Chloride interference during DOC analyses using wet chemical oxidation methods

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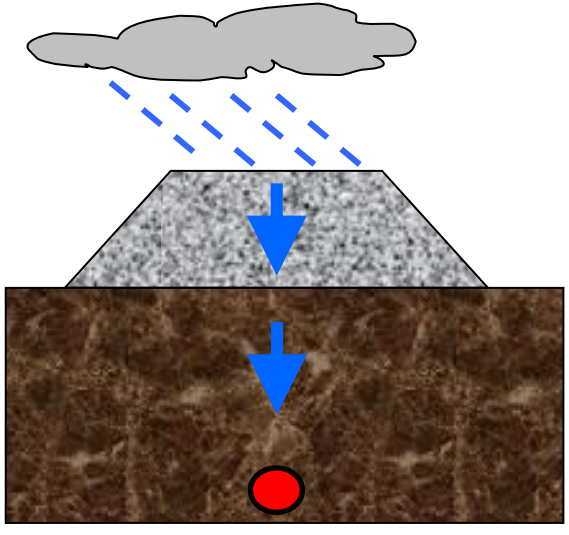
Energy research Centre of the Netherlands

Background: Environmental impact assessment

- Environmental limit values for emissions to soil and groundwater
- →Dutch Soil Quality Decree (2007)

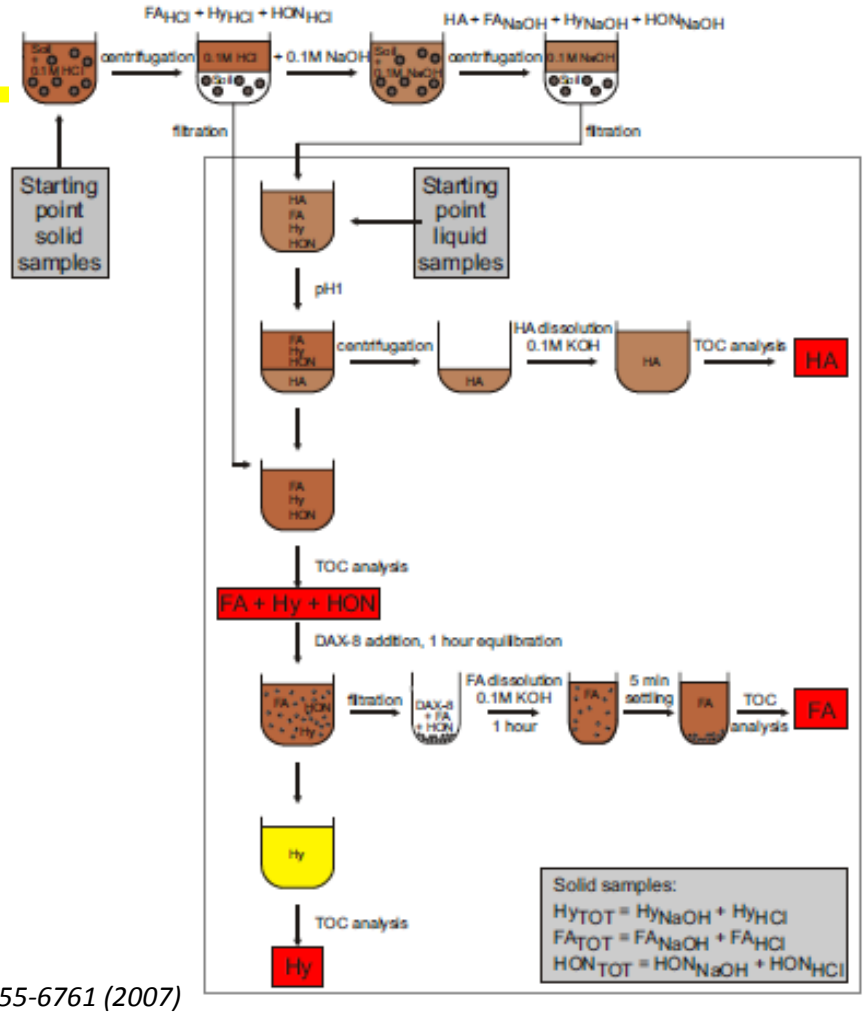
- Validate assumptions on HA/FA concentrations in modelling
- Rapid batch method available: consistent with IHSS methods, suitable for both solid and aqueous samples
- Change DOC analyses from “combustion method” to “chemical oxidation method”



Transport, dilution, sorption, attenuation in soil

Rapid batch method

- Humic acids (HA)
  (precipitate at pH =1)
- Fulvic acids (FA)
  (bind to XAD8, desorbed with NaOH)
- Hydrophobic neutrals (HON)
  (bind to XAD8, not desorbed with NaOH)
- Hydrophylic acids (Hy)
- 1-2 hours per sample



Van Zomeren & Comans, Env. Sci. Technol. ***41****, 6755-6761 (2007)*

Standardisation of rapid batch procedure: ISO 12782-4 and -5

ISO/TC 190/SC 7

Date: 2011-09-01

ISO 12782-4:2011(E)

ISO/TC 190/SC 7/WG 6

Secretariat: DIN

Soil quality — Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials — Part 4: Extraction of humic substances from solid samples

Qualité du sol — Paramètres pour la modélisation géochimique du lessivage et spécifications des constituants des sols et des matières — Partie 4: Extraction des substances humiques des échantillons de sol

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Soil quality — Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials — Part 5: Extraction of humic substances from aqueous samples

Qualité du sol — Paramètres pour la modélisation géochimique du lessivage et spécifications des constituants des sols et des matières — Partie 5: Extraction des substances humiques des échantillons aqueux

Methods: Shimadzu TOC Vcph

- TIC: acidification (H_3PO_4) and detection of CO_2
- TC: catalytic combustion at 680 C
- DOC= TC-TIC

- Combustion of DOC: CO_2 and detection by NDIR
- DTL ± 1 ppm

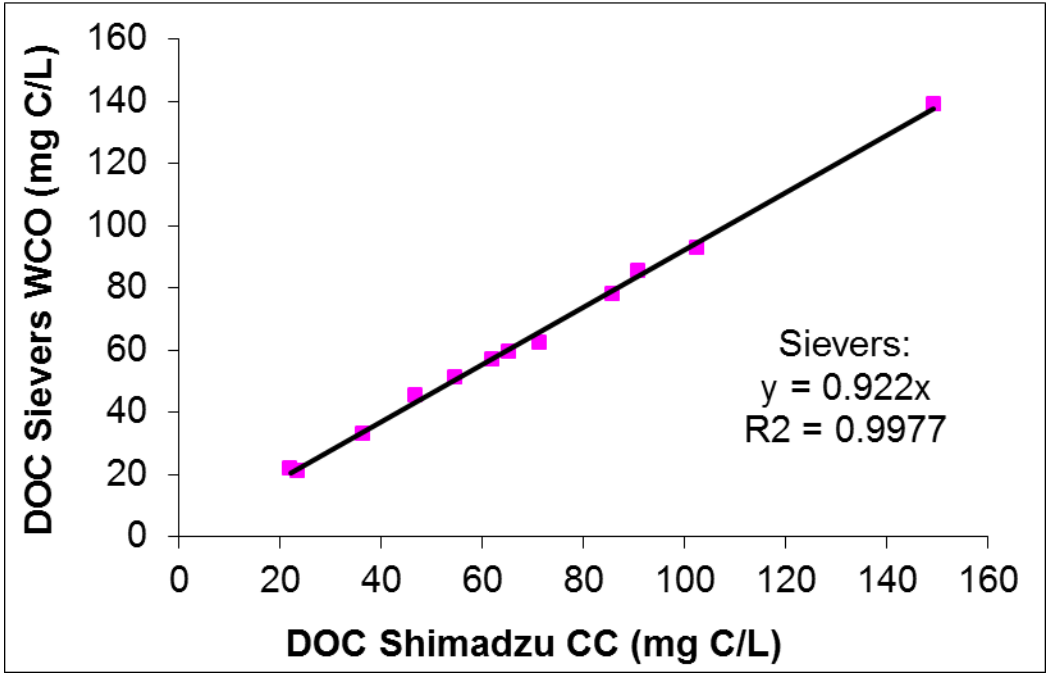
- ISO 17025 accreditated

Methods: Sievers TOC 900

- TIC: acidification (H_3PO_4) and detection of CO_2
- TC: wet chemical oxidation with persulfate and UV
- DOC= TC-TIC

- Radical formation by persulfate and UV light
- Oxidation of DOC: CO_2 and detection by conductometry
- DTL ± 0.1 ppb

Comparison of analytical methods



Fractionation in soil sample extracts

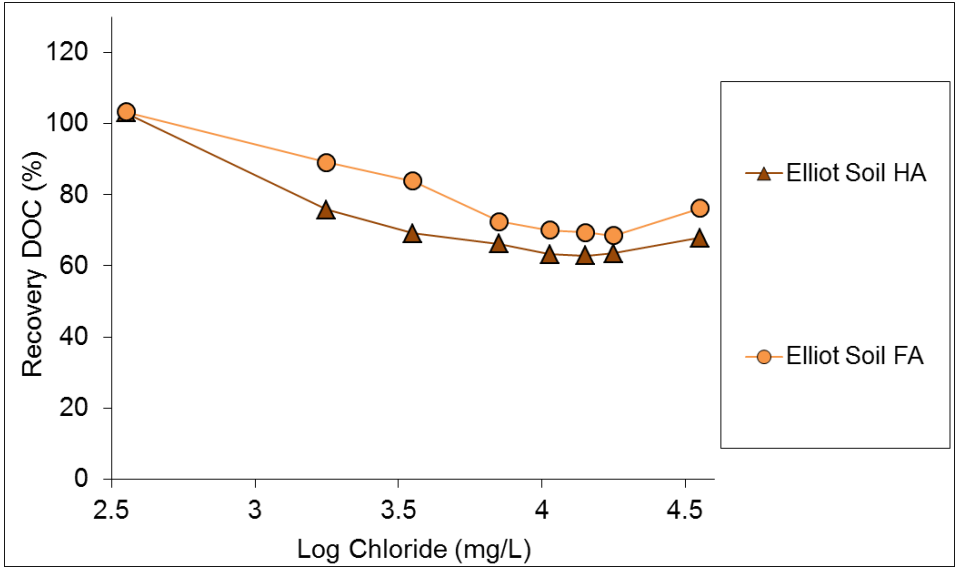
- Method: Sievers WCO

?

Sample data						
Samplecode	HA (mg C/L)	FA (mg C/L)	Hy (mg C/L)	HON (mg C/L)	DOC (mg C/L)	Mass balance (%)
Kloosterzande top	0.00	3.73	0.16	0.00	3.89	147.6
Kloosterzande mid	0.00	0.00	-0.05	0.60	0.55	30.5
Kloosterzande sub	0.00	1.94	0.24	0.00	2.18	65.8
Kerkerdam 1 top	0.00	0.62	0.06	0.27	0.96	29.9
Kerkerdam 1 mid	0.01	3.45	0.02	0.00	3.47	110.2
Kerkerdam 1 sub	0.00	0.42	-0.12	0.17	0.46	46.1
Kerkerdam 2 top	0.00	4.15	0.04	0.00	4.19	107.3
Kerkerdam 2 mid	0.00	0.00	-0.01	0.77	0.76	35.2
Kerkerdam 2 sub	0.00	0.56	-0.12	0.11	0.55	42.2
Arnhem top	0.00	0.00	-0.03	0.98	0.95	31.6
Arnhem mid	0.00	0.63	-0.07	0.10	0.66	41.5

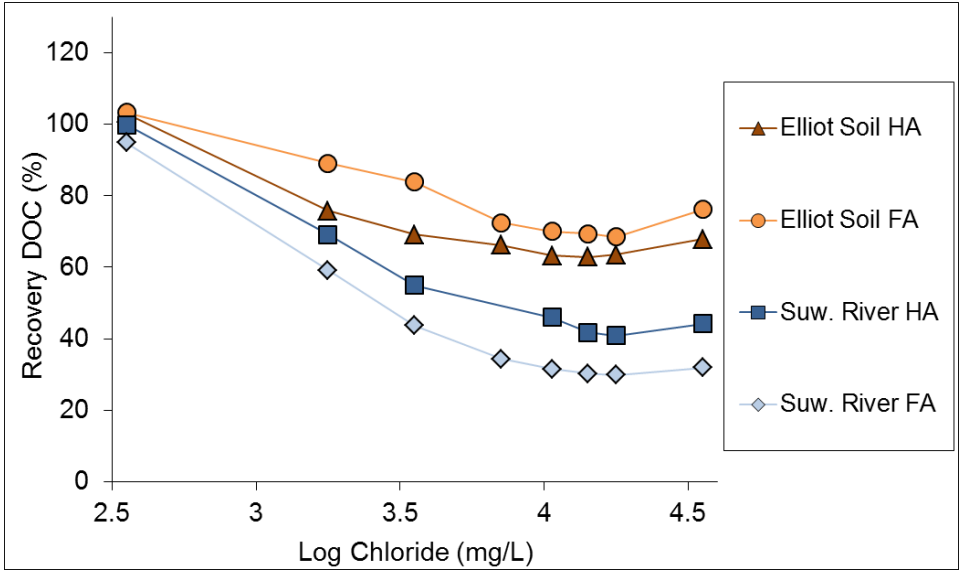
Oxidation efficiency HS as a function of chloride concentration

- Dissolution of 5 mg C/L HS and addition of increasing NaCl to each bottle



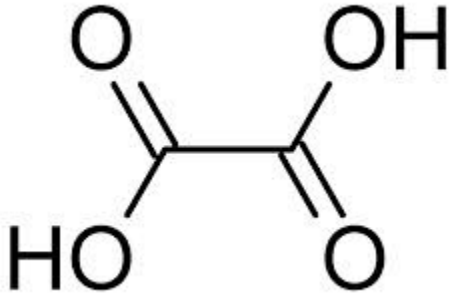
Oxidation efficiency HS as a function of chloride concentration

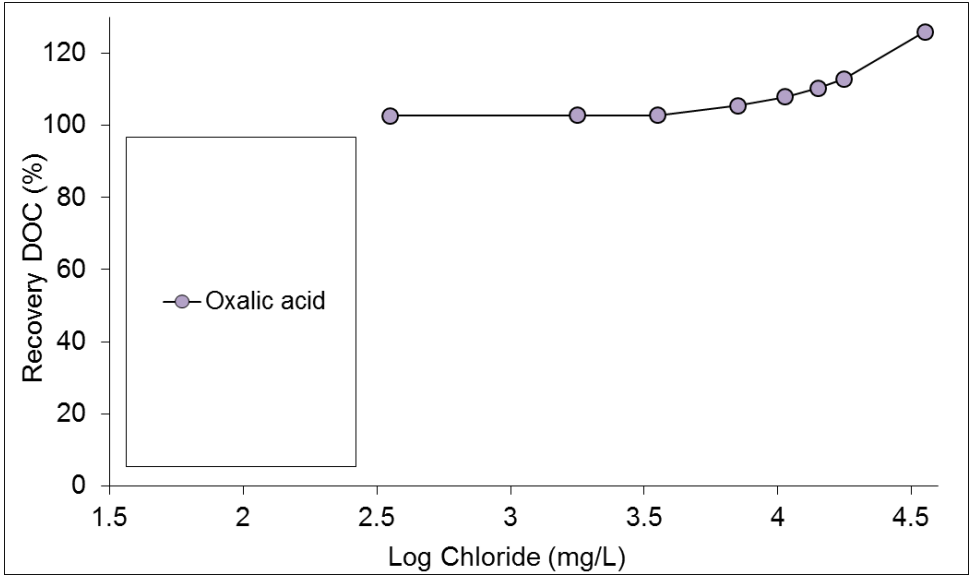
- Distinct differences between aquatic and soil HS
- Soil HS more easily oxidised than aquatic HS
- In soil FA is more easily oxidised than HA
- In Aquatic sample, HA is more easily oxidised than FA



Oxidation efficiency as a function of chloride concentration

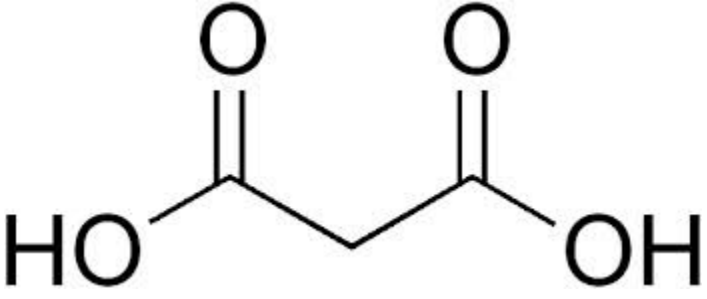
- Insensitive to chloride concentration
- Increase of oxalic acid to >100%?

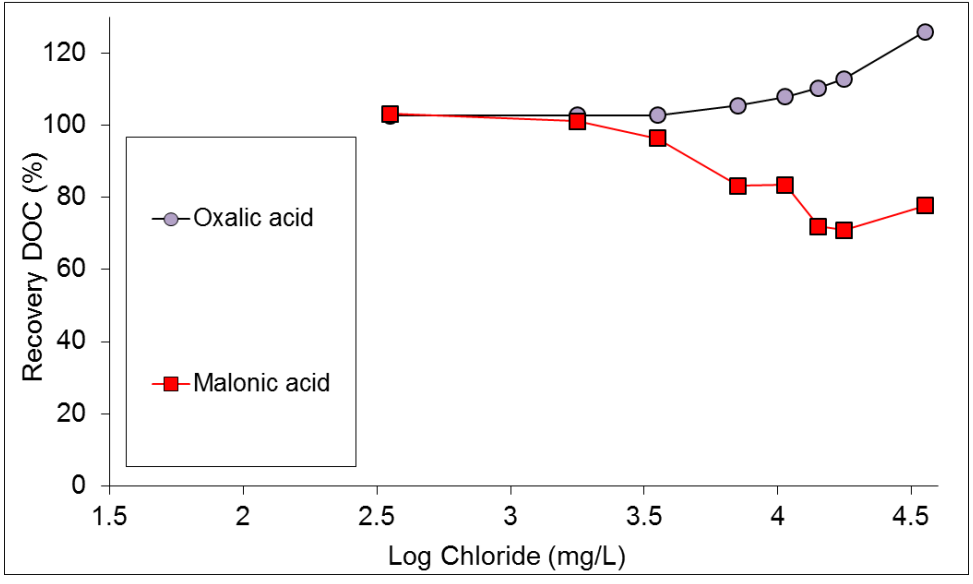




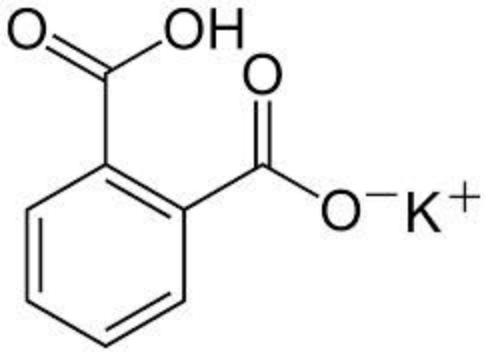
Oxidation efficiency as a function of chloride concentration

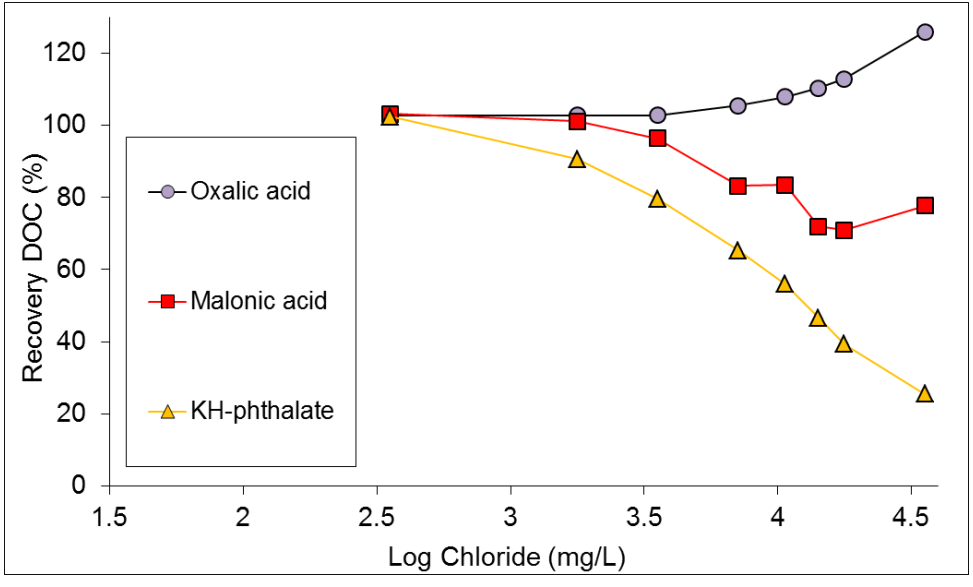
- Decrease in oxidation efficiency at relatively high chloride concentrations



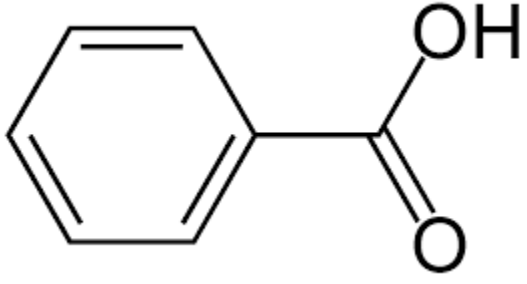


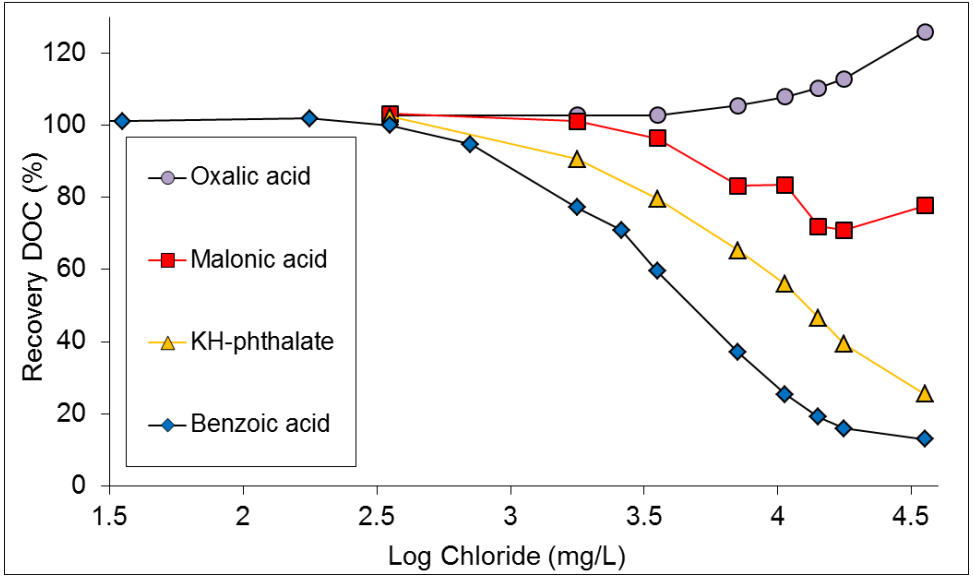
Oxidation efficiency as a function of chloride concentration



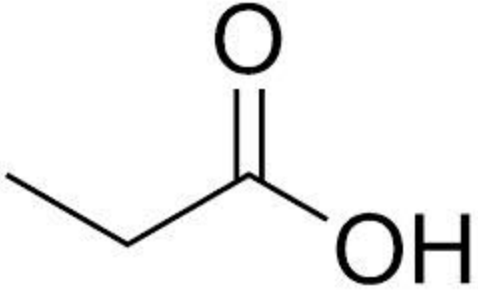


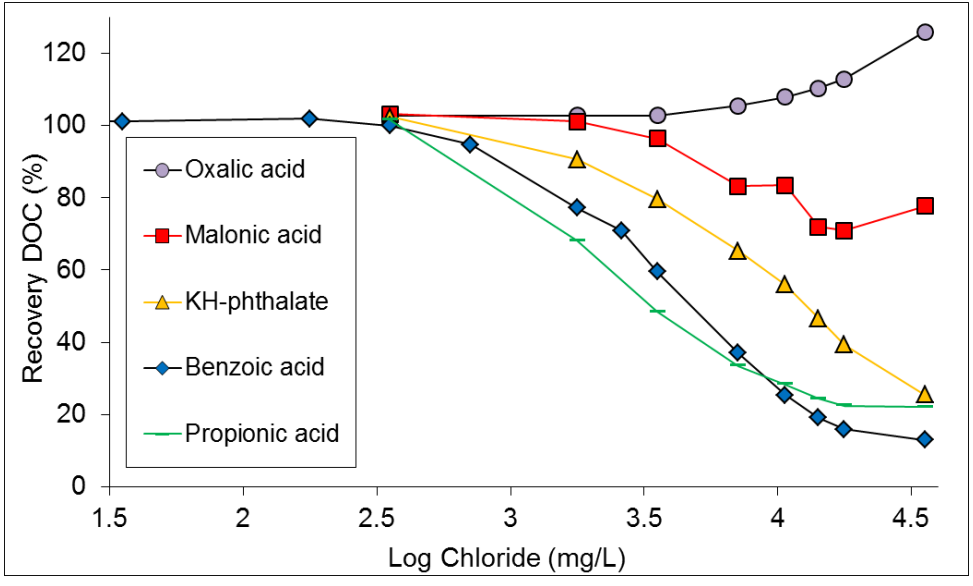
Oxidation efficiency as a function of chloride concentration





Oxidation efficiency as a function of chloride concentration

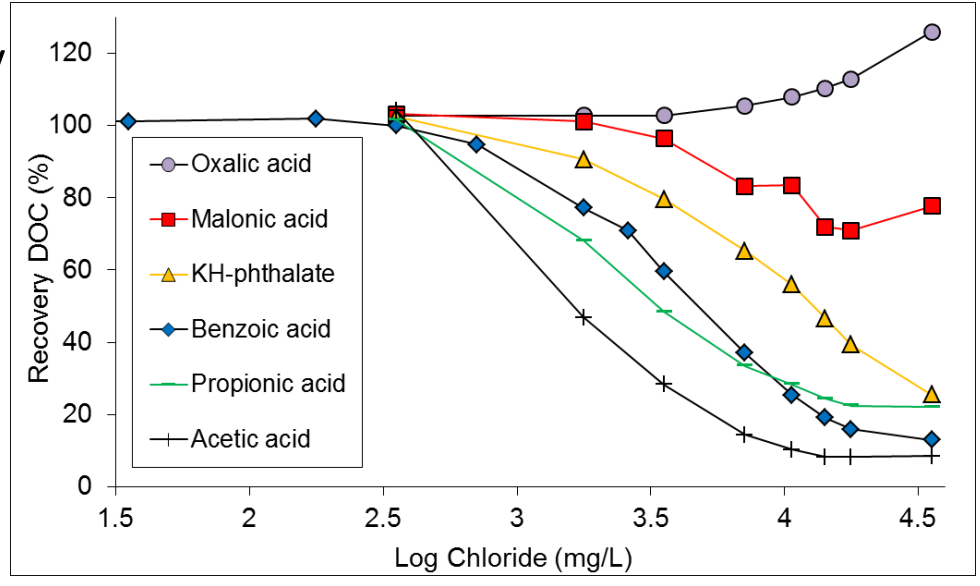


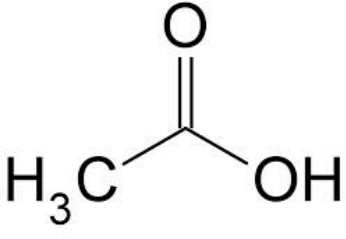


Oxidation efficiency as a function of chloride concentration

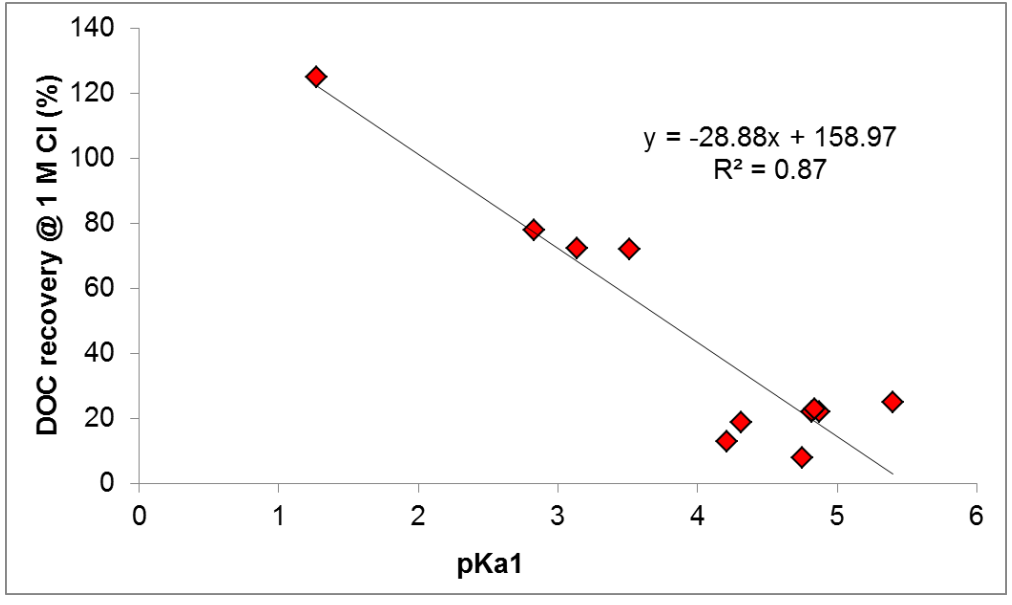
- Acetic acid has lowest recovery
- Oxalic and malonic acid relatively high recovery

- Increase of oxalic acid to >100%?
- Why different recovery for each substance?
- Overall, HS seem to be more easily oxidised than small organic acids



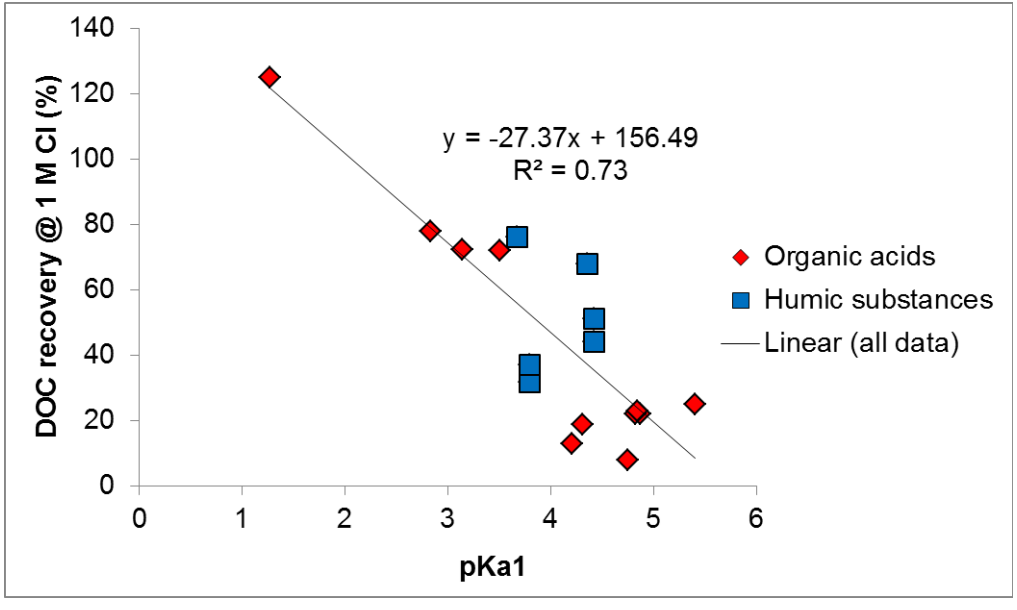


Oxidation efficiency as a function of pKa1



Oxidation efficiency as a function of pKa1

- Stronger acids are more easily oxidised
- Since pKa reflects part of the chemical structure, this is probably important to explain results
- No indication of exact mechanism



Conclusions

- Use of standardised methods important for research and geochemical modeling tools
- HS concentrations at low levels are challenging to analyse
- Chloride interference substantial for both organic acids and HS
- pKa seems to have relation with oxidation efficiency
- Exact mechanisms remain unknown but type of organic carbon is important
- Measurement of chloride concentrations is important when using WCO

Thanks for your attention!

More information:
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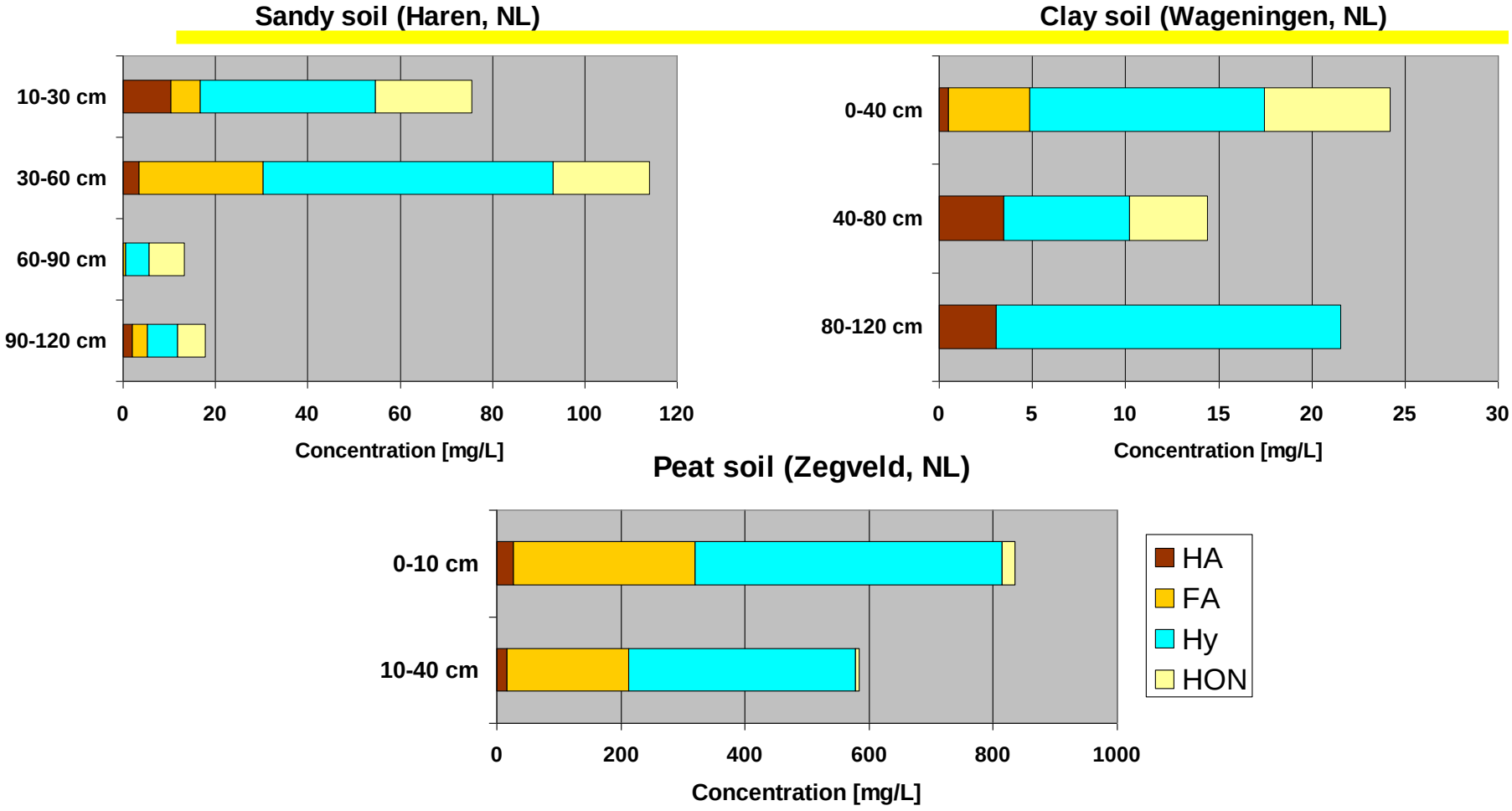
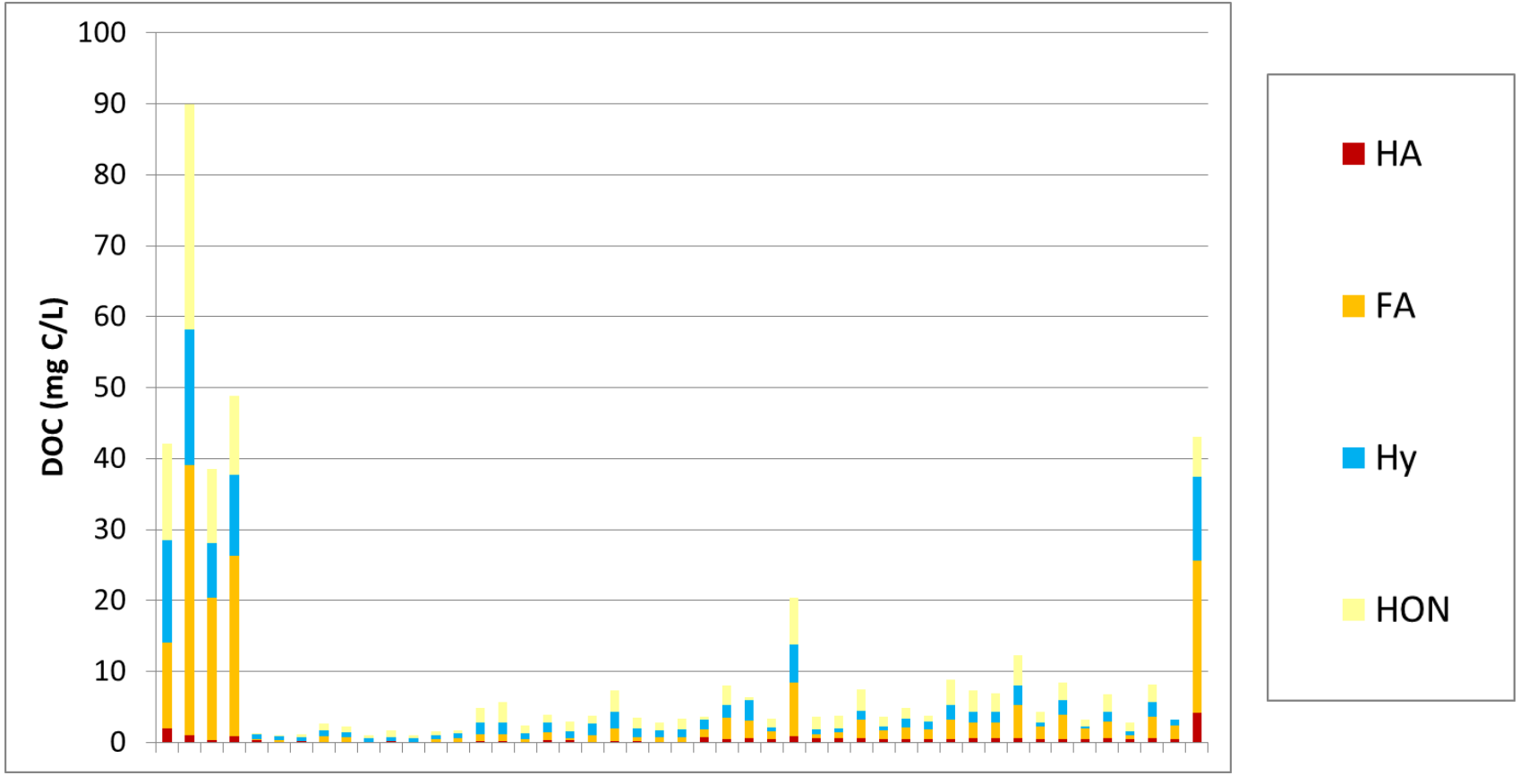
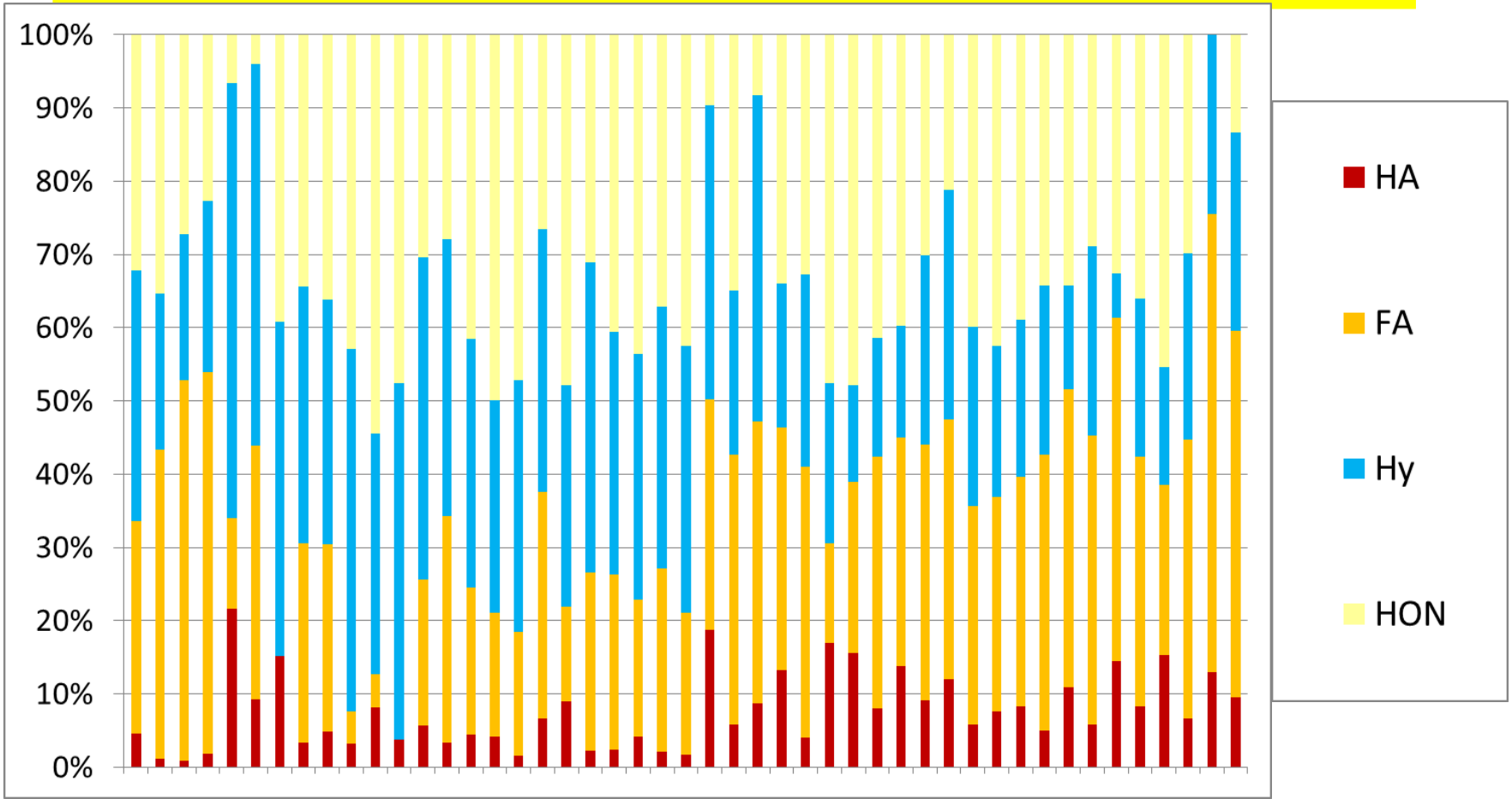
Example of DOC fractions in soil profiles



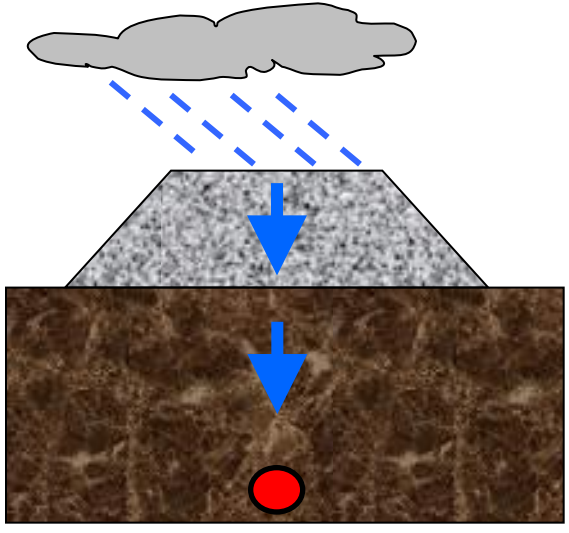
Variation in DOC concentrations in soil extracts (L/S=10 l/kg)



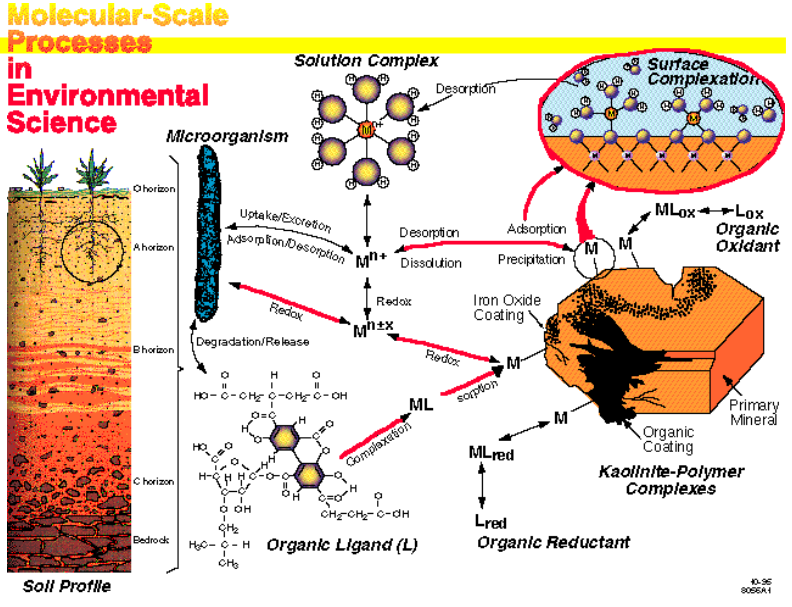
Example of DOC fractions in soil samples (L/S=10 extractions)



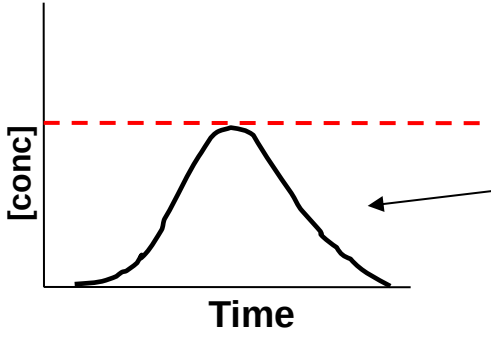
Background: Environmental impact assessment



Transport, dilution, sorption, attenuation in soil



protection level at "point of compliance" (POC)



Estimated / predicted concentration in groundwater at POC

Rationale for a rapid procedure for NOM fractionation

- Classical isolation and purification procedures (IHSS) are very elaborate:

- Throughput time for samples is typically 2-4 weeks
- Labour time is approximately 20-40 hours/sample
- Not suitable for routine analysis

- → Development of insight in the concentrations of sub-fractions of NOM in soils and natural waters and their role in ecosystem services such as soil carbon storage, food production and quality of groundwater

- → Rapid batch method, consistent with IHSS methods, suitable for both solid and aqueous samples

Background

- Involved in deriving environmental limit values for emission of dangerous substances from construction products
- Long-term scenario modelling using state of the art approach:
  - Geochemical speciation modelling
  - Adsorption to iron-oxides
  - Complexation with humic substances
- Indications that the assumed HS concentration in soil pore water and ground water was too low
- Possible implication: under estimation of predicted emissions and emission limits should be more strict
- Need for analytical methods to determine HS at low concentrations

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