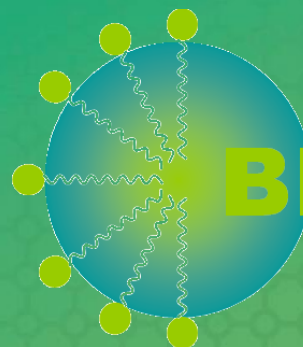




MATERIALS
RESEARCH
CENTRE

/ Brno University of Technology



FACULTY OF CHEMISTRY
BRNO UNIVERSITY OF TECHNOLOGY

BIOCOL
BIOCOLLOID
RESEARCH GROUP

MATERIALS-RESEARCH.EU

The function of carboxyls in the structure of humic acids to binding of organic substances

Jiri Smilek,

Anna Belusova, Michal Kalina and Petr Sedlacek



EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND
INVESTING IN YOUR FUTURE



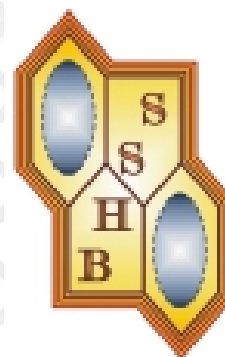
OP Research and
Development for Innovation



Acknowledgement



**NATURAL
ORGANIC
MATTER
RESEARCH**



GRANT AGREEMENT

for the

DATE

between

INSTITUTION /

GRANTEE

GRANT PERIOD

(begin and end)

and

YOUNG INVESTIGATOR RESEARCH GRANT (YIG)

“Interaction of different (methylated) humic acids with organic ionic compounds”

July 12, 2018

**Brno University of Technology, Faculty of Chemistry,
Purkynova 464/118**

CZ-612 00 Brno, Czech Republic

Dr. Jiri Smilek

2 years

from September 1st 2018 to August 31st 2020

International Humic Substances Society (IHSS)

Aims of the YIR project

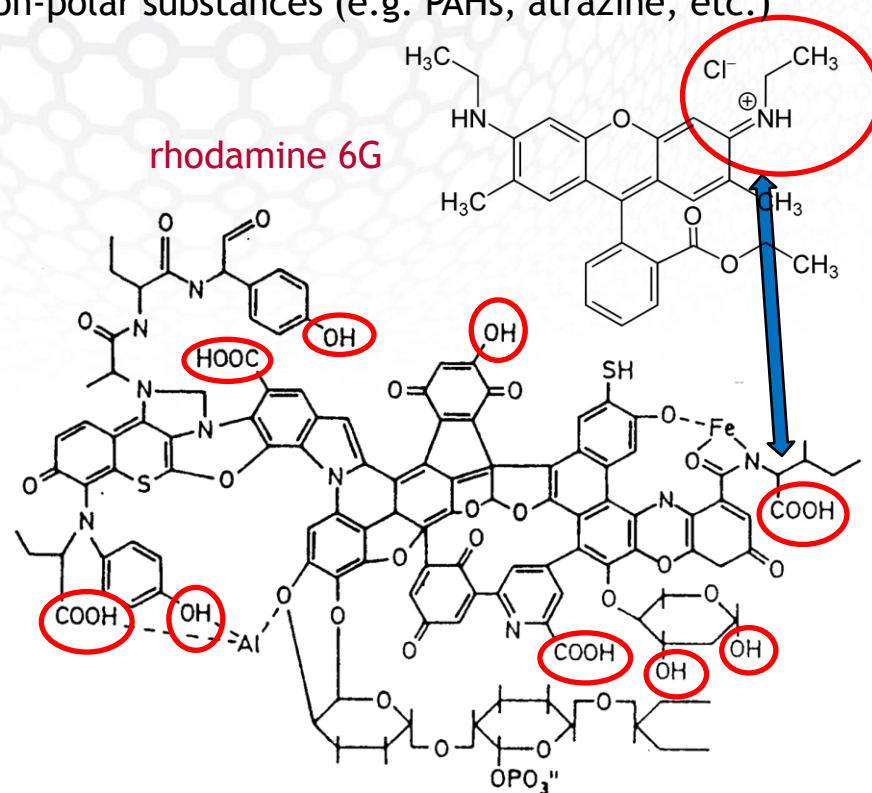
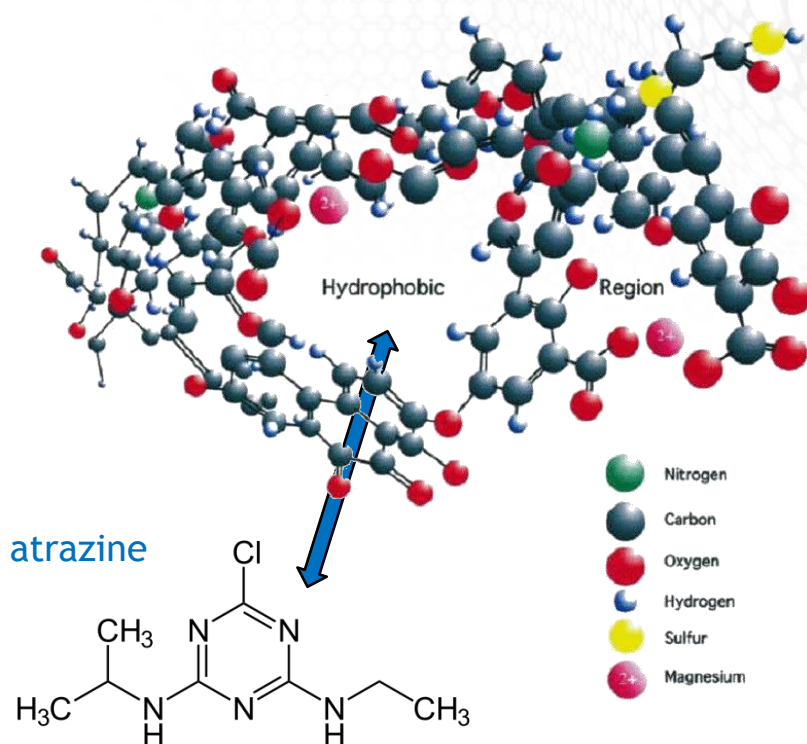
- verify the influence of COOH on the barrier properties of humic substances and interactions with ionic species
- prove the nature of interactions between native/methylated humic substances and ionic compounds
- assess and compare the interactions of HS and ionic compounds with respect to nature and origin of humic substances
- correlate the rate of interaction with advanced physico-chemical characterization of feedstock materials

Reactivity of humic acids

!!! Enormous diversity of different functional groups predict HA as universal binding agent !!!

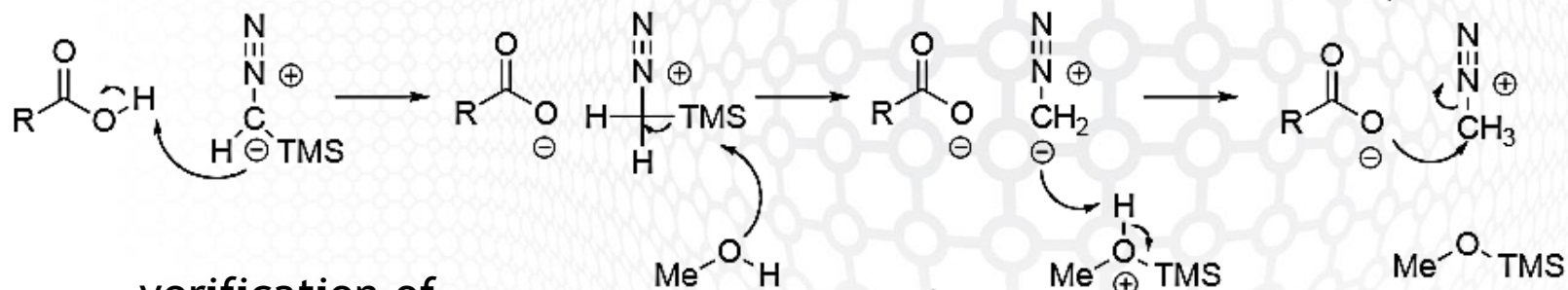
Amphiphilic structure of humic acids

- Hydrophilic functional groups (-COOH, -OH) - ionic compounds (e.g. dyes, heavy metal ions)
- Hydrophobic nature (-aromatic groups) - non-polar substances (e.g. PAHs, atrazine, etc.)



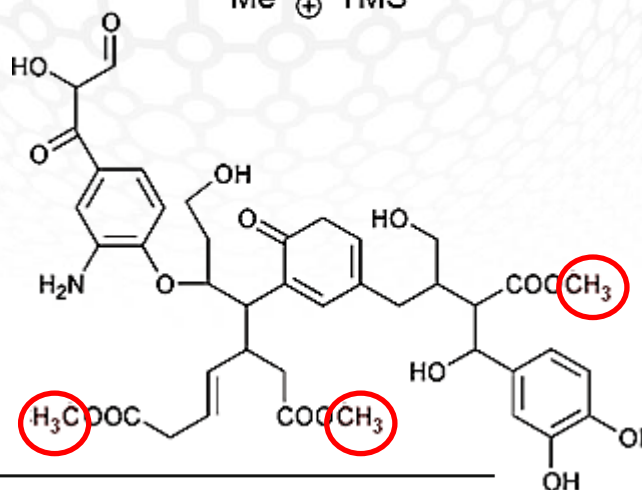
Modification of humic acids ... METHYLATION

Role of -COOH functional groups on the reactivity of humic acids



verification of
methylation

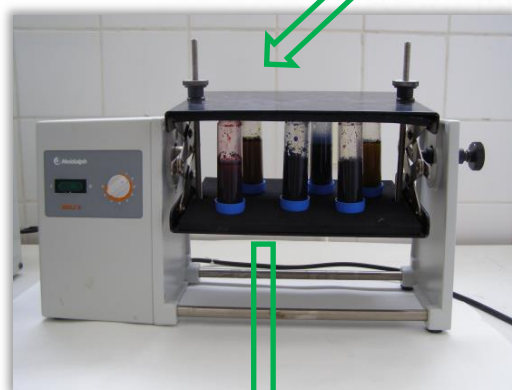
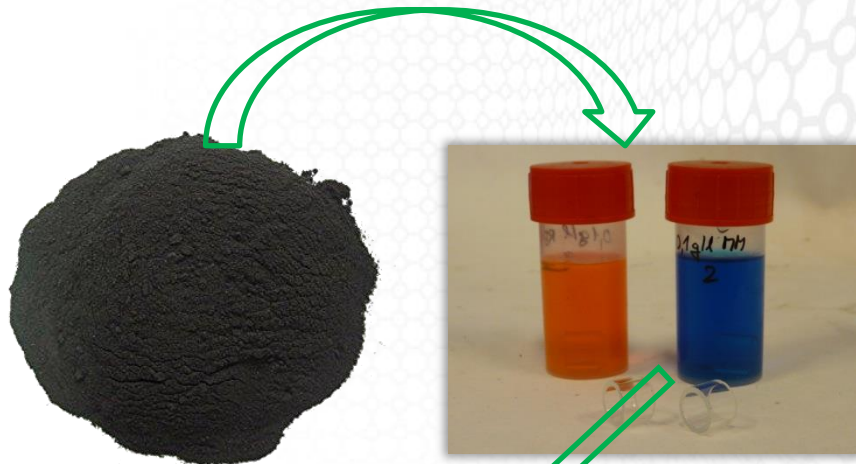
infrared spectroscopy,
titration,
elemental analysis



Sample	C (at.%)	H (at.%)	N (at.%)	S (at.%)	O (at.%)	COOH (mmol/g)	Total acidity (mmol/g)
HA	39.97	40.74	0.81	0.26	18.22	4.24	4.45
MHA	37.72	46.84	0.83	0.09	14.52	0	0

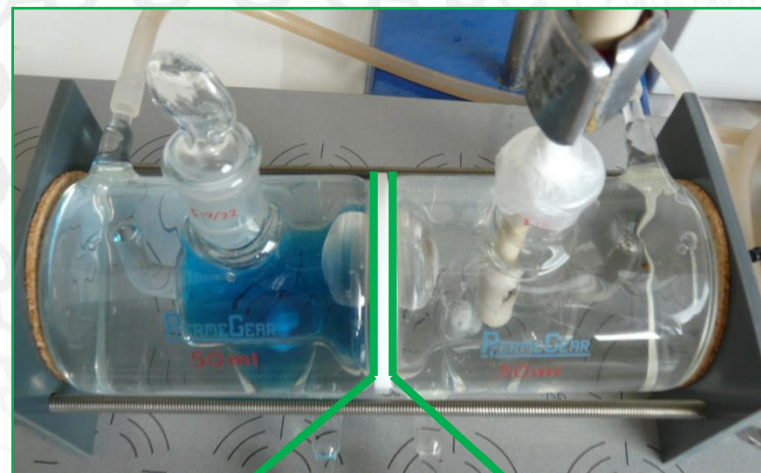
Diffusion techniques vs. sorption experiments

SORPTION EXPERIMENTS



Adsorbed mass
 % mass removal

DIFFUSION TECHNIQUES



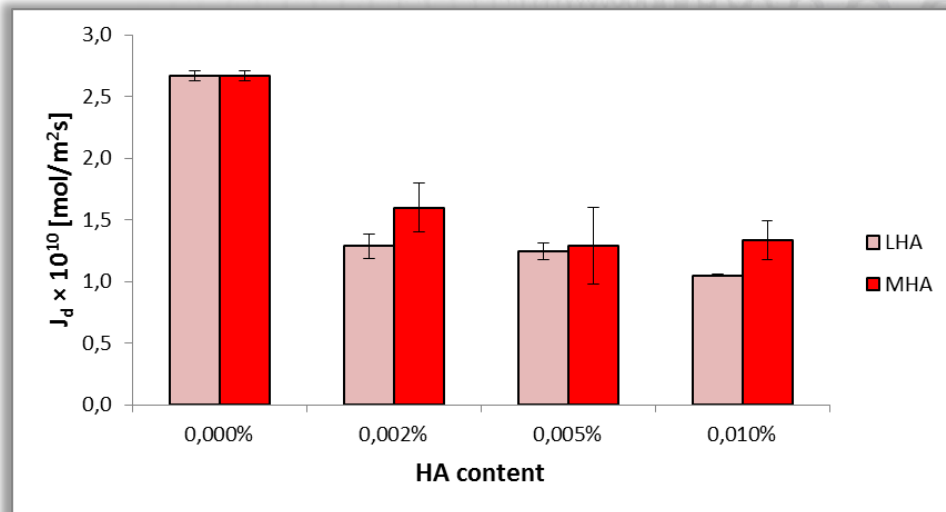
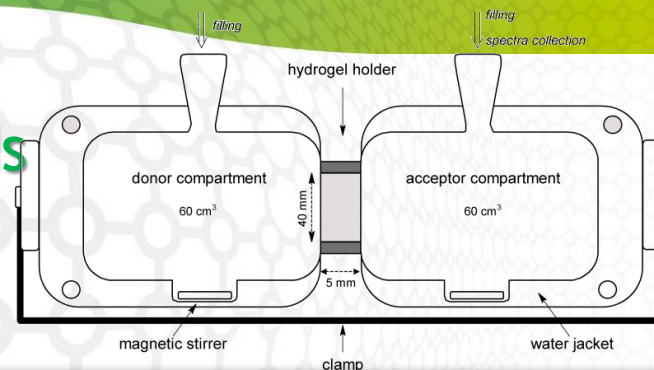
J_d
 diffusion flux

t_{bt}
 break-through
 time

Diffusion results

stationary & transient diffusion methods

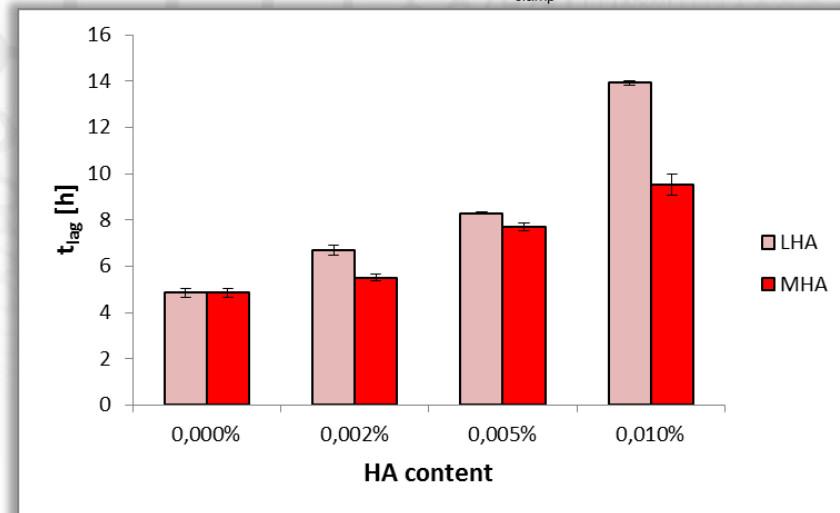
- through-diffusion in diffusion cells



... steady-state diffusion flux

decreases with the HA content!

→ small effect of methylation



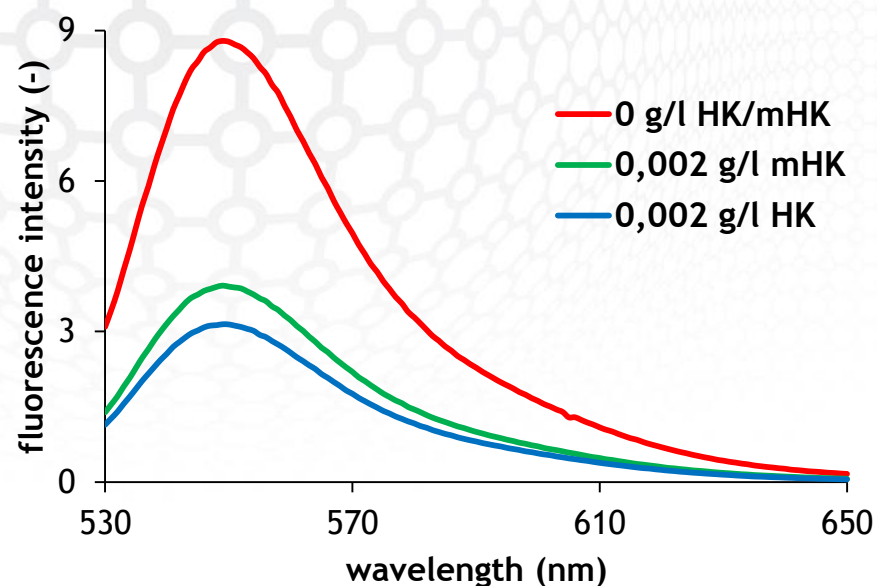
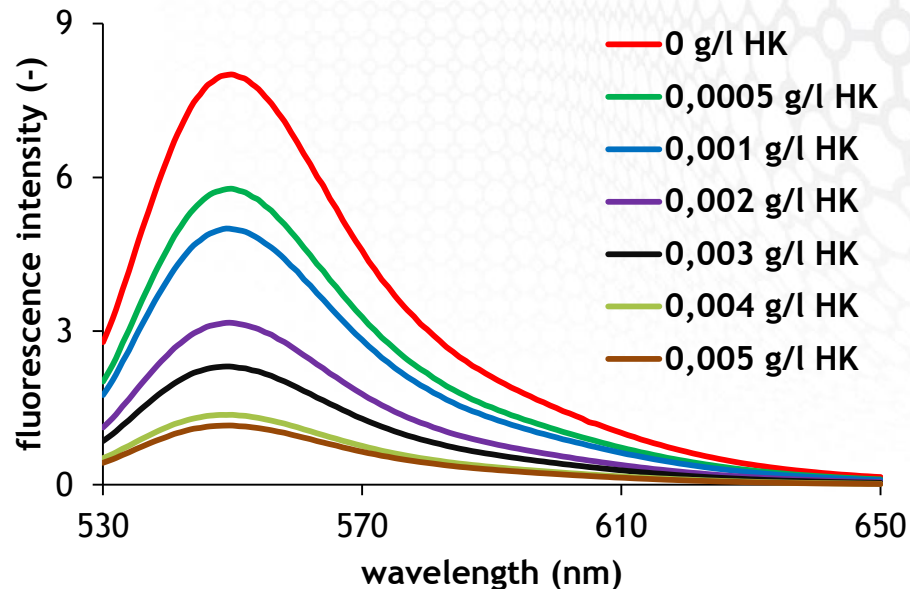
... break-through time

increases with the HA content!

→ caused by immobilizing interactions

Advanced spectroscopic techniques (FLUO)

- quenching of rhodamine fluorescence in presence of HA
- comparison of native / methylated humic acids



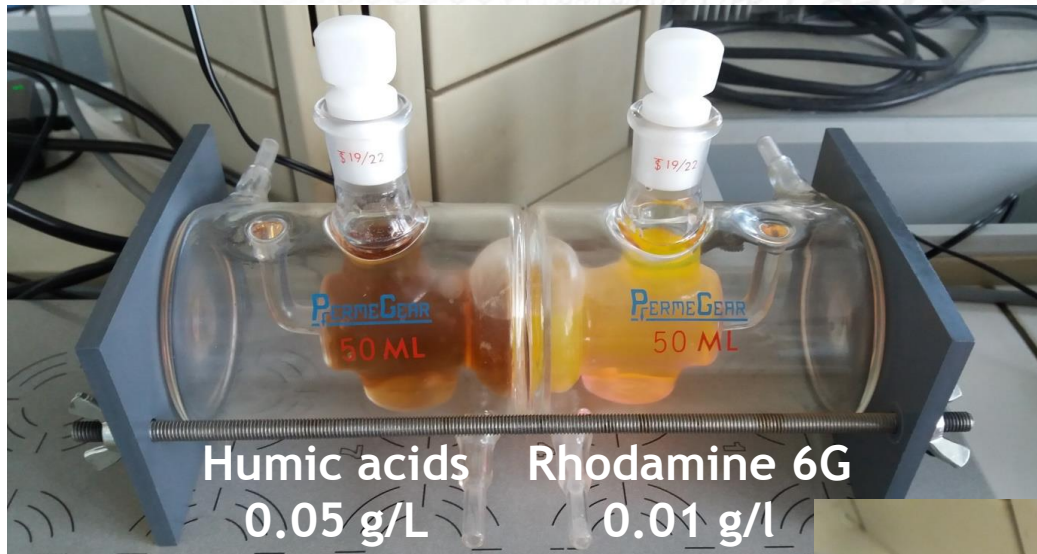
➤ quenching of rhodamine fluorescence higher for native HA

a premise that **MUST BE** verified !!!



methylated HA show less interactions with rhodamine 6G in comparison with native

Dialysis experiments



Beginning of experiment

$$K_{app} = \frac{[c_{bonded}]}{[c_{free}]}$$

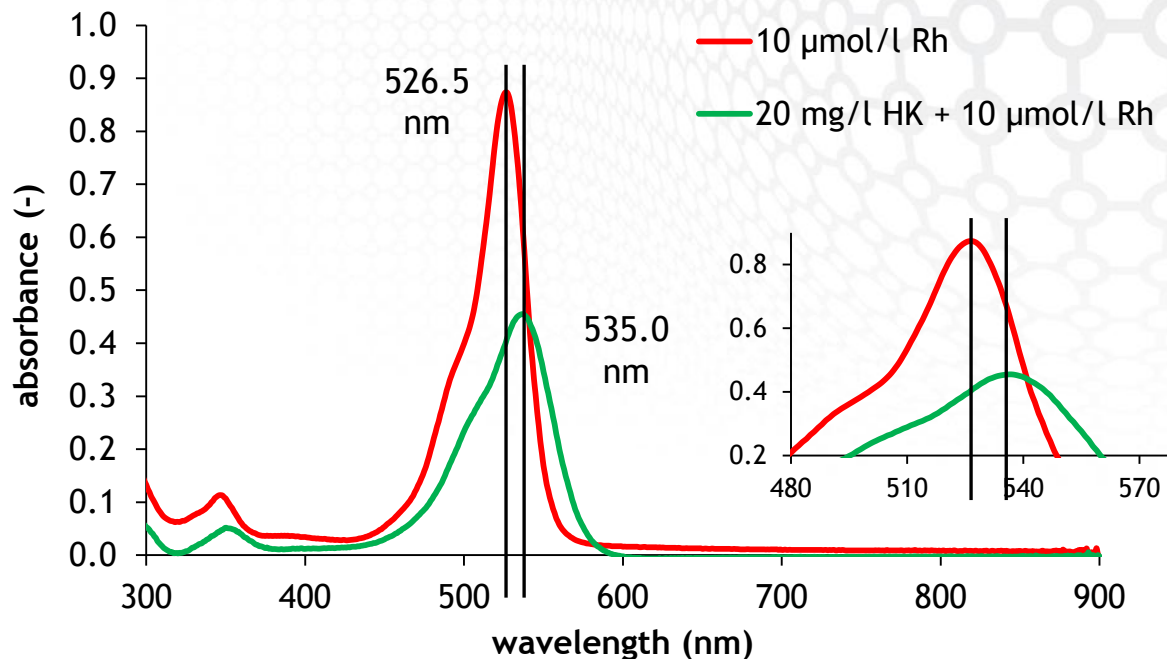
c ... rhodamine concentration

- membrane: Spectra/Por (3.5 kDa)
- method: UV-VIS spectroscopy
- output: app. equilibrium constant
- different concentration of HA and rhodamine 6G
- native vs. methylated humic acids



Differential UV-VIS spectroscopy

- verification of the nature of interactions
- structural changes in rhodamine after the interaction with HA
- UV-VIS spectra - rhodamine + HA (blank sample HA solution)



bathochromic shift



presence of π - π
interactions

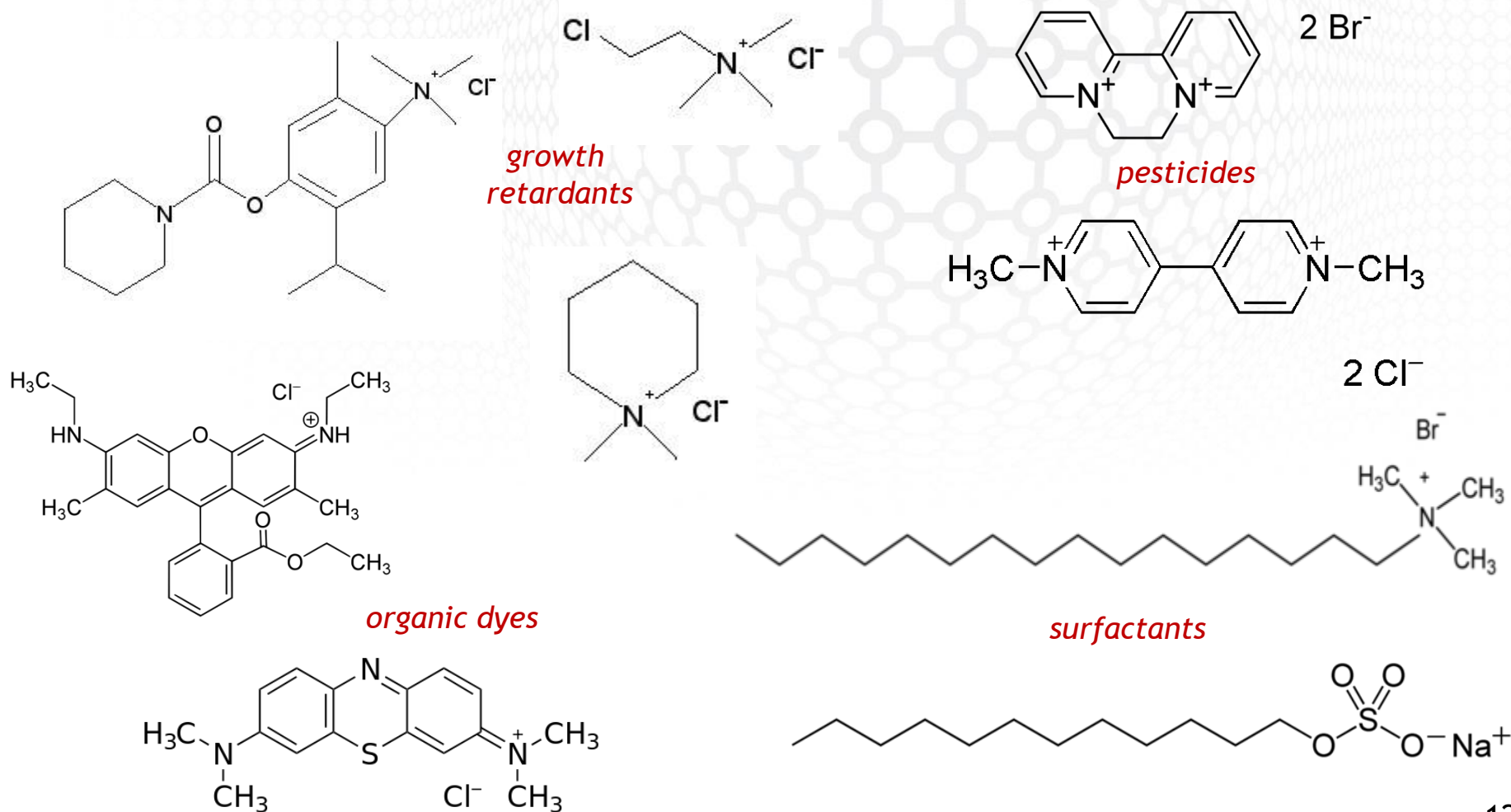
both methylated
and native HA

Humic substances from different sources

- **Elliot soil humic acid standard V (5S102H)**
- **Leonardite humic acid standard (1S104H)**
- **Humic acids isolated from high (e.g. Chernozem) and low (e.g. Cambisol) content of SOM**
- **Humic acids isolated from bulk solid standard soil (Elliot silt loam soil 1BS102M)**
- **Suwannee River NOM (2R101N)**
 - all methylated equivalents ...

Common “pollutants”

Interaction of humic acids with common (non)polar substances



THANK YOU FOR YOUR ATTENTION

... and I AM LOOKING FORWARD TO DISCUSS THE RESULTS ON THE NEXT IHSS MEETING ...



... and thanks all involved members of BIOCOL research group