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Interaction of Dissolved Organic Matter with Free Metal Ions in Heavy Metal Contaminated Soil Solution

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Introduction

Free or non-complexed metal ion (FMI) is considered as the key factor in determining heavy metal bioavailability and toxicity (Li et al., 2009).

Dissolved organic matter (DOM) is a polyfunctional complex and heterogeneous mixture of components. It can interact with metal ions to form organometal complexes, thus strongly affecting the metal speciation(Huguet et al., 2010).

Donnan membrane technology has advantage of allowing simultaneous measurement of multi-metal free ions at low concentration, with minimized disturbance of soil chemical equilibrium.(Li et al., 2009)

Optical properties of DOM in aquatic system have been investigated for decades. Optical measurements (3D Fluorescence Spectroscopy and UV-visual Absorption Spectra) are relatively simple to obtain and non-destructive.

It has been proved that they offer the possibility to determine the types and relative concentration of DOM in aquatic system. (qualitative and semi-quantitative) (Huguet et al., 2009; Chin et al., 1994; Helms et al., 2008)

A strong correlation was observed between optical properties and the average molecular weights(Chin et al., 1994; Helms et al., 2008).

Wrobel et al. (2003) found that both bridging between small molecules and complexation/chelation by individual molecules are involved in metal ion binding to humic substances obtained from compost.

Scientific Questions

1. Donnan Membrane Technique is suitable for different kinds of soil to measure free metal ions?

2. For various kinds of soil solution, what's the relationship between FMI and DOM properties (size fractions and optical properties)?

⇩

to interpret the mechanism that DOM strongly facilitates the transport of heavy metals

Materials & Methods

15 French soil samples:

groupe I : sols non contaminés
groupe II : origine géogénique
groupe III : contamination par apport de PRO
groupe IV : contamination d'origine inorganique sur Mortagne-du-Nord
groupe V : autres contaminations d'origine inorganique

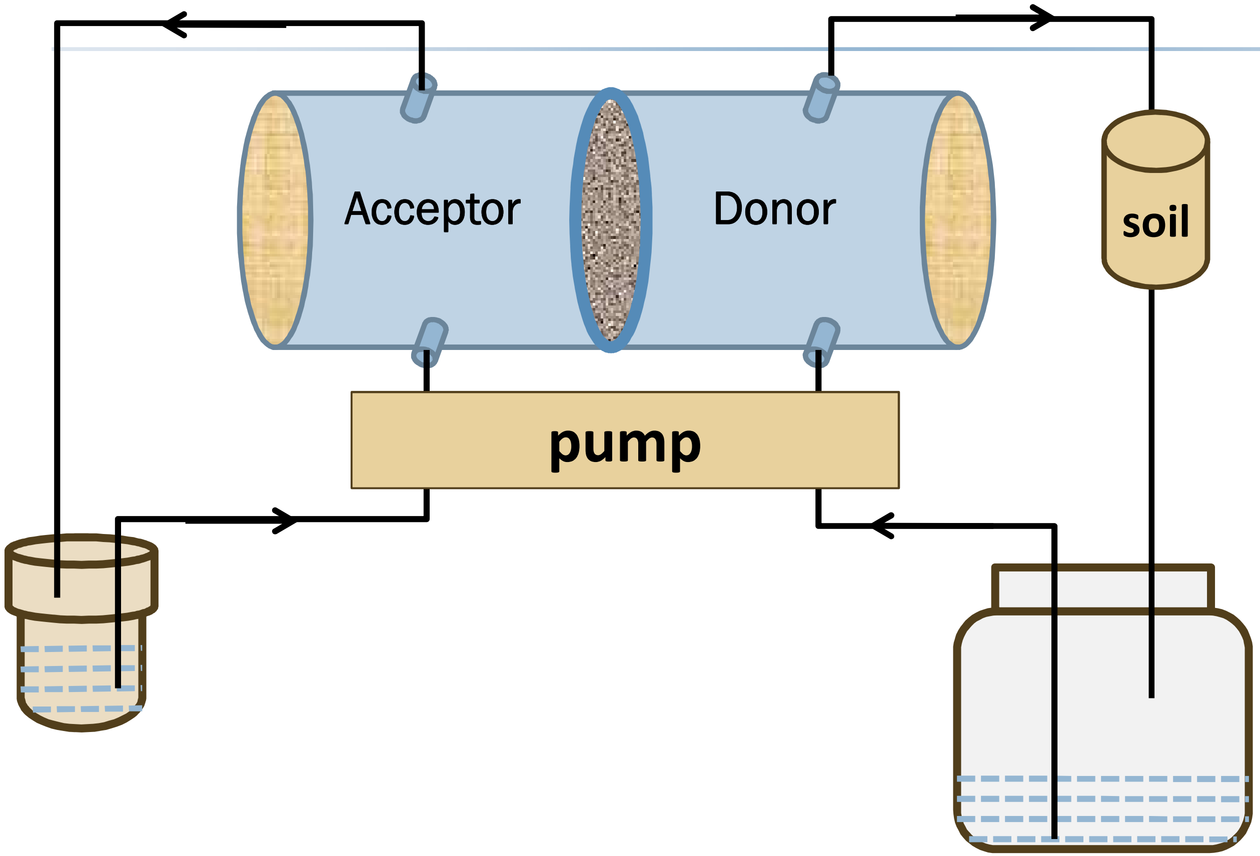
↘ Weak acid /neutral and alkaline

9 Chinese soil samples:

groupe I : sols non contaminés
groupe II : contaminated by acid mine drainage

↘ Paddy soil, very low pH, high clay, reductive

Donnan Membrane Technique



Initially:

Donor: 100 mL 2mM $Ca(NO_3)_2$

Acceptor: 20 mL 2mM $Ca(NO_3)_2$

Equilibrium:

Donor**: free ions** together with inorganic and **organic complexes**

Acceptor: **free ions** and inorganic complex

Donnan membrane: semipermeable, negatively charged, cation exchange membrane

(Temminghoff et al., 2000)

$$\left(\frac{C_{i,\,don}}{C_{i,\,acc}}\right)^{1/Z_i} = \left(\frac{C_{j,\,don}}{C_{j,\,acc}}\right)^{1/Z_j}$$

Free metal ions in donor solution

$$C_{\textit{organic complexes}} = C_{\textit{total dissolved metal}} - C_{\textit{corrected free ion}}$$

Activity: Davies

Concentration unit: Molal

Temperature: 25 deg C

pH: Calculated from mass balance

Ionic strength: To be calculated

Component name: Select from list

● Total concentration: 0 Molal

○ Fixed activity

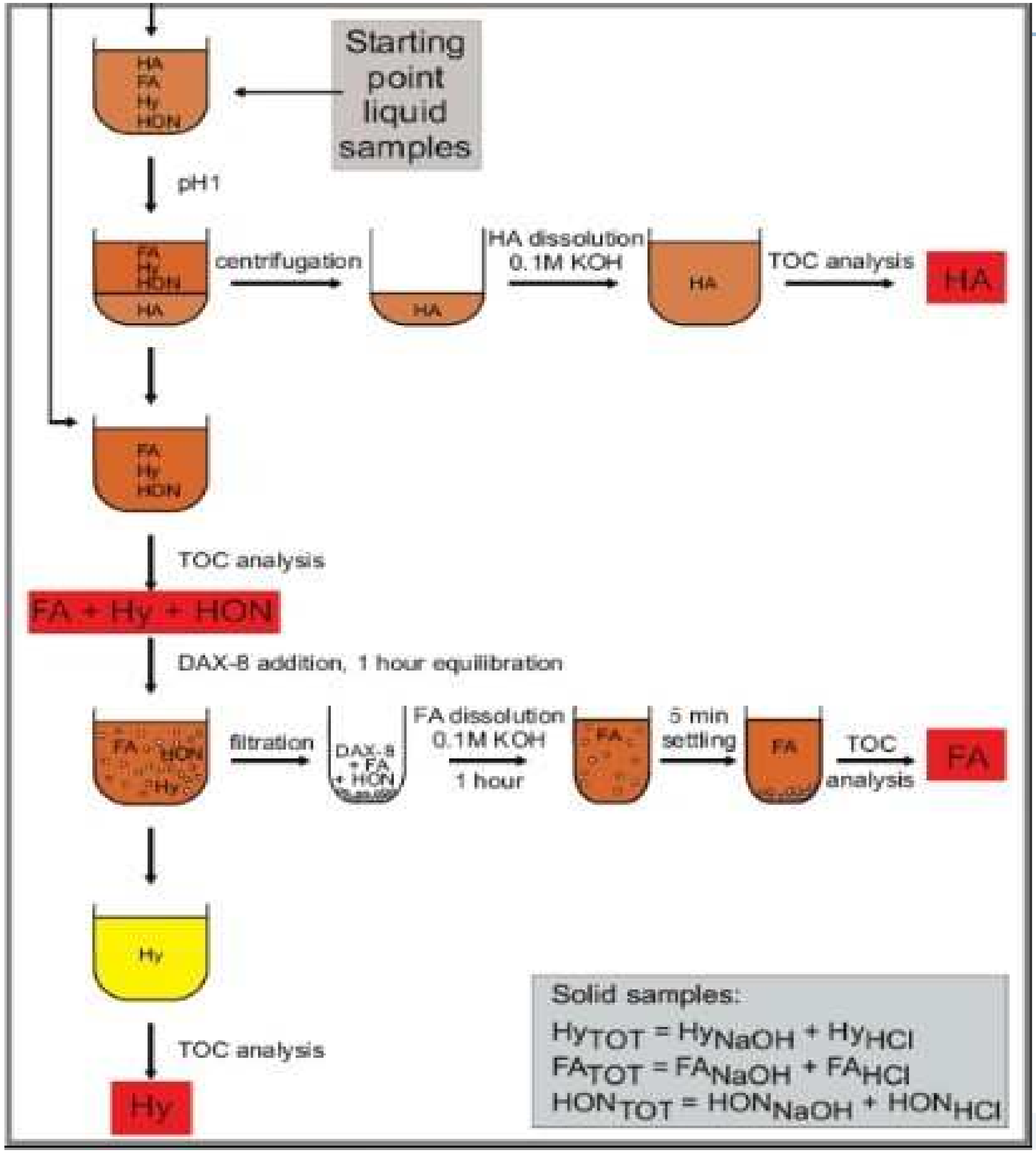
☐ Show organic components

NICA-Donnan model

C_{FMI} modelled

(Li et al, 2009)

Chemical Batch Experiment of Isolating the Humic Substances



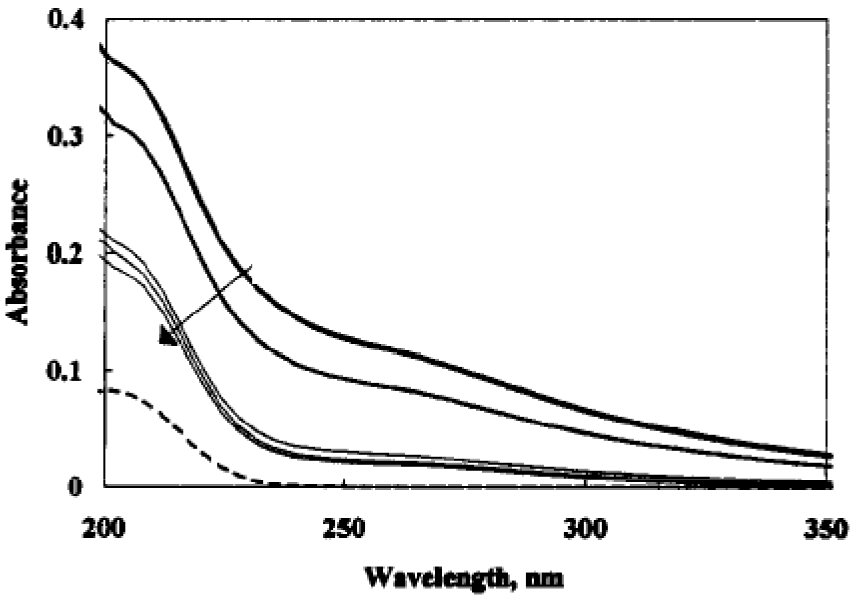
☺Traditional , widely used , but procedures are laborious

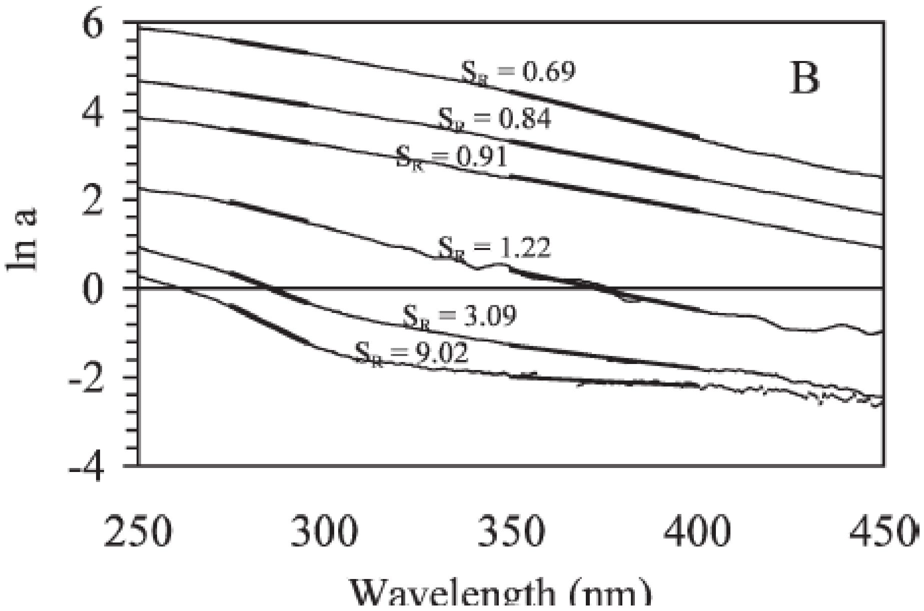
☺ It makes HA and FA quantification dependent on the chemical extraction procedure rather than an intrinsic property of the HS.

☺ Specific conditions in the isolation procedure, which affect the chemical behavior of HS, can change their classification in terms of HA and FA.

(**van Zomeren and Comans, 2007**)

UV-visual Absorption Spectra





$$\mathrm{SUVA} = \frac{\mathrm{Abs}_{254}}{[\mathrm{COD}]} \times 100$$

Percentage of aromaticity

$$a_\lambda = a_{\lambda_{\mathrm{ref}}} e^{-S(\lambda - \lambda_{\mathrm{ref}})}$$

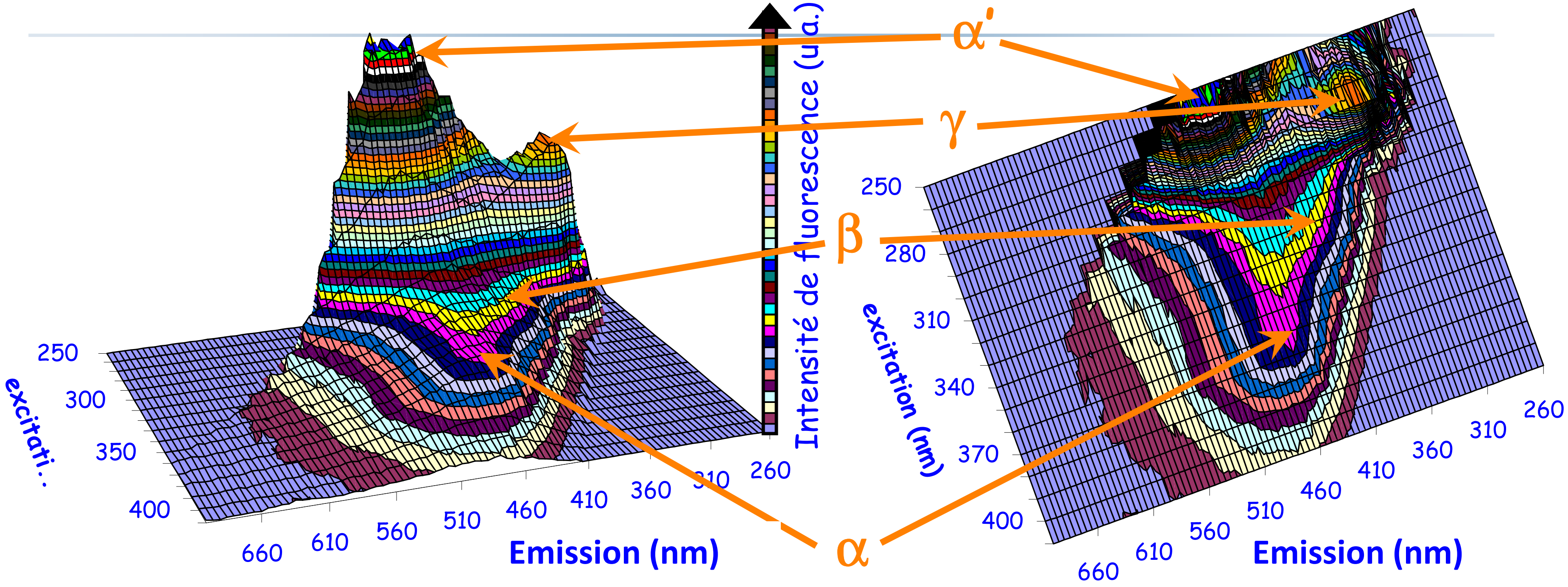
S correlates strongly with molecular weight of isolated fulvic acids but not humic acid

$\mathrm{E2:E3} = \mathrm{Abs}_{250}/\mathrm{Abs}_{365}$ ⇒ To track changes in the relative size of DOM molecules

$\mathrm{E4:E6} = \mathrm{Abs}_{465}/\mathrm{Abs}_{665}$ ⇒ DOM aromaticity

(Hayase and Tsubota, 1985; Helm et al., 2008)

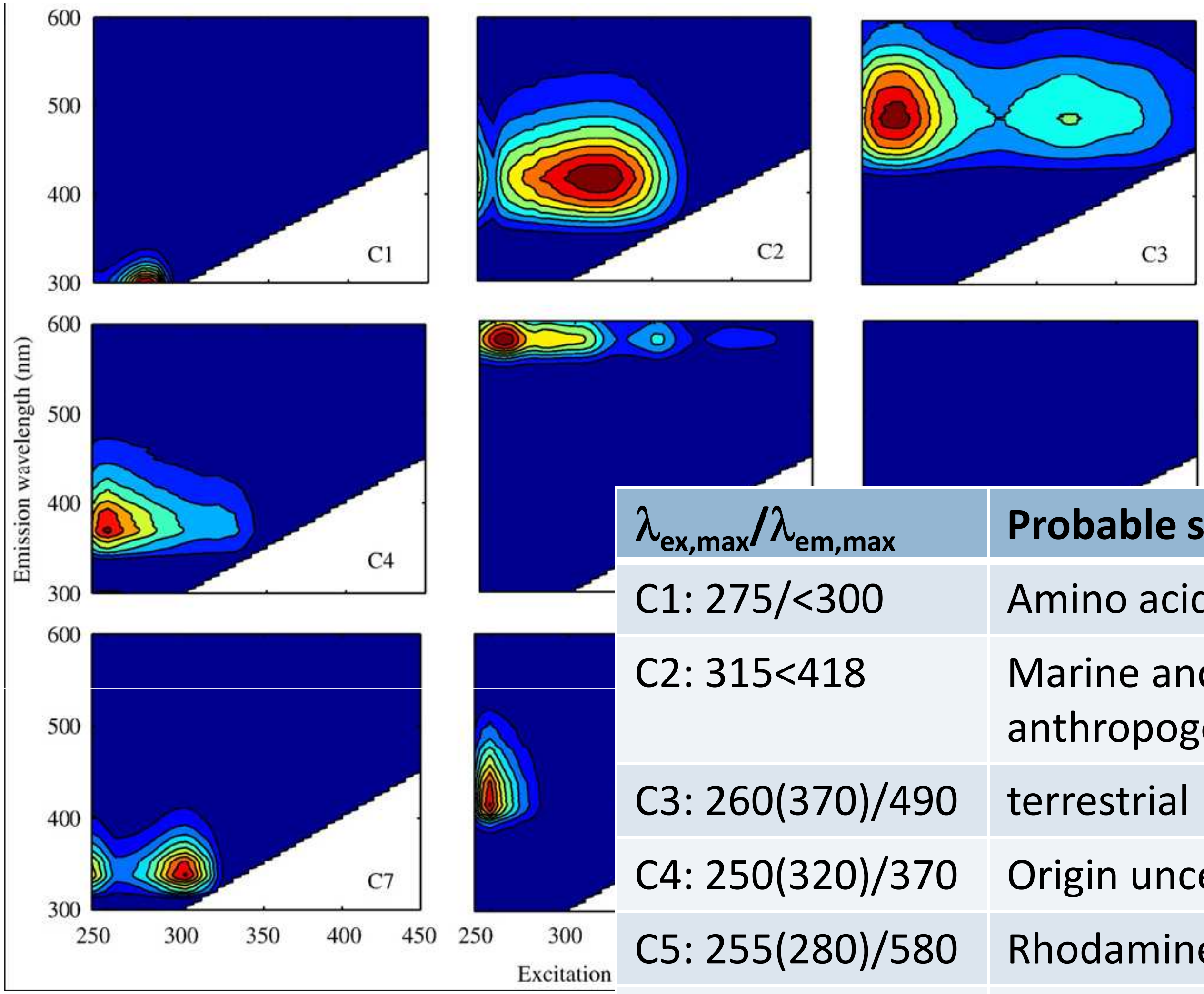
3D Fluorescence Excitation- Emission Matrix (EEM) Spectroscopy



Pics	Longueur d'onde d'excitation (nm)	Longueur d'onde d'émission (nm)	Type de composés
α	330 - 350	420 - 480	Substances type humiques
α'	250 - 260	380 - 480	Substances humiques + matériel plus récent
β	310 - 320	380 - 420	Matériel récent - composante biologique
γ	270 - 280	300 - 320	Tyrosine, tryptophane ou protéines + activité bactérienne

HIX = H/L
H: $435<\lambda em< 480$nm
L: $300<\lambda em<345$nm

(Huguet et al., 2009, 2010)



Parallel Factor Analysis (PARAFAC)

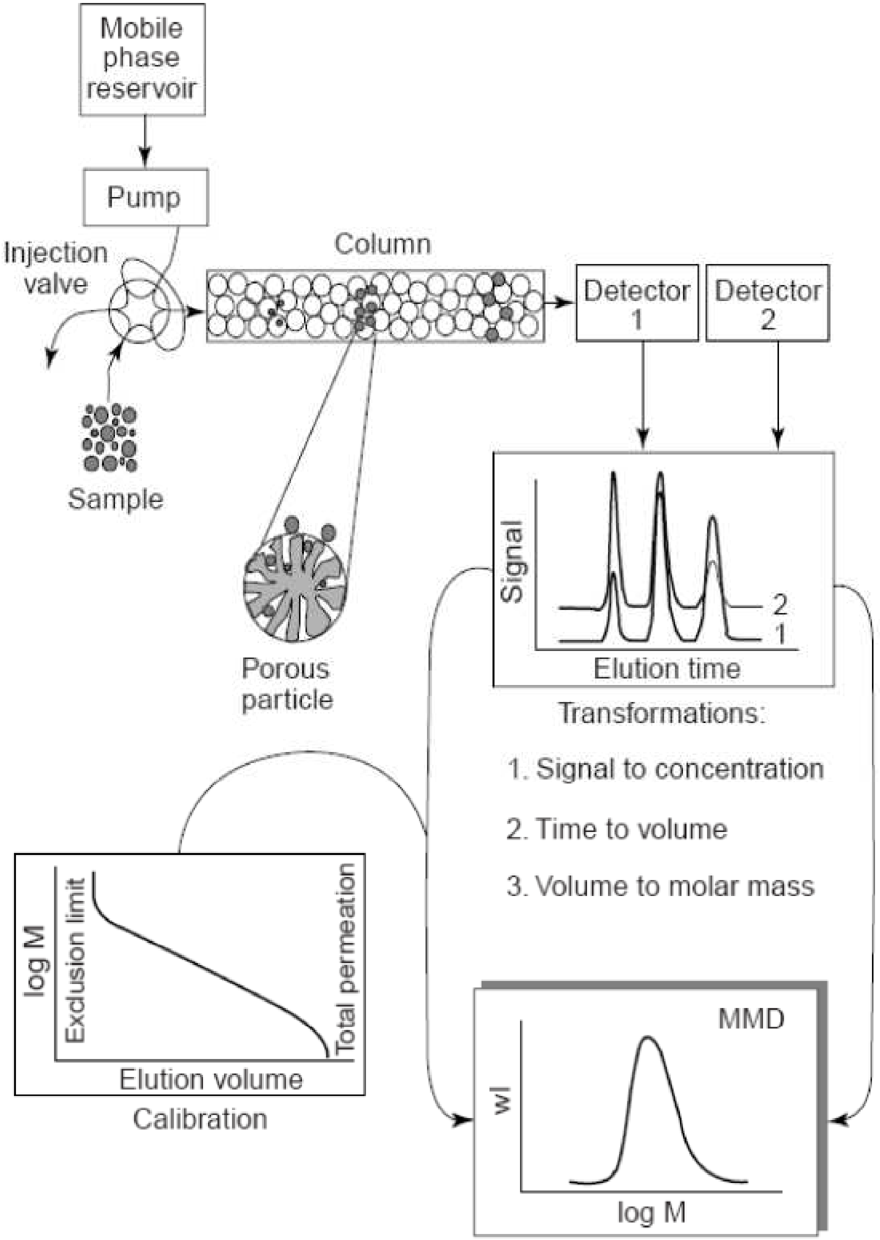
N-way toolbox for Matlab

$\lambda_{ex,max}/\lambda_{em,max}$	**Probable source**
C1: 275/<300	Amino acid, free or bound in proteins
C2: 315<418	Marine and terrestrial humic materials; anthropogenic humic materials, agricultral;
C3: 260(370)/490	terrestrial humic substances, widespread
C4: 250(320)/370	Origin uncertain, possible PAH
C5: 255(280)/580	Rhodamine WT dye
C6: 280/328	Trytophan
C7: 240(300)/338	Amino acid, free or bound in proteins
C8: 250(380)/416	terrestrial humic substances
C9: <240/422	Photochemical product of terrestrial organic matter

$$\frac{\mathbf{Ci}}{\mathbf{Cj}} = \frac{\textbf{Fluorescence Intensity i}}{\textbf{Fluorescence Intensity j}}$$

(Murphy et al., 2008)

Size Exclusion Chromatography

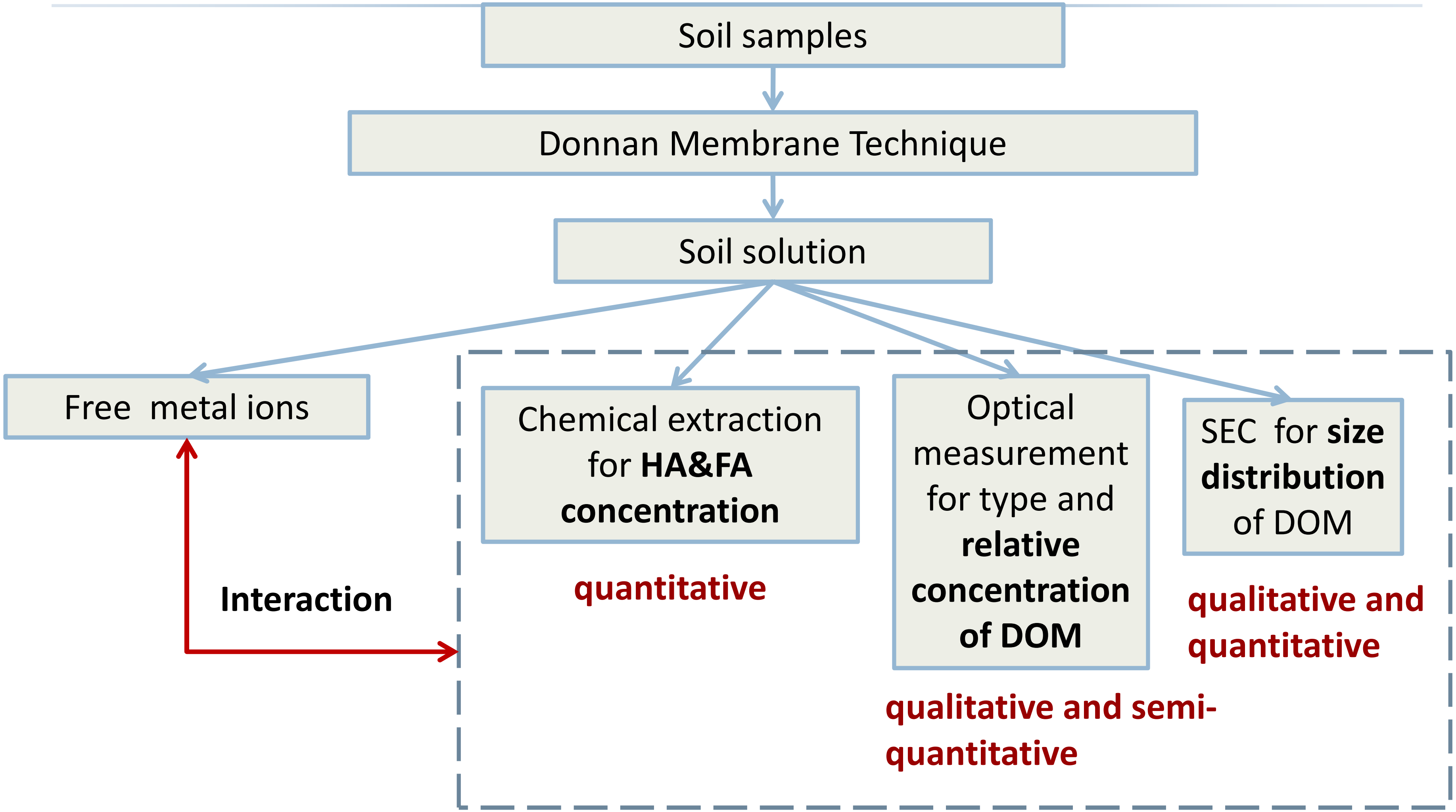


Principle of SEC:

Due to limited accessibility of the pore volume within the particles of the column packing, polymer molecules are separated according to their hydrodynamic volumes, with the larger size molecules exiting first followed by the smaller. Residence time can be correlated with molar mass.

(Trathnigg, 2000)

Schematic Design



Soil samples

Donnan Membrane Technique

Soil solution

Free metal ions

Chemical extraction for **HA&FA concentration**

Optical measurement for type and **relative concentration of DOM**

SEC for **size distribution** of DOM

Interaction

quantitative

qualitative and semi-quantitative

qualitative and quantitative

Probable Problems

1) Will Ca^{2+} and NO_3^- affect the spectra of DOM?

→ Use soil solution extracted by MQ water

2) What if free metal ions in alkaline soil samples are lower than the detective limit of DMT?

→ Add ligand (Weng et al., submitted)

3) ……

Main References

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Thank you very much for

your attention!