

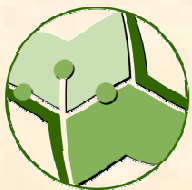
Proposal of evaluation of soil organic matter sorption capacity

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VUPOP Humic Substances in Ecosystems 8, Šoporňa 13.-17.9.2009 Slovakia

Soil organic matter (SOM) is responsible for:

- *stable crop production (production function)*
- *maintaining of good soil quality*

SOM has been widely promoted as a *key indicator* of soil quality and plays an important role in soil. SOM affects

:

- *biological*
- *chemical*
- *physical properties.*



SOM

```
graph TD; SOM([SOM]) --> 1[1. organic matter at various degree of decomposition]; SOM --> 2[2. completely decomposed material (humus)]; 2 --> 2.1[2.1. nonhumified organic material]; 2 --> 2.2[2.2. humified organic material (humic substances)]; 2.2 --> 2.2.1[2.2.1. humic acids]; 2.2 --> 2.2.2[2.2.2. fulvic acids]; 2.2 --> 2.2.3[2.2.1. humin];
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1. organic matter at various degree of decomposition

2. completely decomposed material (humus)

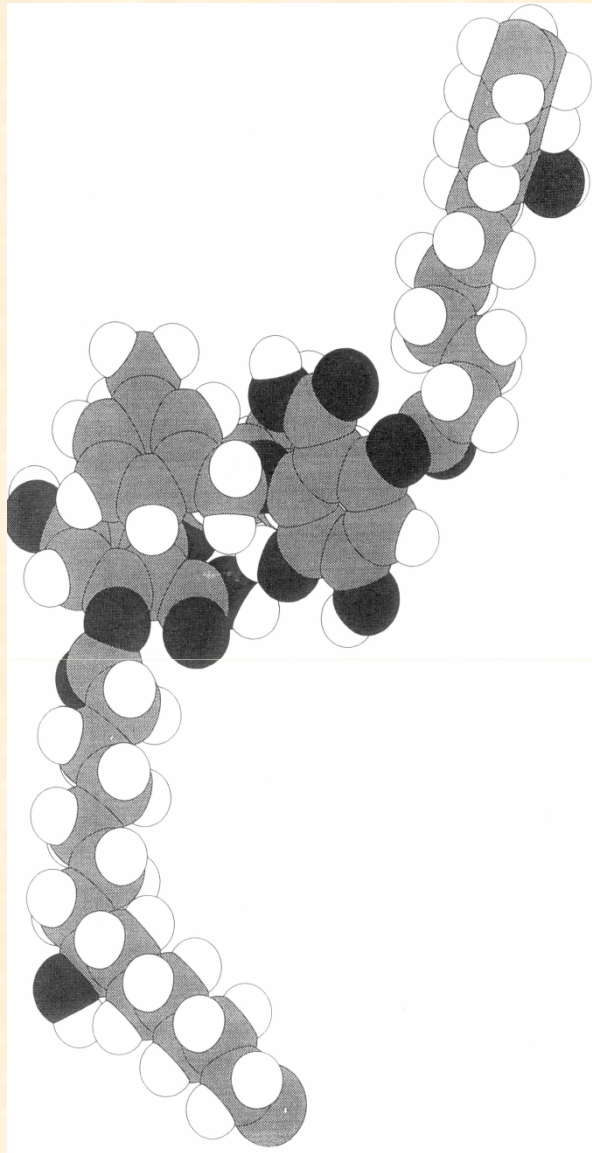
2.1. nonhumified organic material

2.2. humified organic material (humic substances)

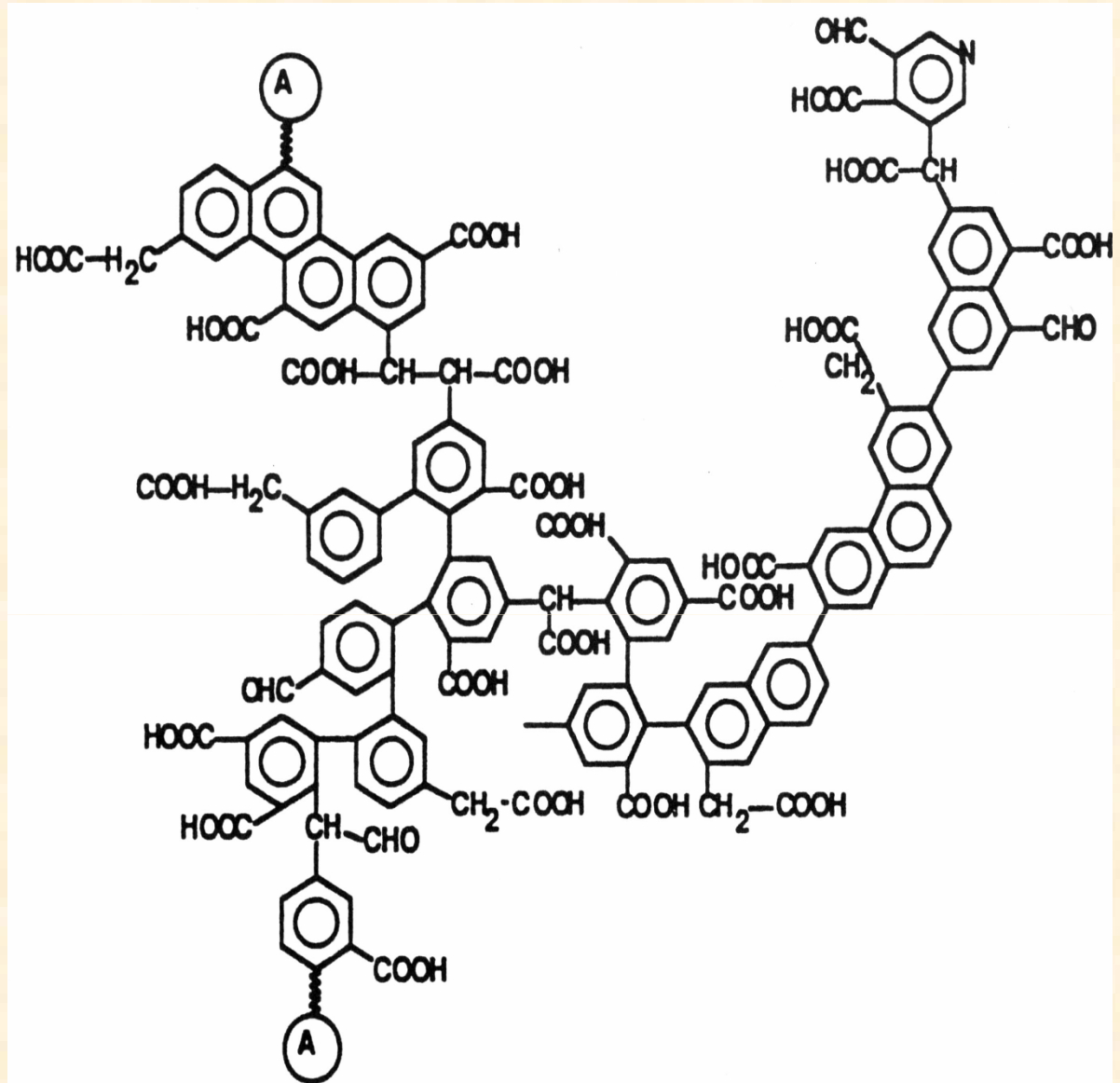
2.2.1. humic acids

2.2.2. fulvic acids

2.2.1. humin

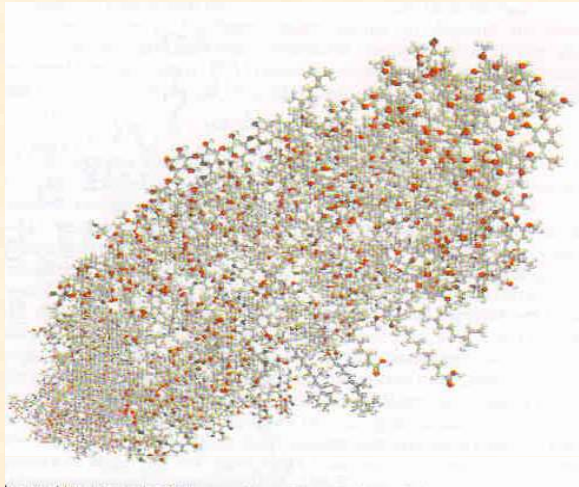


Three-dimensional model of a hypothetical HA (Schulten, 1996)



A two-dimensional structure of HA from andosol (Hatcher et al., 1994)

Humic substances (HS) are amphiphilic with hydrophobic and hydrophilic, internal and external reactive surfaces



Hypothetical structure of a humic acid macromolecules

include lignin-like backbone (mainly part of model), some polysaccharide-like components, protein residues, and alkyl molecules visible in peripheral location

Chestworth, 2008

SOM – high specific surface (up to $800 \text{ m}^2 \text{ g}^{-1}$)
CEC ranging from 150 to 300 cmol kg^{-1}

SOM plays fundamental role in:

Sorption

Binding

Entrapment

of plant macro and micronutrients, variety of chemicals, including inorganic pollutants (heavy metals) and organic substances as enzymes, proteins and xenobiotics

Humic substances– amphoteric compounds with **positive** and **negative** charges

Negative charges - dissociation of protons from **functional groups** in the humic molecule

Two the most important **functional groups**:

- **Carboxyl (COOH)**
- **Phenolic- hydroxyl (Phe-OH)**

Functional groups (COOH, phe-OH) are responsible for:

- Adsorption
- Cation exchange
- Complex and chelation reactions

Humic acids - HA

- substantially larger molecules
- more complex structure

Fulvic acids - FA

- smaller molecules
- less complex

Total acidity : FA > HA

Binding sites : HA > FA

Binding capacity: HA > FA

Forces responsible for adsorption reactions of HS with ionic and non polar substances:

Physical forces
Chemical forces
Hydrogen bonding
Hydrophobic bonding
Electrostatic bonding
Coordination reactions
Ligand bonding
Covalent bonds

Importance of HA chemical structure on HM sorption

Statistically significant Spearman's coefficients of Cu fraction and selected HA parameters

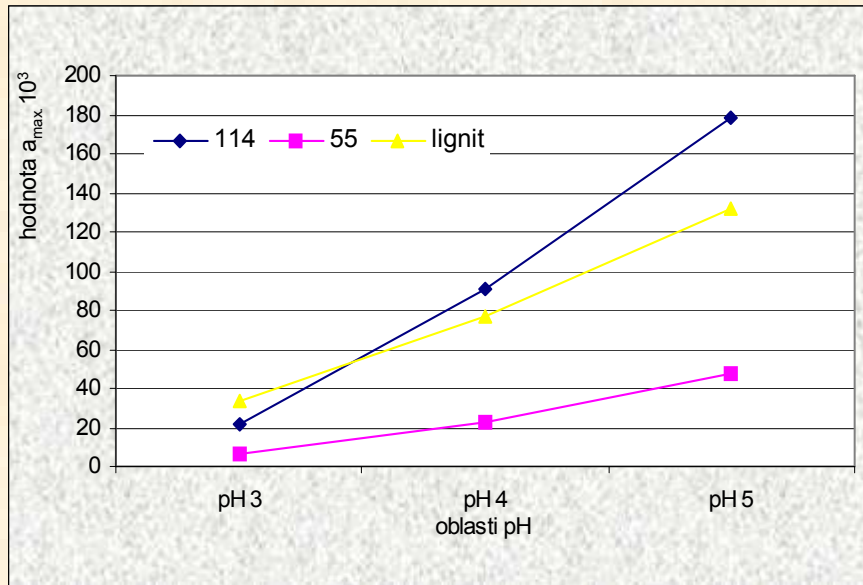
HA parameter	Cu fraction IV (HM associated with SOM)
Corg	0.59*
Cha/Cfa	0.55*
C	0.6*
H/C	-0.72*
Car	0.63*
Caliph	-0.69*
α	0.59*

Barančíková & Makovníková, 2003

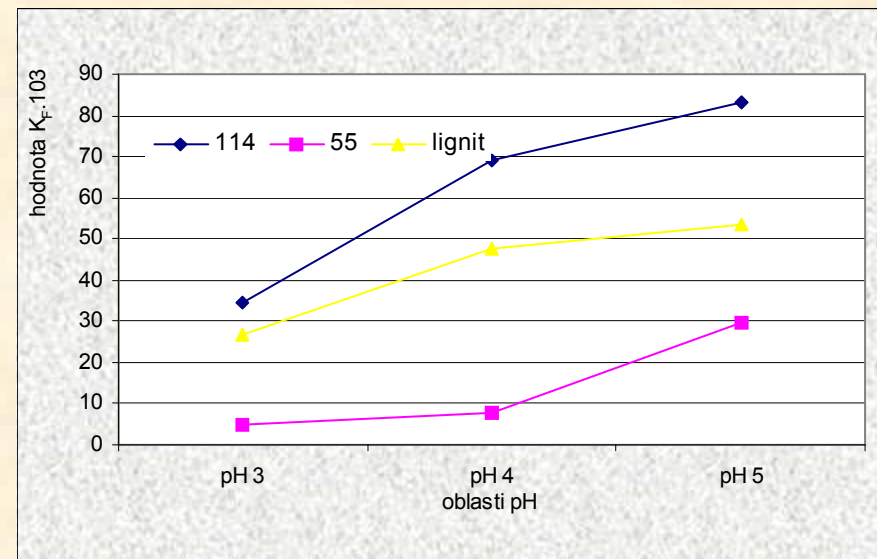
Influence of HA sorption characteristics at soil detoxifications Cd sorption

Source of HA	-COOH	Caliph	Car	α
	meq/1 g HA	%	%	%
Chernozem 114	4,2	33,7	42,2	55,6
Cambisol 55	2,76	48,6	29	37,7

Maximum sorption capacity a_{max} in context with pH



Freundlich distribution coefficient K_F in context with pH



Madaras et al., 2004

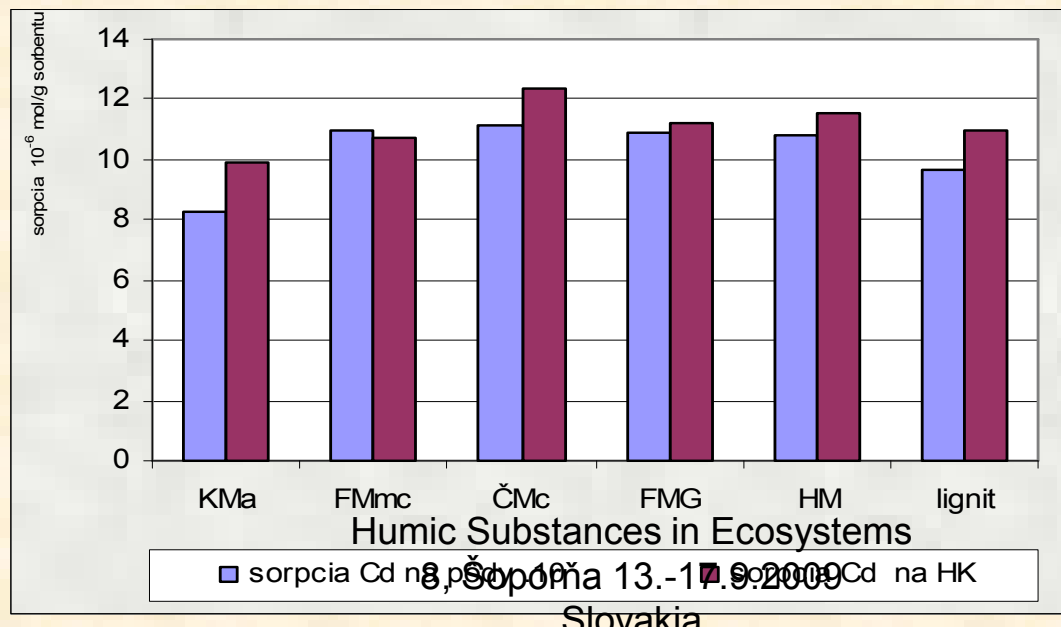
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Soil and HA parameters

soil

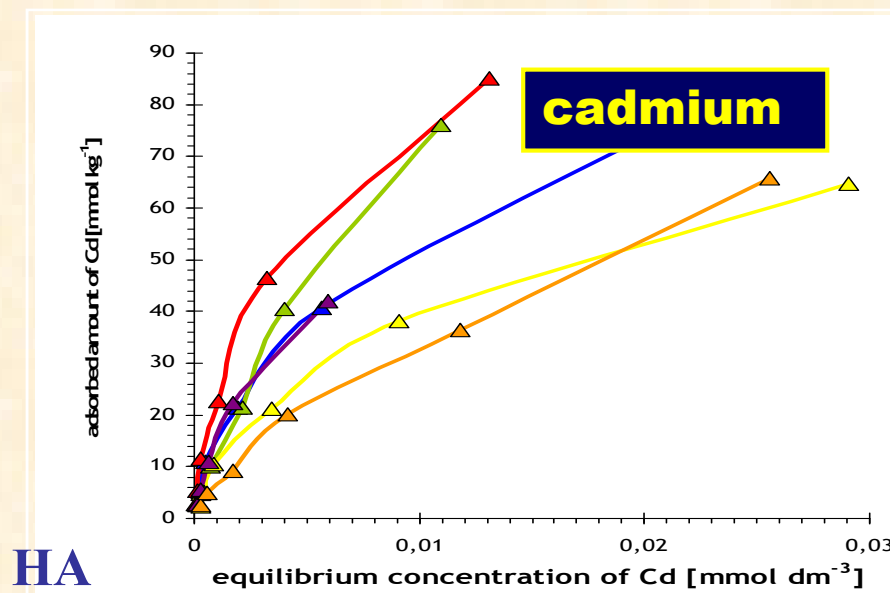
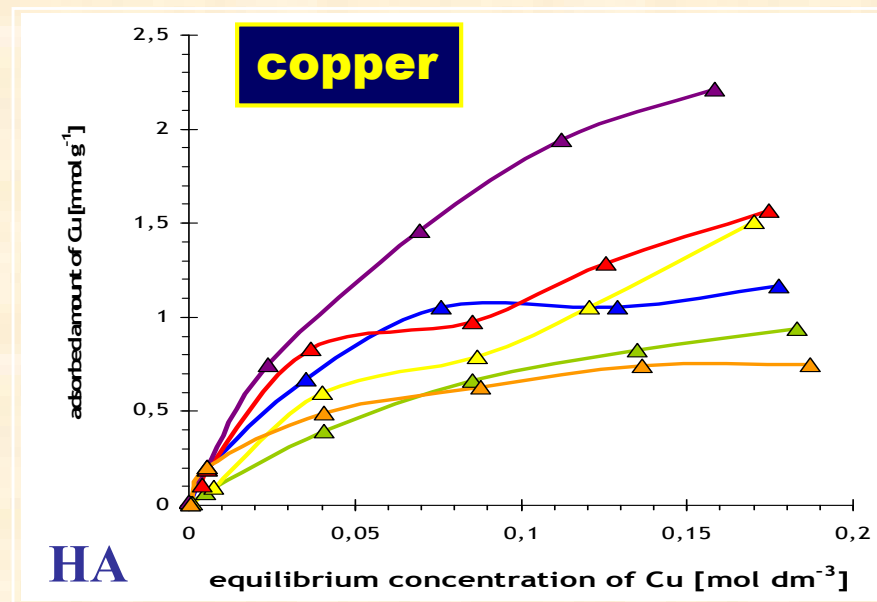
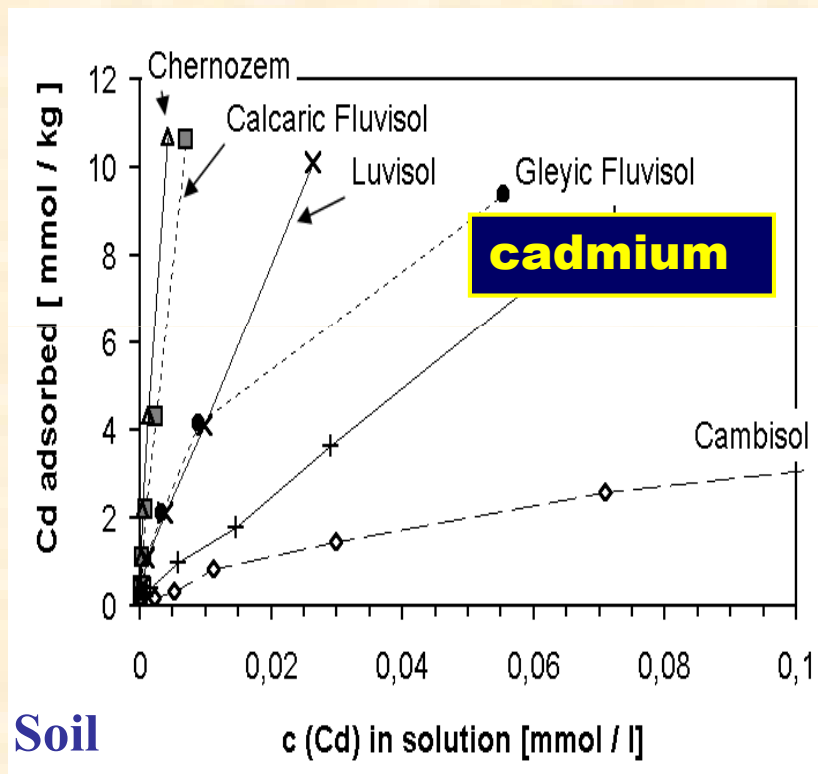
HA

Soil type	pH (CaCl ₂)	Corg (%)	Q ₆ ⁴	COOH meq/1gHA	Caliph (%)	Car (%)
Calcaric Fluvisol	7.89	0,97	3,73	3,62	41,8	37,2
Gleyic Fluvisol	5.46	1,43	4,83	3,1	43,1	34,7
Calcaric Chernozem	7.77	1,16	3,80	4,2	33,7	42,2
Orthic Luvisol	5.56	1,09	3,96	2,52	46,9	32,8
Dystric Cambisol	3.63	3,00	6,06	2,76	48,57	28,99



Makovníková et al., 2003

Adsorption isotherms of soil and HA



chernozem fluvisol 1 luvisol fluvisol 2 cambisol lignite

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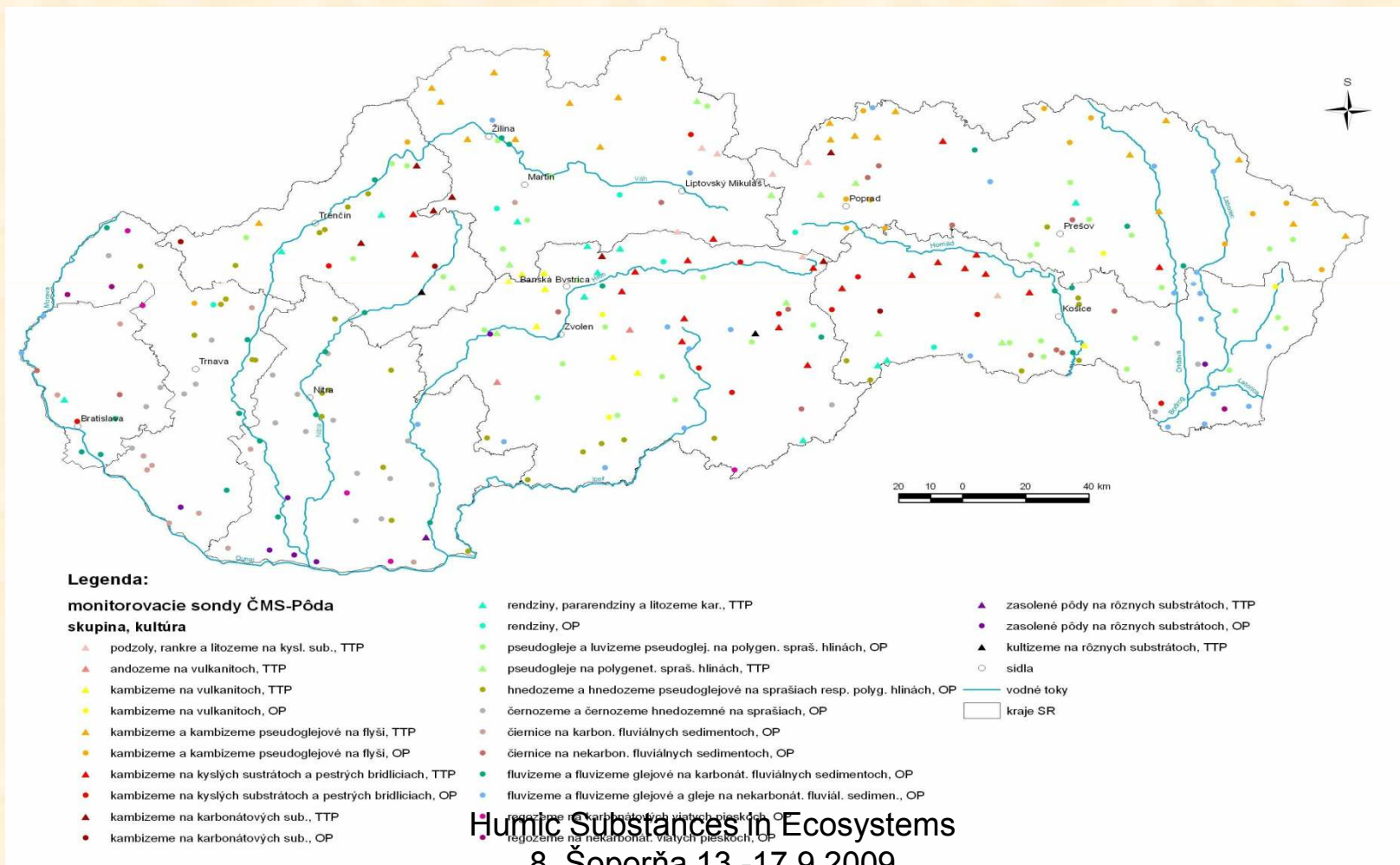
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Soil monitoring

➤ The **basic network** of monitoring sites (300) at 5 years regular interval (agriculture and alpine soils)

➤ The **key monitoring sites** (21) at 1 year regular interval



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Monitoring of soil organic matter

Basic monitoring network

- quantitative parameter: Soil organic carbon SOC (%)
% humus = SOC x 1,724
- basic qualitative parameters: C_{HA} / C_{FA} , Q_6^4

Key monitoring localities

selected parameters of chemical structure of humic acids:

- Elemental analyses (C H N)
- Carboxylic groups (COOH meq/1 g HA)
- UV-VIS spectra ($E_{6}^{1\%}$)
- ^{13}C NMR spectra

Main parameters of soil organic matter which influence its sorption capacity

Content of soil organic carbon (SOC)

Ratio of HA and FA carbon (C_{HA}/C_{FA})

Optical parameter of HA (Q^4_6)

Content of carboxylic groups (COOH)

Degree of aromaticity ($\alpha = (C_{ar} + C_{aliph})/C_{ar} \times 100$)

Proposal of humus sorption capacity assessment on agricultural soils

category	SOC (%)	$C_{HA/FA}$	Q_6^4	COOH (meq/1g HA)	α (%)
I.	≥ 2	> 1	< 4.5	> 4	> 50
II.	1.5 - 2	0.8 - 1	4.5 - 5	3 - 4	40 - 50
III.	< 1.5	< 0.8	> 5	< 3	< 40

I. - high humus sorption capacity

II.- medium humus sorption capacity

III. - low humus sorption capacity

Notice: Humus belongs to particular category if fulfil minimum three qualitative parameters

I. – high humus sorption capacity

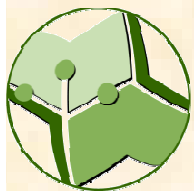
- **Chernozem**
- **Phaeozems**
- **Andosols**

III. Medium sorption capacity

- **Luvisols**
- **Rendzinas**
- **Regosols**
- **Fluvisols**
- **Part of Cambisols**

III. – low humus sorption capacity

- **Planosols**
- **part of Cambisols**



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Thank you for your attention

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