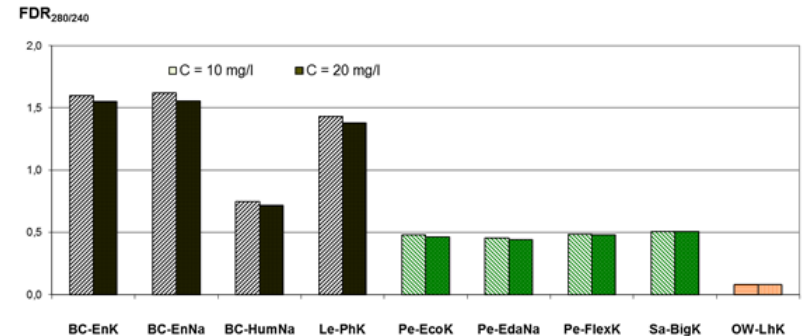
Derivative spectroscopy:

indexes $FDR_{280/240}$ and $SDR_{267/280}$ calculated using first and second-orders derivatives of absorption spectra for solutions of HA ($C = 10$ and 20 mg/L) isolated from various humic products

$FDR_{280/240}$



$SDR_{267/280}$



According to values of $FDR_{280/240}$ and $SDR_{267/280}$, all the studied HA can be segregated in three groups:

- from fossil-derived HPs,
- from peat- and sapropel- derived HPs,
- from lignosulphonate-derived HP.

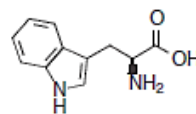
Those indexes show good ability to classify the samples independently of HA concentration in solution.

Fluorescent spectroscopy of DOM

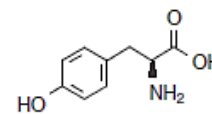
Fulvic acids, humic acids and proteins (due to the presence of phenylalanine, tyrosine and triptophane) are fluorophores

Structures of some common aquatic fluorophores

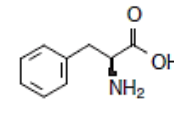
Structure of tryptophan, tyrosine, phenylalanine



trp w Tryptophan



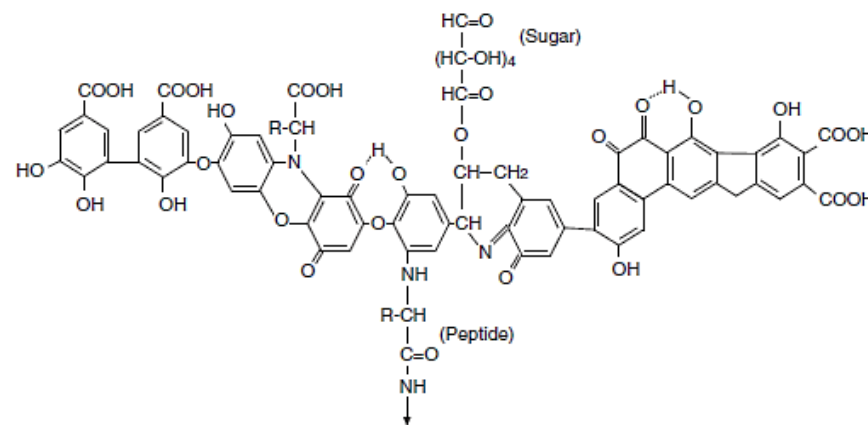
tyr y Tyrosin



phe f Phenylalanin

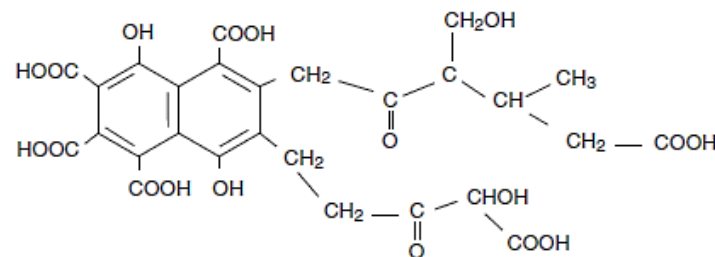
Theoretical humic acid

Stevenson, (1982) cited in Aitken et al., (1985)

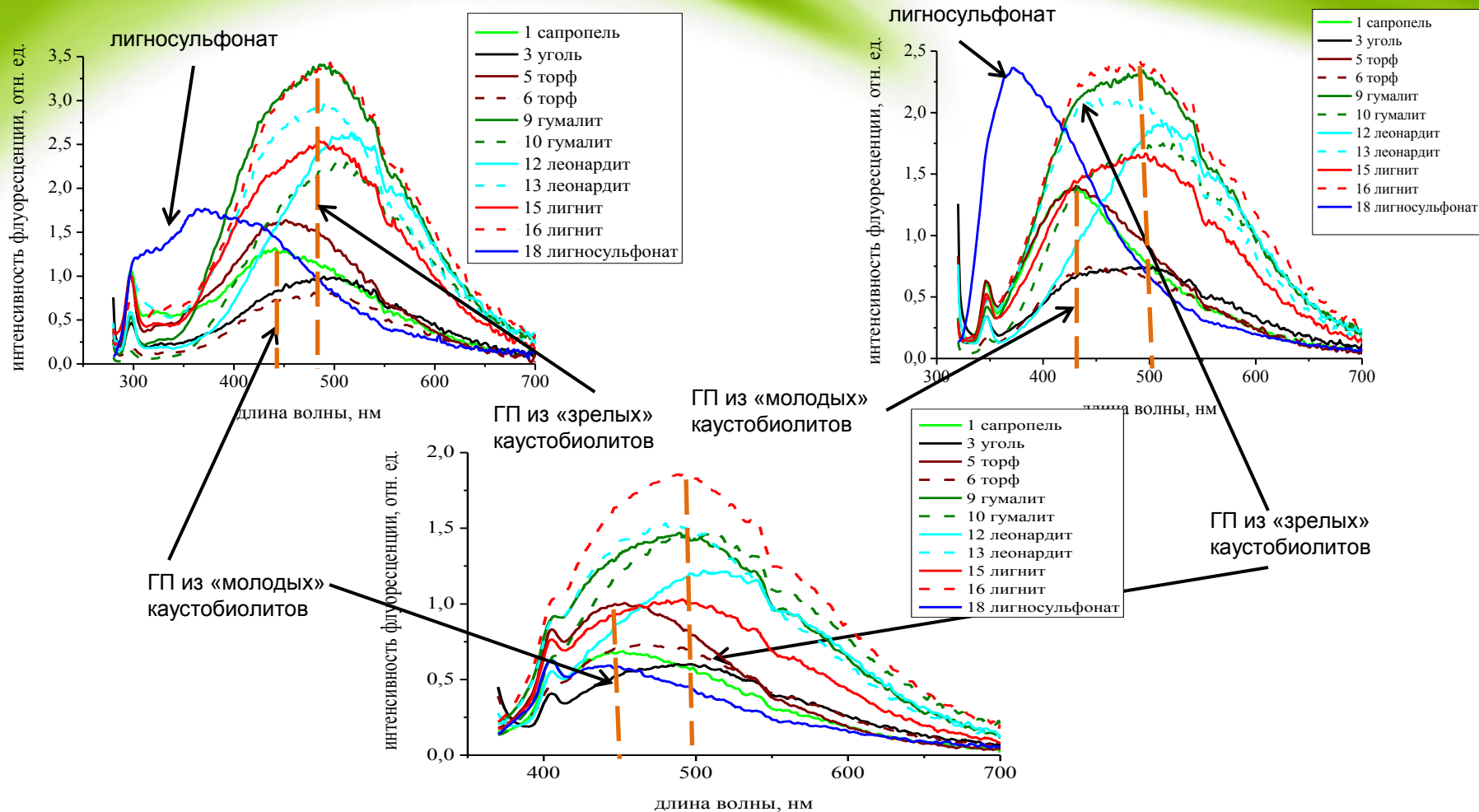


Theoretical fulvic acid

Buffle, (1977) cited in Aitken et al., (1985)

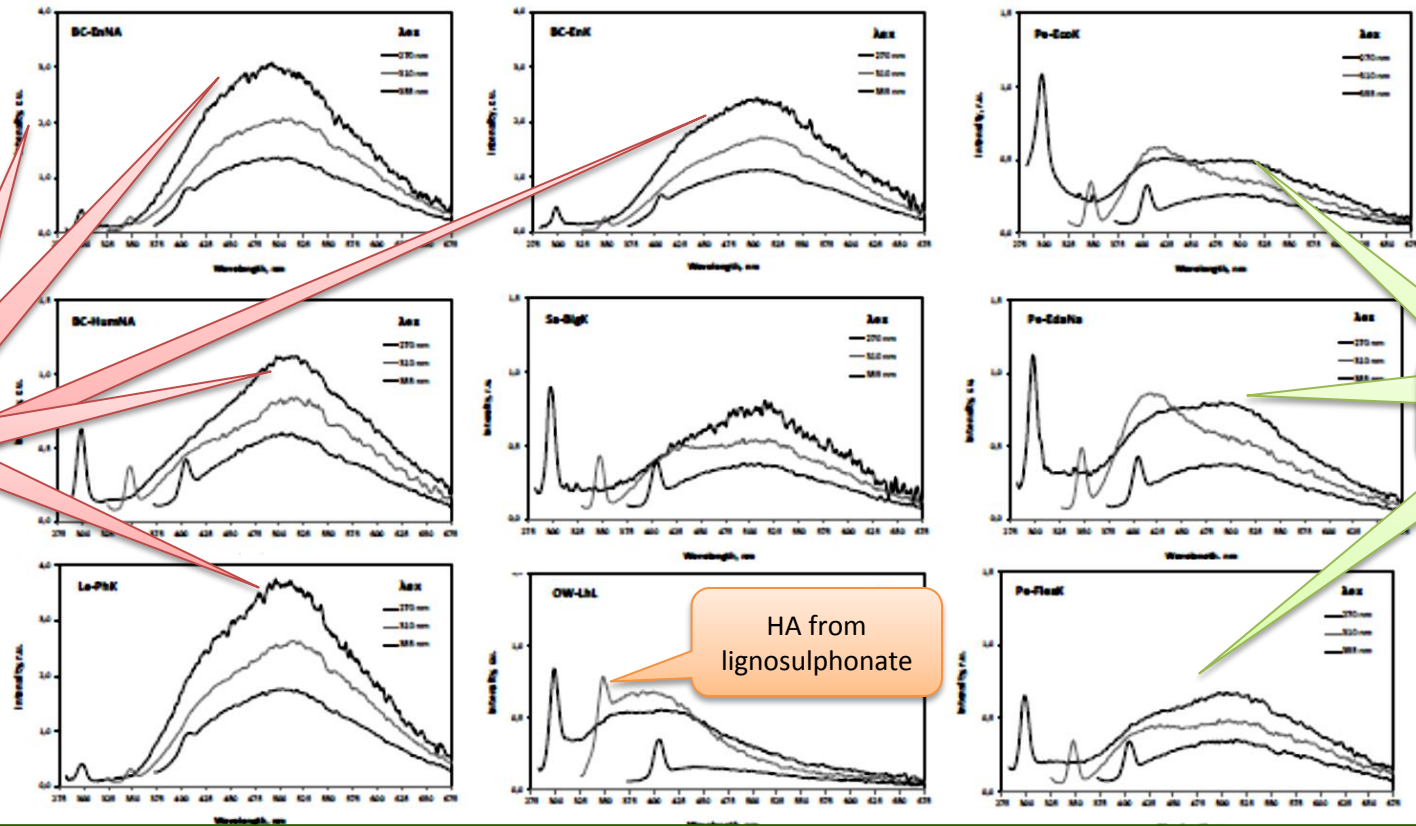


Fluorescence emission spectra of HP from different sources with excitation at 270, 310, and 355 nm



in HA, isolated from peat- and lignosulphonate-derived HPs, fluorescence maximum was accounted at shorter wavelengths than for HA from coal- and sapropel-derived HPs.

Fluorescence emission spectra of HP from peat, lignite, sapropel and lignosulphonate with excitation at 270, 310, and 355 nm



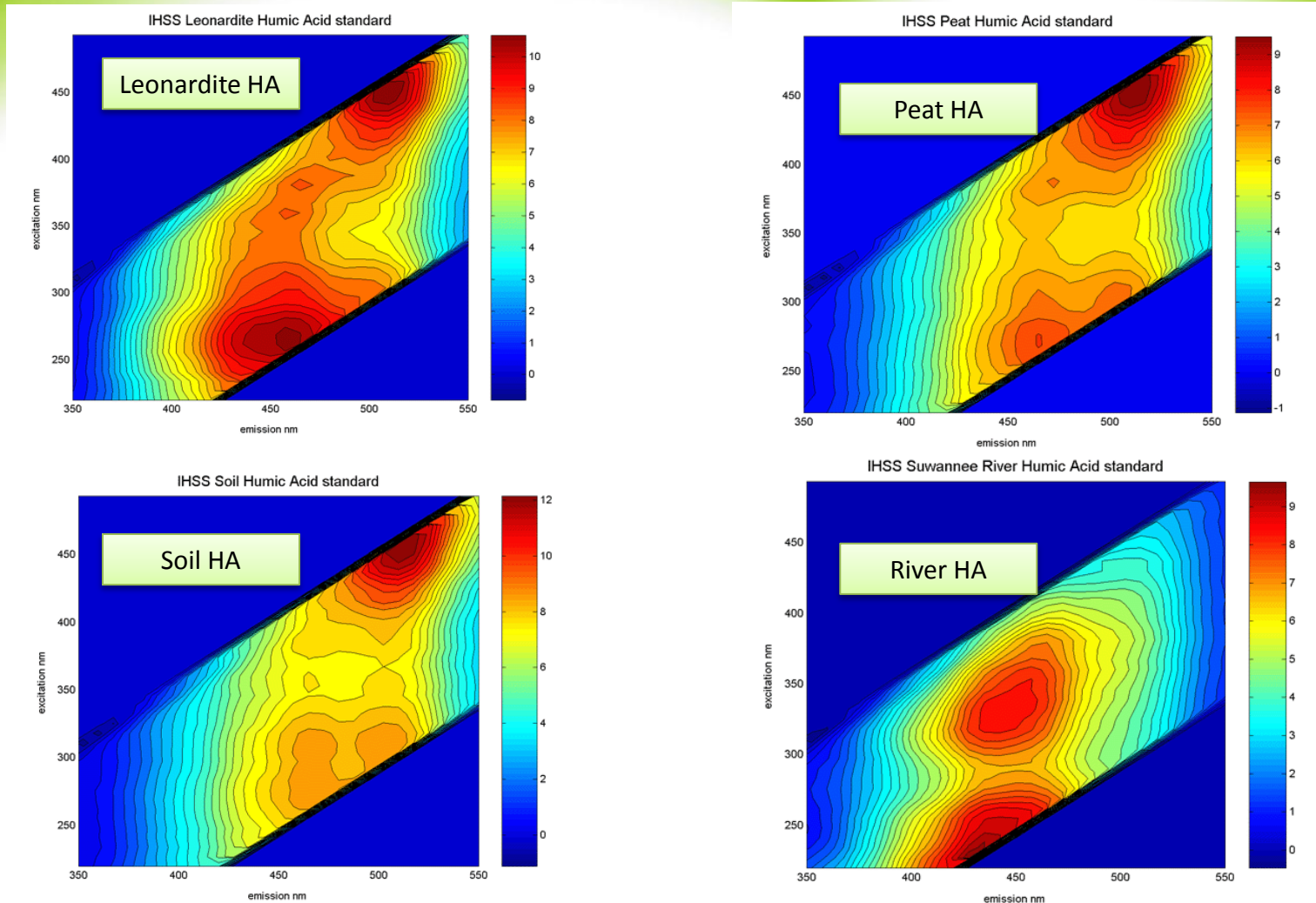
HA from fossils

HA from peat

HA from lignosulphonate

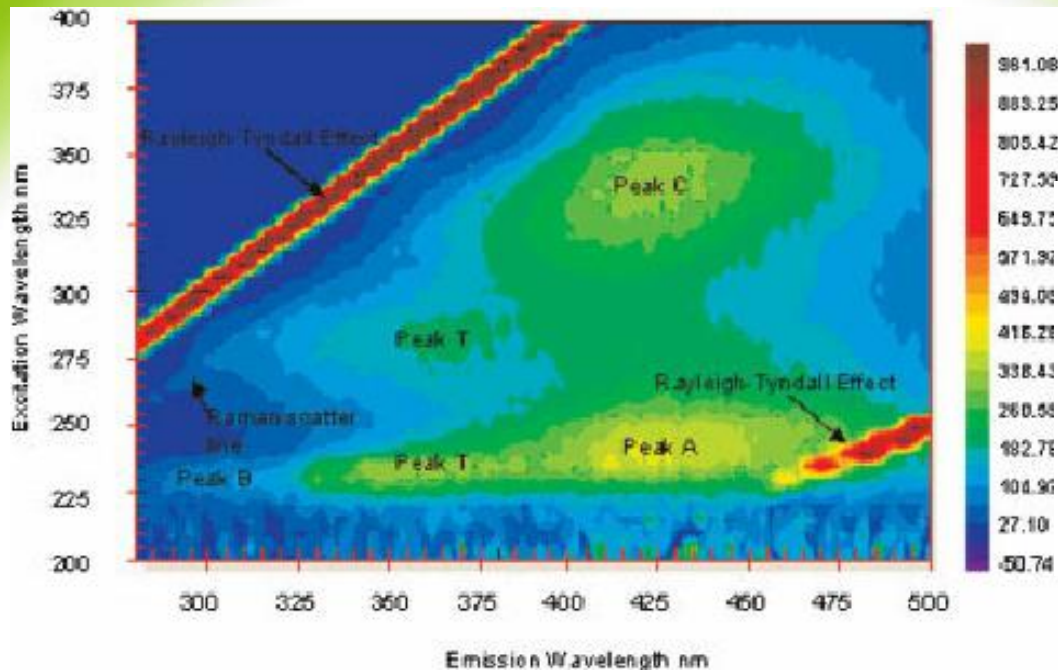
HP from “young” materials show the BS, whether HP from fossils do not

Fluorescence mapping: EEM



Fluorescence properties of IHSS standard Samples

Fluorescence mapping



Major fluorescent components in bulk seawater. FDOM component peaks are designated by letters because the actual chemical composition is unknown at this time

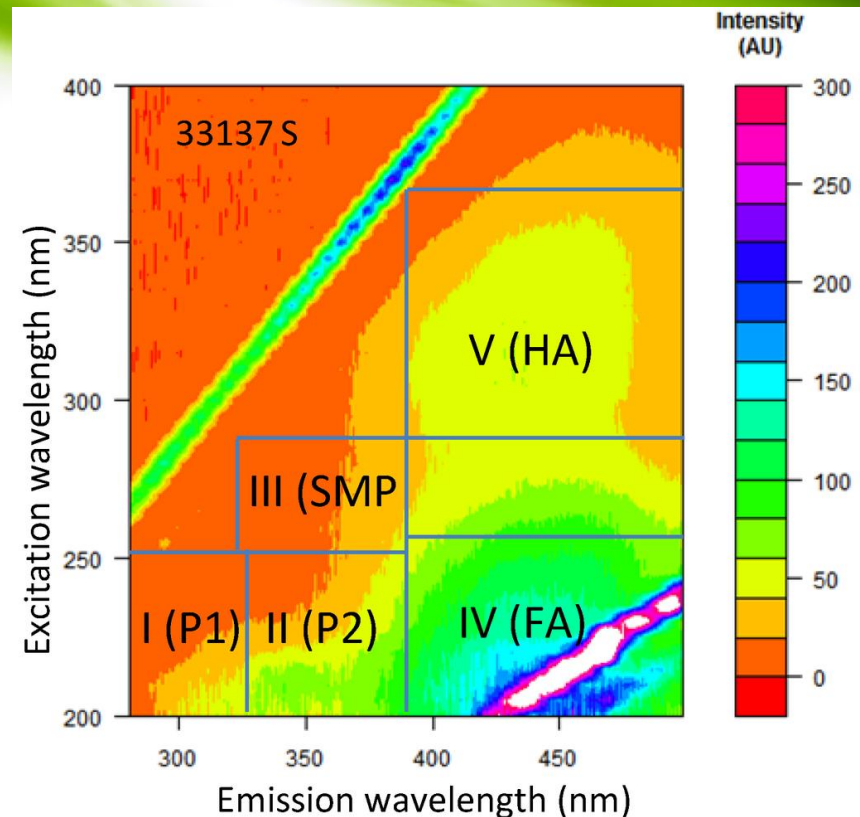
Peak	Ex _{max} (nm)	Em _{max} (nm)	
B	275	310	Tyrosine-like, protein-like
T	275	340	Tryptophan-like, protein-like
A	260	380–460	Humic-like
M	312	380–420	Marine humic-like
C	350	420–480	Humic-like

EEM showing common EEM features and the position of peaks A, C, B and T as named by Coble, 1996

(Hudson et al 2007)

Five major regions in excitation emission matrix (EEM) spectra according to Chen et al. (2003)

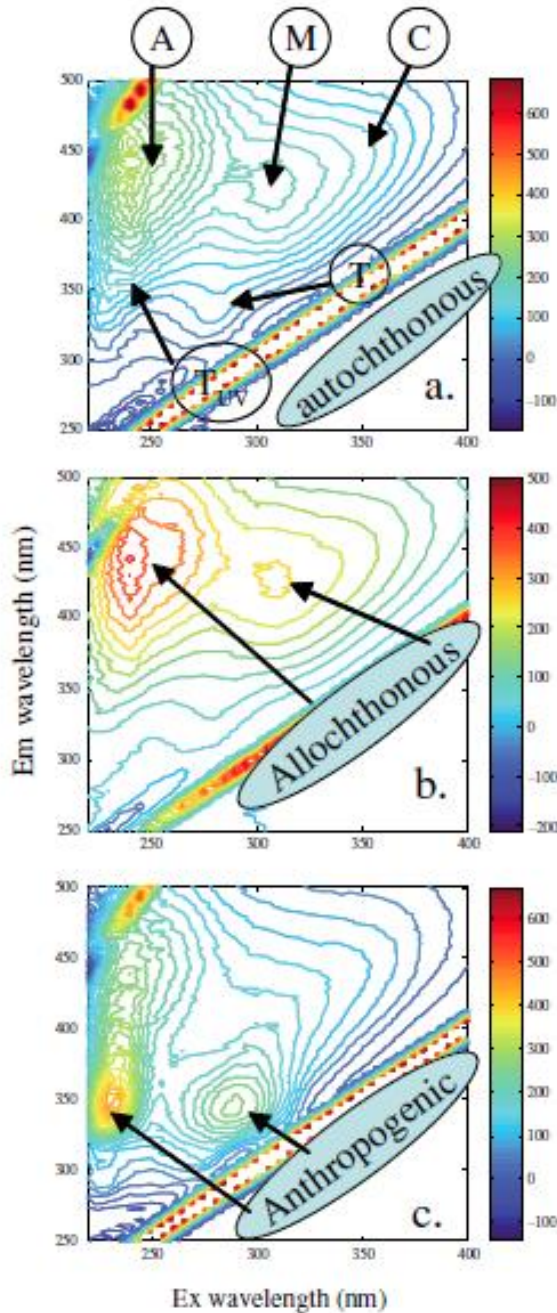
Region	Chemical composition of organic matter
I (P1): Ex:Em 200–250:280–330	lower molecular weight tyrosine-like aromatic amino acids
II (P2): Ex:Em 200–250:330–380	low molecular weight aromatic proteins
III (SMP): Ex:Em 250–340:280–380	large molecular weight peptides and proteins (microorganism related by-products)
IV (FA): Ex:Em 200–250:380–500	fulvic acid type substances
V (HA): Ex:Em 250–500:380–500	humic acid type substances



Five EEM regions from the surface water of Site 33137 (regions plotted according to Chen et al., 2003) (Aryal et al 2014)

SMP, soluble microbial by-product; FA, fulvic acid; HA, humic acid, P1 and P2 = proteins,
Ex = excitation, Em = emission,

Typical examples of the EEM fluorescence spectra of DOM



- EEM fluorescence spectra of DOM collected in the lakes Hongfeng and Baihua showing the excitation/emission (Ex/Em) positions of
- fulvic acid-like (peak M, peak A),
 - autochthonous DOM or fulvic acid-like (peak C),
 - tryptophan-like or anthropogenic DOM (peak T and peak T_{uv}) fluorescence (*Fu et al 2010*)

Thank you for your attention

