Colloidal vectors of Uranium in various aqueous environments: case of the former mining site of Rophin (Puy-de-Dôme, France)

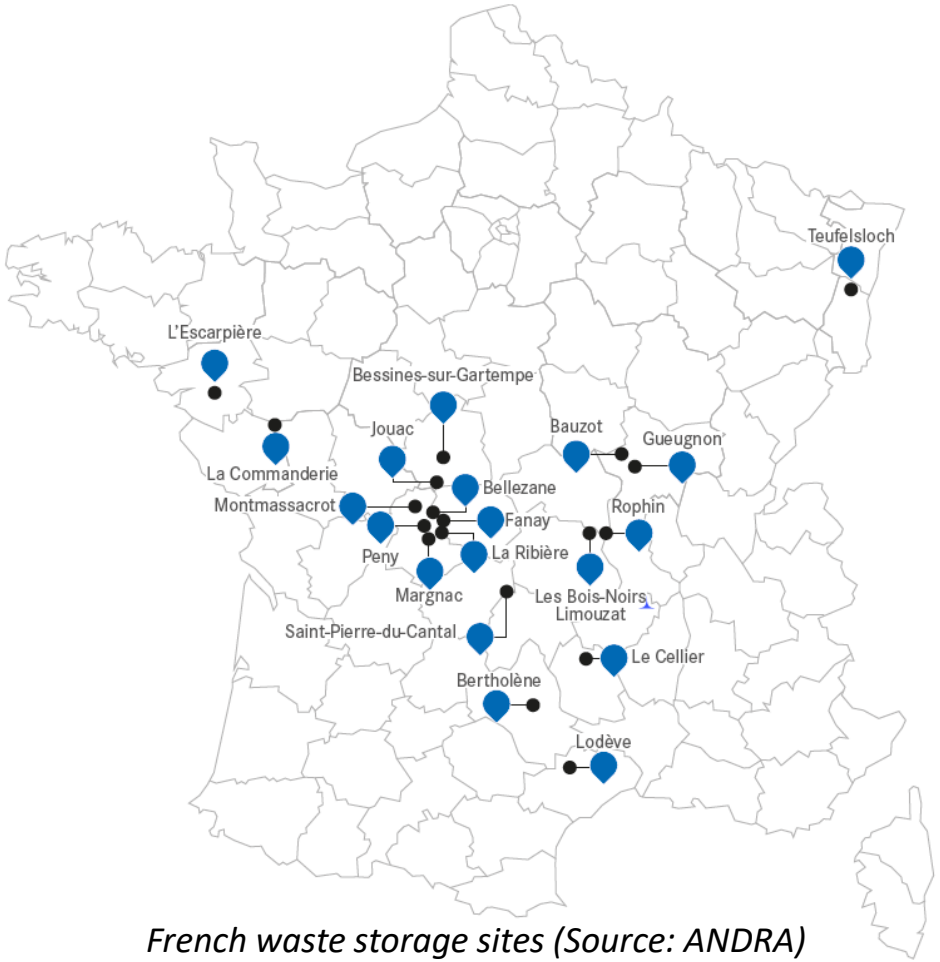
Chaillou Maxime – PhD Hours – 09/01/2025

Supervising Team

- ***Subatech*** Nivesse Anne-Laure, Landesman Catherine, Montavon Gilles
- ***KIT-INE*** Bouby Muriel
- ***LMGE*** Mallet Clarisse

Uranium mining in France:

- From 1948 to 2001
- 50 millions tons of tailings with activities > 10^5 Bq/kg
  - Waste stored in 17 sites registered as ICPE



French waste storage sites (Source: ANDRA)

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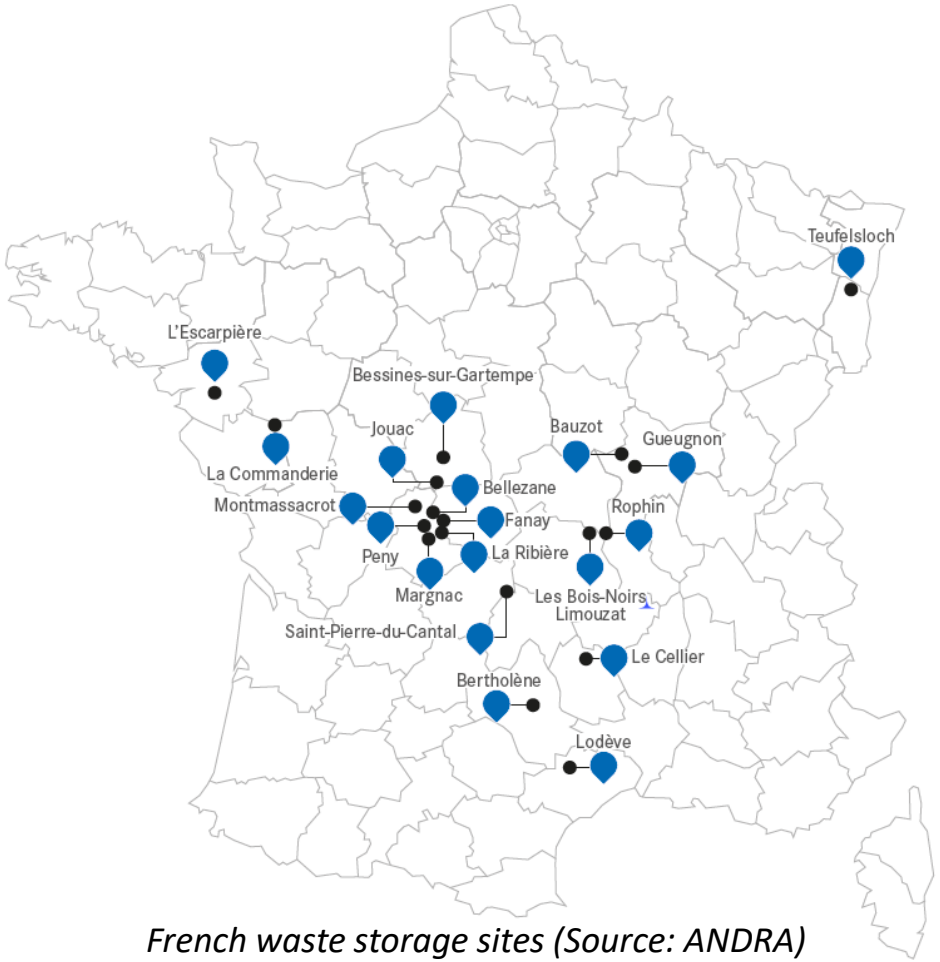


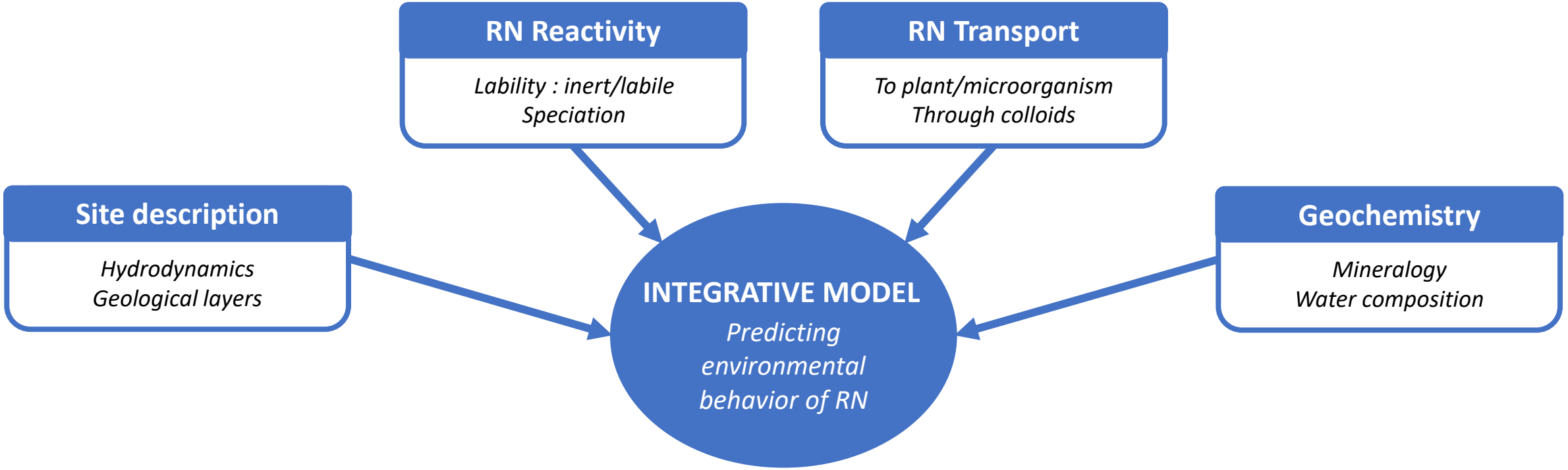
French waste storage sites (Source: ANDRA)

Societal and Environmental issues :

- Long term behavior of radionuclides (RN)
- Safety of tailings waste storage sites
- Effects of low concentrations RN on ecosystems

ZATU program: A multidisciplinary approach towards a better understanding of RN behavior in the environment

Application to the old mining site of Rophin (Puy-de-Dôme, France)



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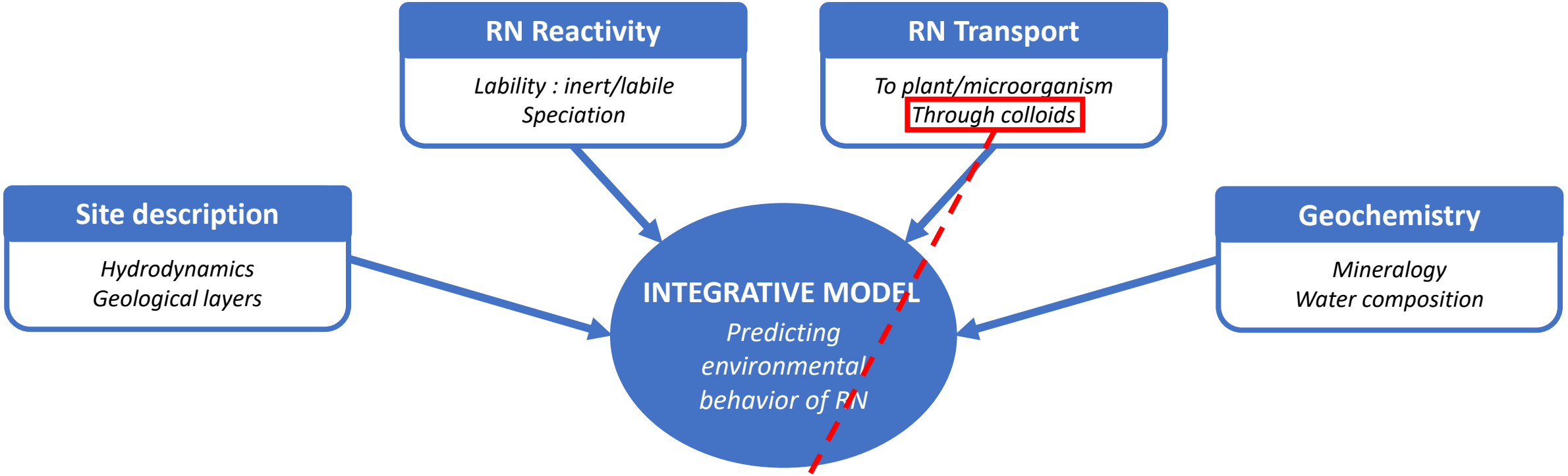
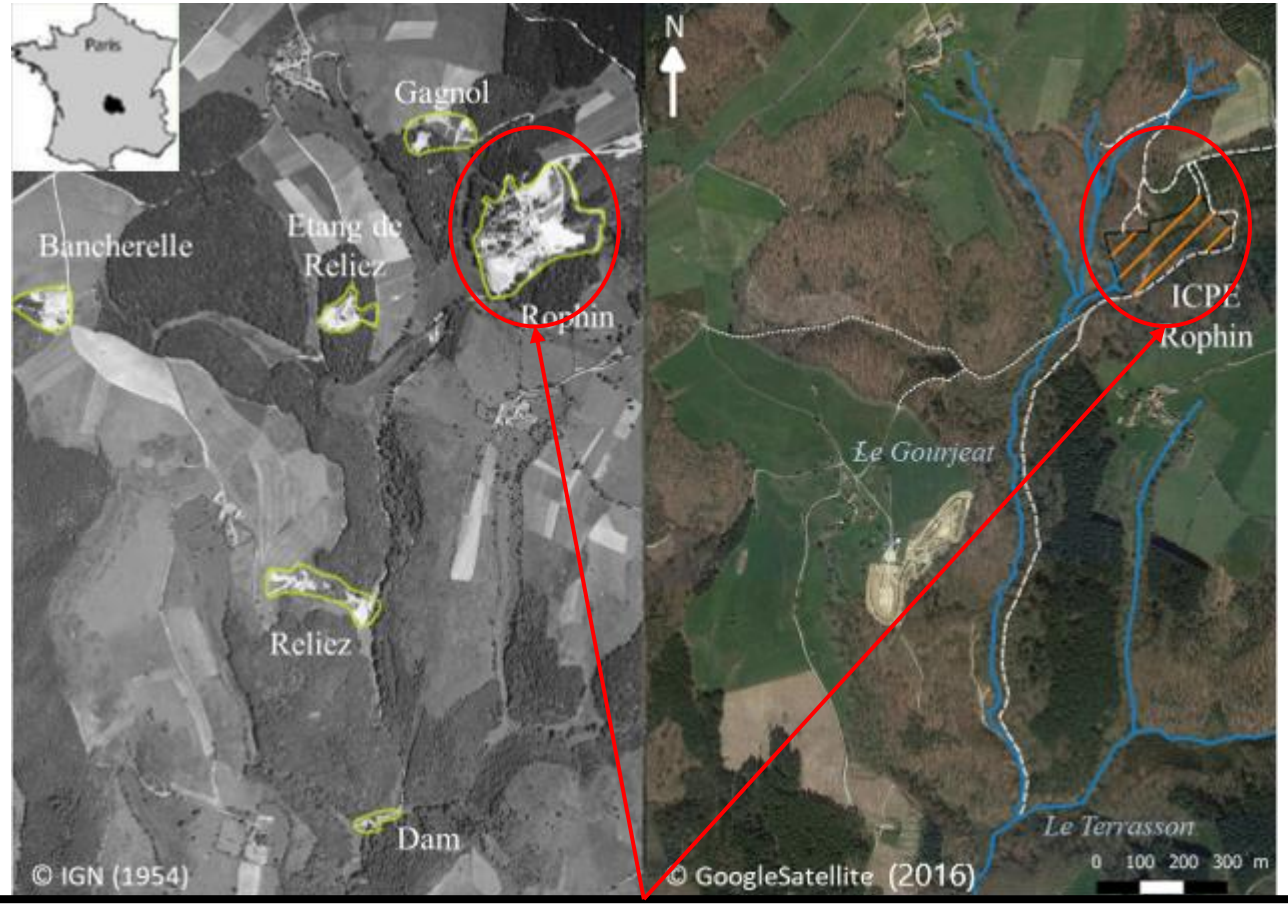


This study

Identifying colloidal particles involved in Uranium migration across Rophin wetland



Rophin Site (Puy-de-Dôme, France)

- High concentration of radioactive materials (≈30 000 tons of mining waste)
- Practically untouched since the 1950s
- Storage in environmental conditions

ROPHIN KEY DATES

Mining

1948
Start of mining activities

1952
End of ore extraction

1957
End of ore processing
Conversion into a storage site

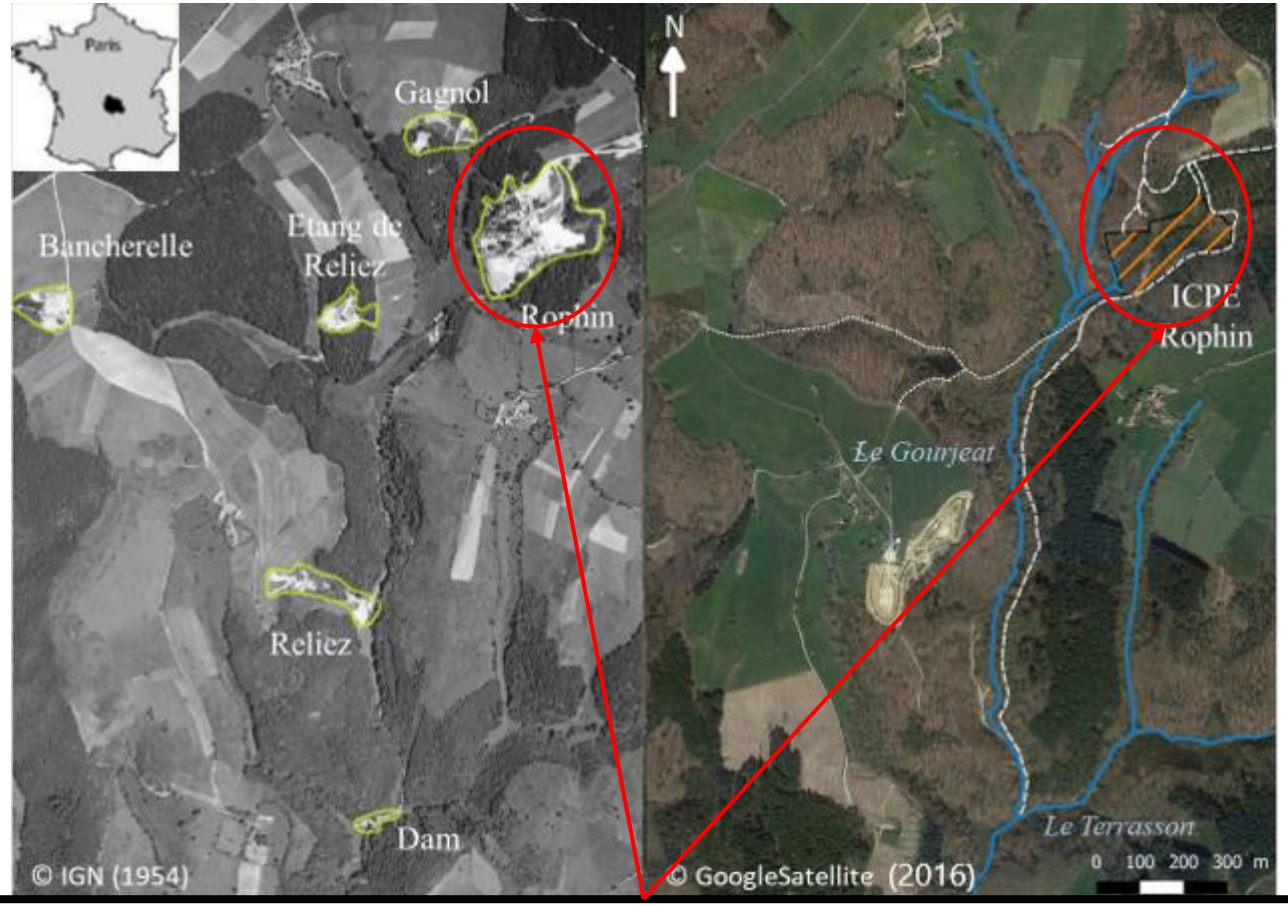
Storage

1982
Waste covered with vegetated soil

1985
Registration as an *Installation Classified for the Proctection of the Environment (ICPE)*

2002
Underground effluents redirected to the downstream river

2010
Access to the site restricted with fences



Rophin Site (Puy-de-Dôme, France)

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- Practically untouched since the 1950s
- Storage in environmental conditions

A very valuable site to study long term behavior of RN in environmental conditions

ROPHIN KEY DATES

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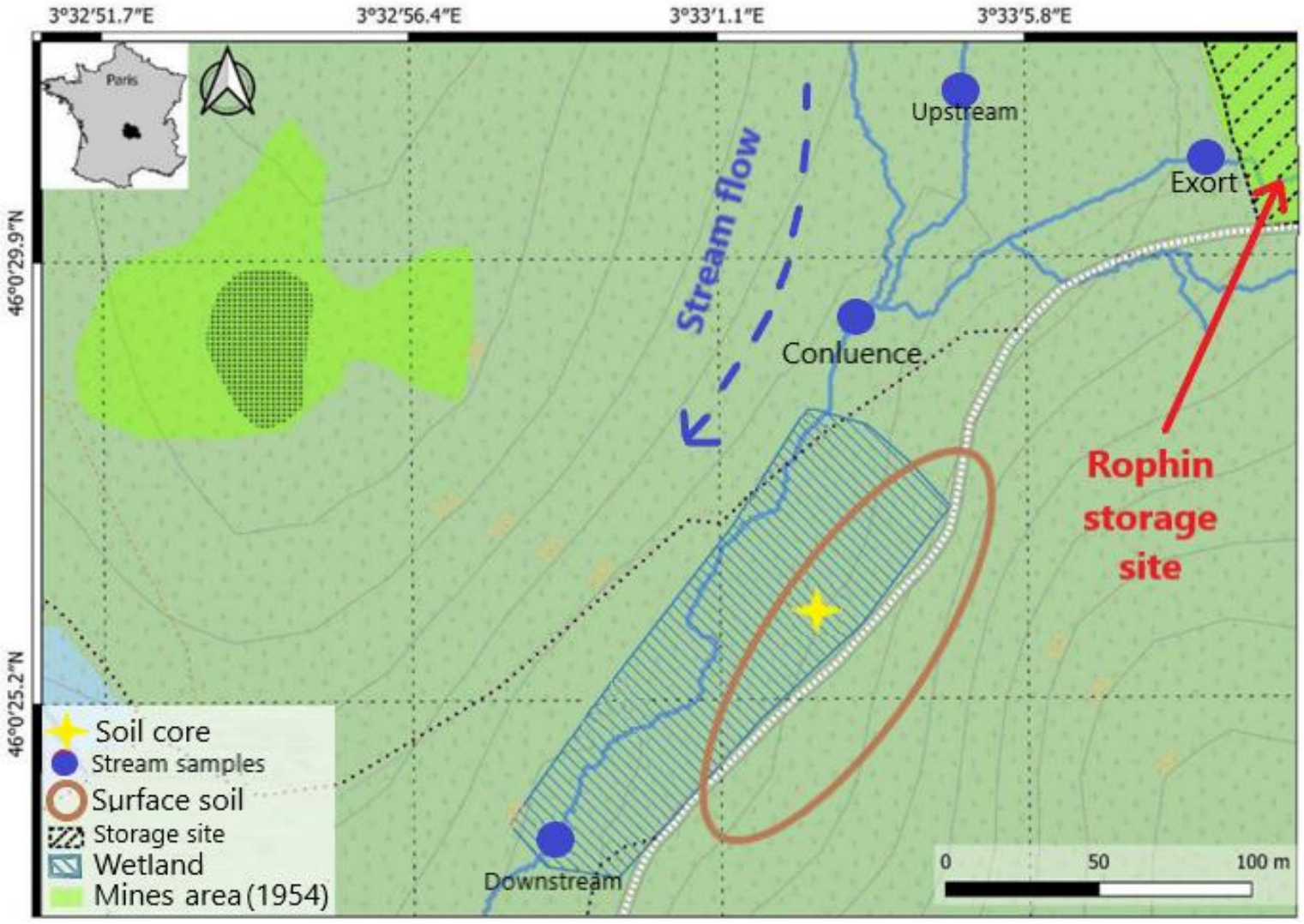


Sampling points location (January 2023 / March 2024)

Stream Water

4 collection points along the stream crossing the wetland

- Upstream
- Confluence
- Exort
- Downstream

Pore Water

Pore water obtained by centrifugation of the 4 layers from a soil core

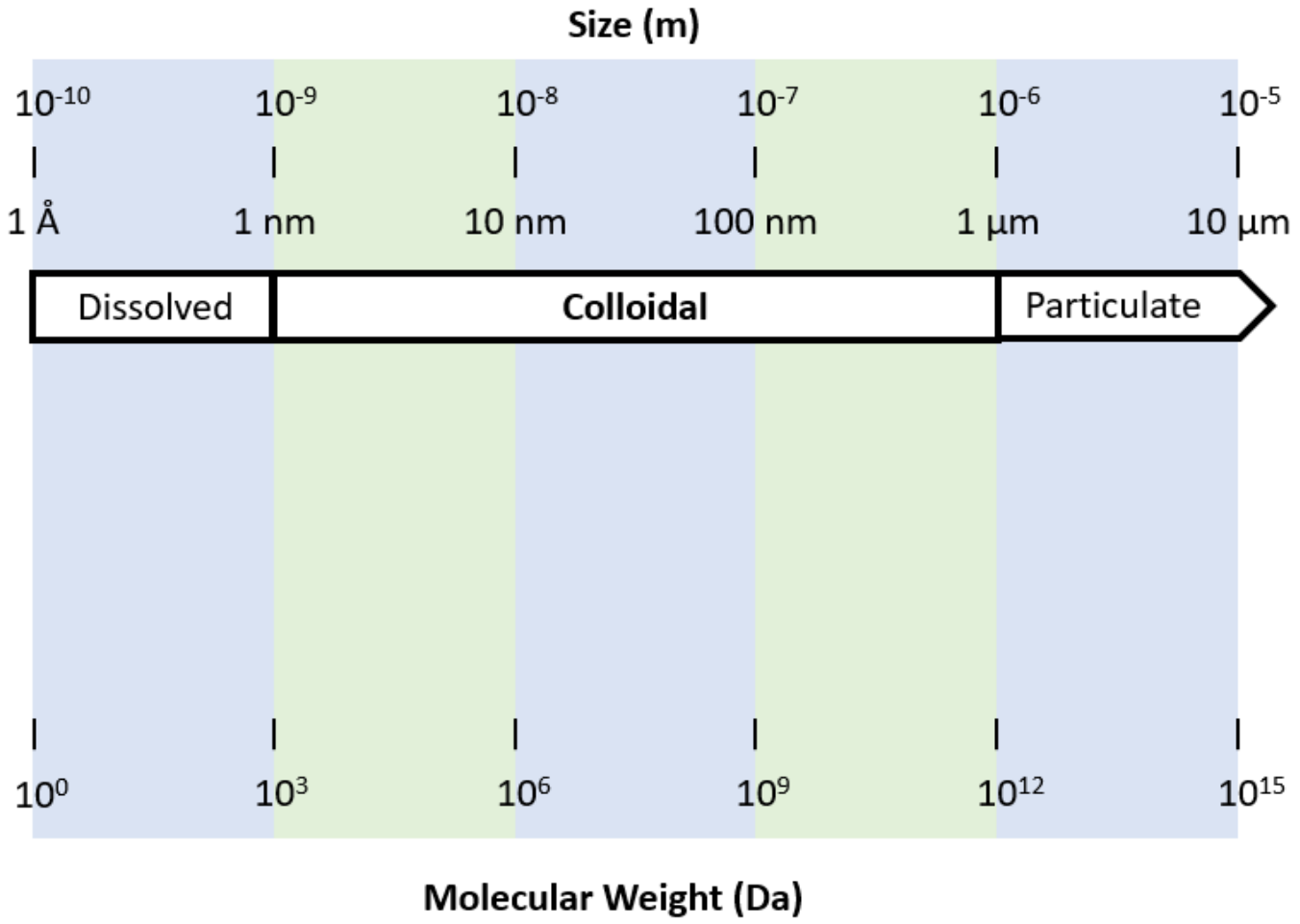
Natural Organic Matter (NOM) Extracts

<u>Surface soil sampled :</u>

6 Successive extractions

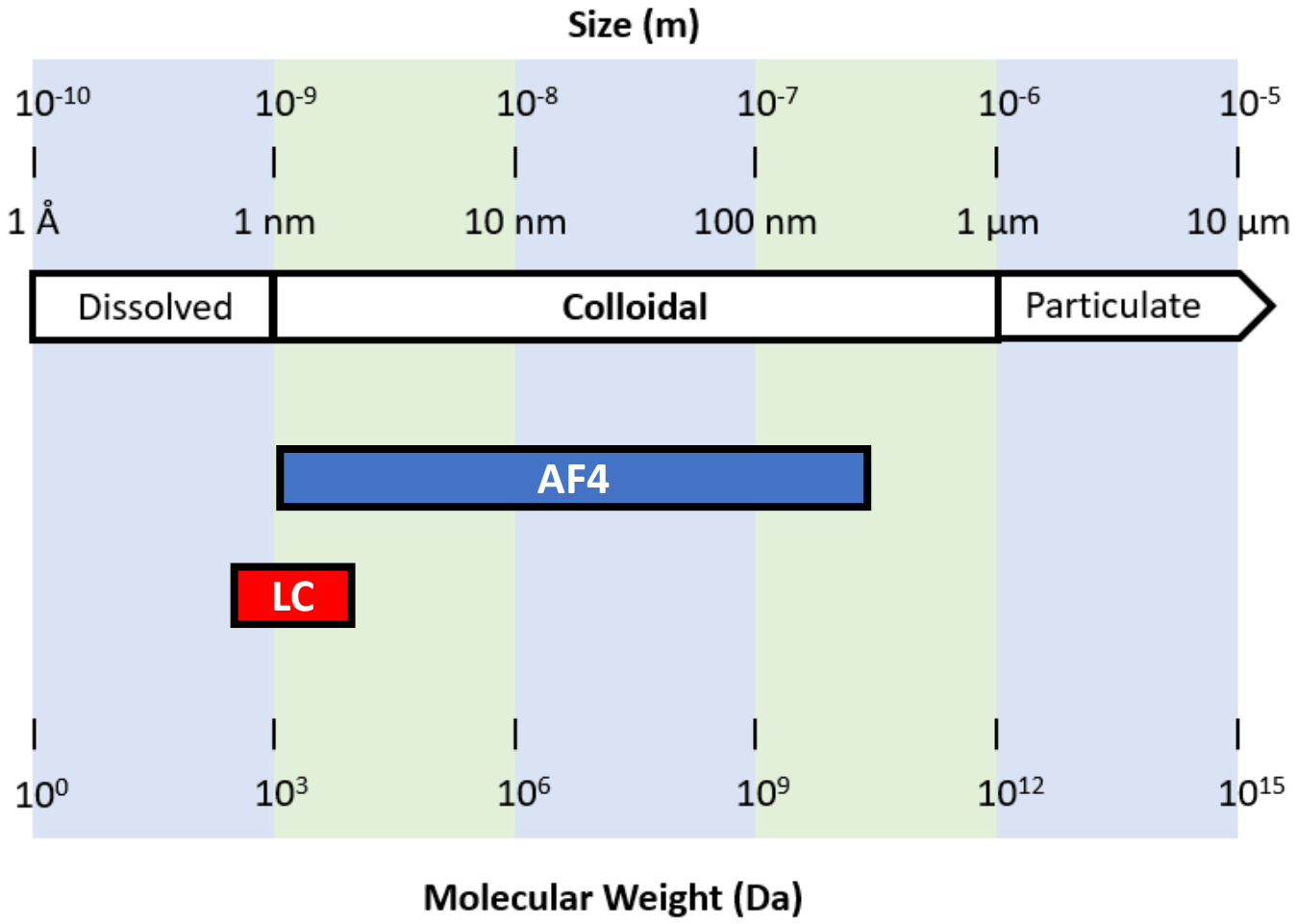
-3 using HCl 0.1M

-3 using NaOH 0.1M



Colloidal : *"Refers to a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have, at least in one direction, a dimension roughly* ***between 1 nm and 1 µm****"*

(IUPAC, 2019)



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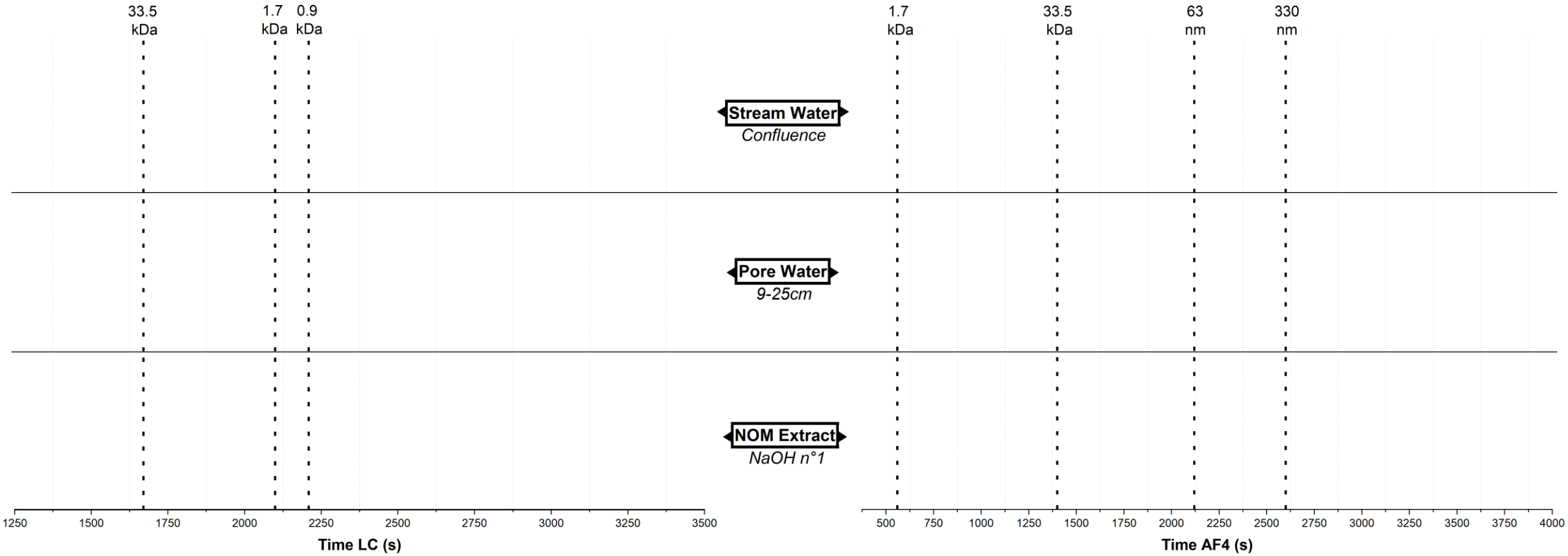
Two size-based fractionation methods coupled to multiple detectors

Asymmetric Flow Field-Flow Fractionation	
UVD	MALS
ICP-MS	RI

Liquid Chromatography	
UVD	OCD
ICP-MS	OND

Presented here

UVD : Ultra-Violet Detector
MALS : Multi Angle Light Scaterring
RI : Refractive Index
OCD : Organic Carbon Detector
OND : Organic Nitrogen Detector
ICP-MS : Inductively Coupled Plasma – Mass Spectrometer


33.5 kDa
1.7 kDa
0.9 kDa
1.7 kDa
33.5 kDa
63 nm
330 nm
Stream Water
Confluence
Pore Water
9-25cm
NOM Extract
NaOH n°1
1250 1500 1750 2000 2250 2500 2750 3000 3250 3500
Time LC (s)
500 750 1000 1250 1500 1750 2000 2250 2500 2750 3000 3250 3500 3750 4000
Time AF4 (s)

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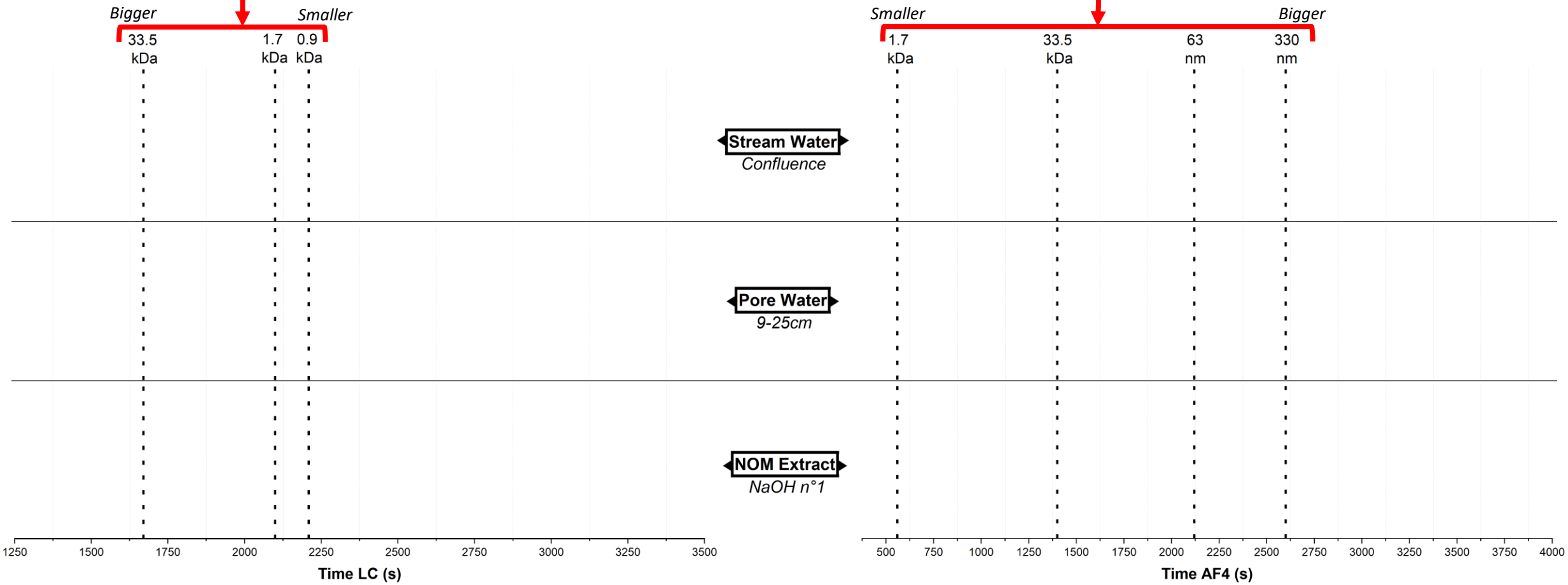
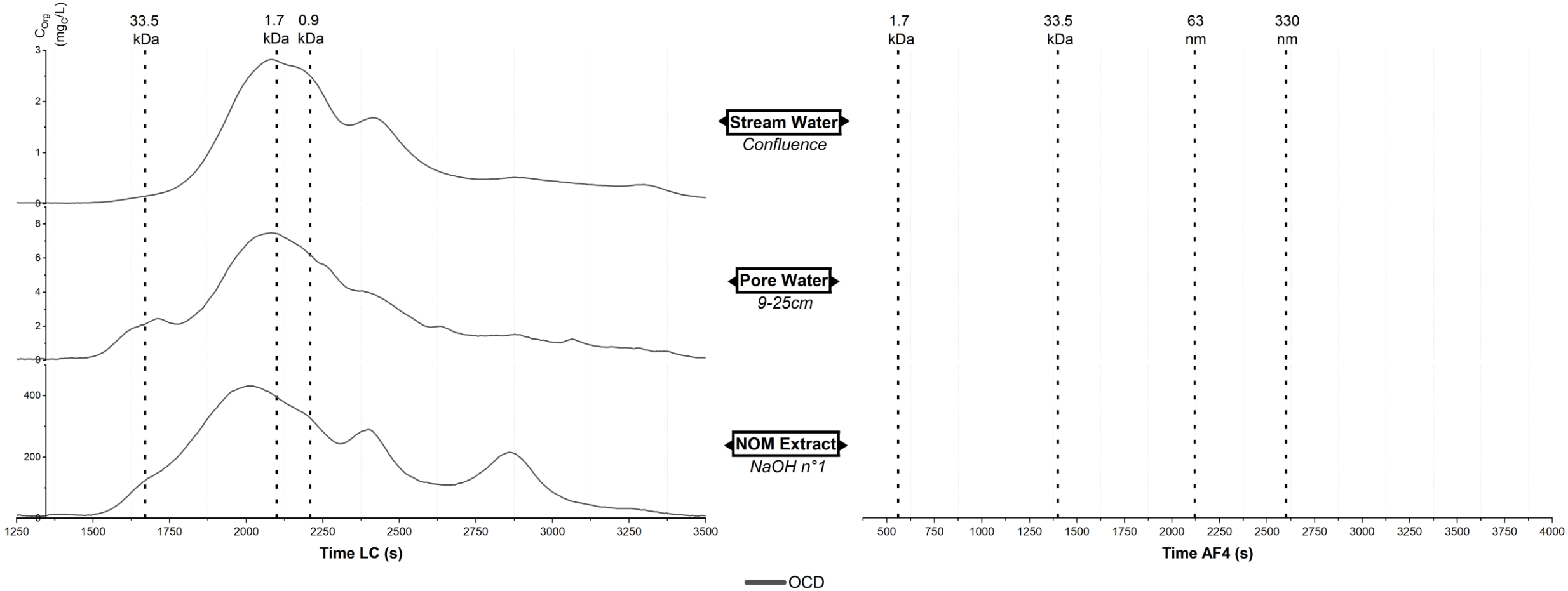
Size Calibration: Injection of monodisperse particles of known size



Organic Colloids Characterization



- Size of detected organic colloids range from 1 to 6 kDa
- Humic-like Substances are the most abundant fraction (>50% of TOC) for all samples

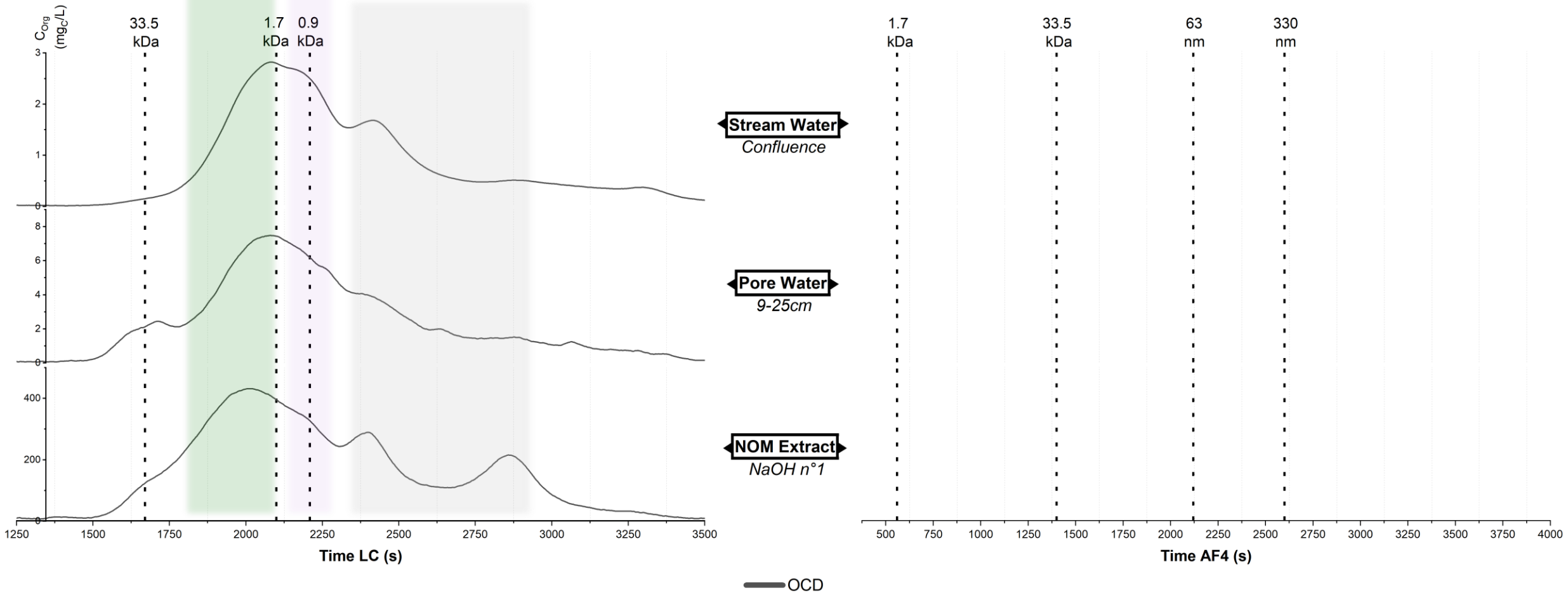
Organic Colloids Characterization

Karlsruhe Institute of Technology

Humic-like Substances = Biomass residues

Building Blocks = Breakdown products of HS

Low Molecular Weight compounds



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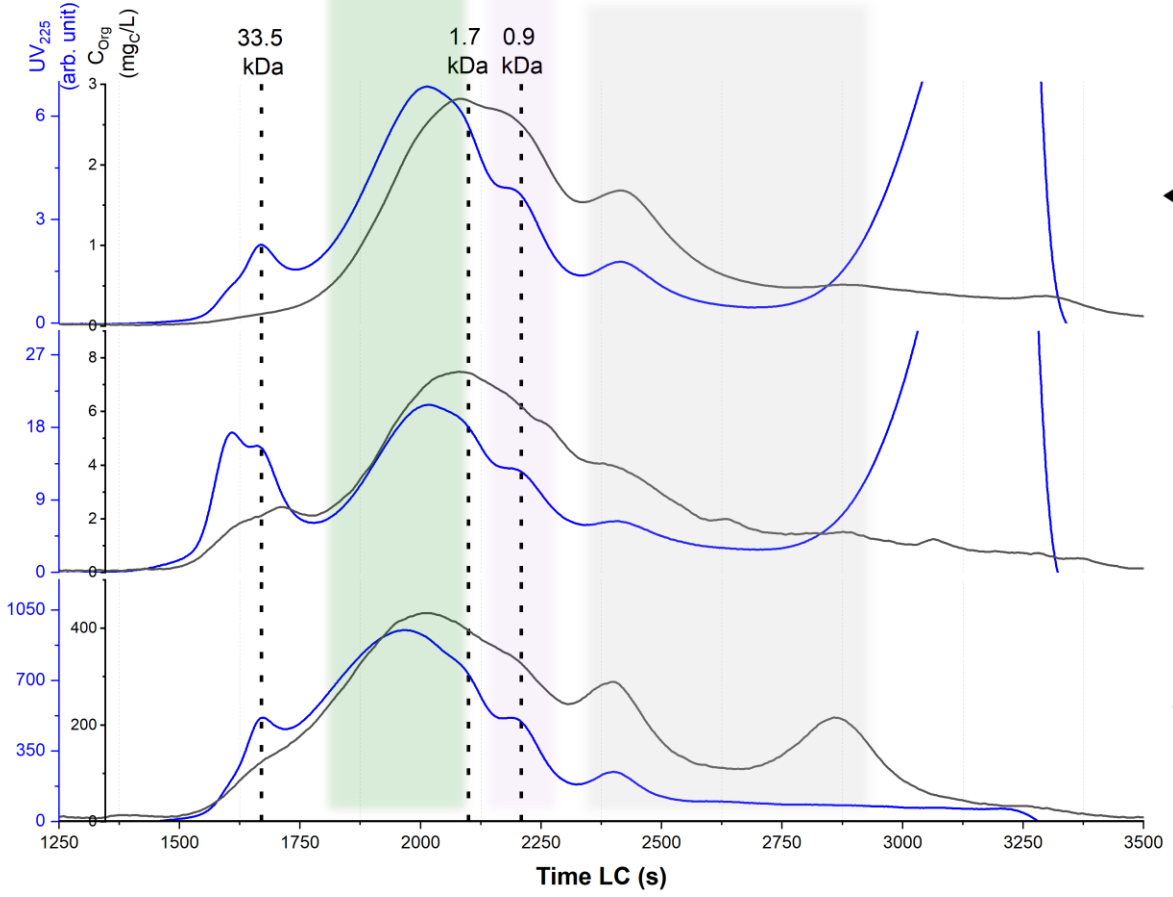

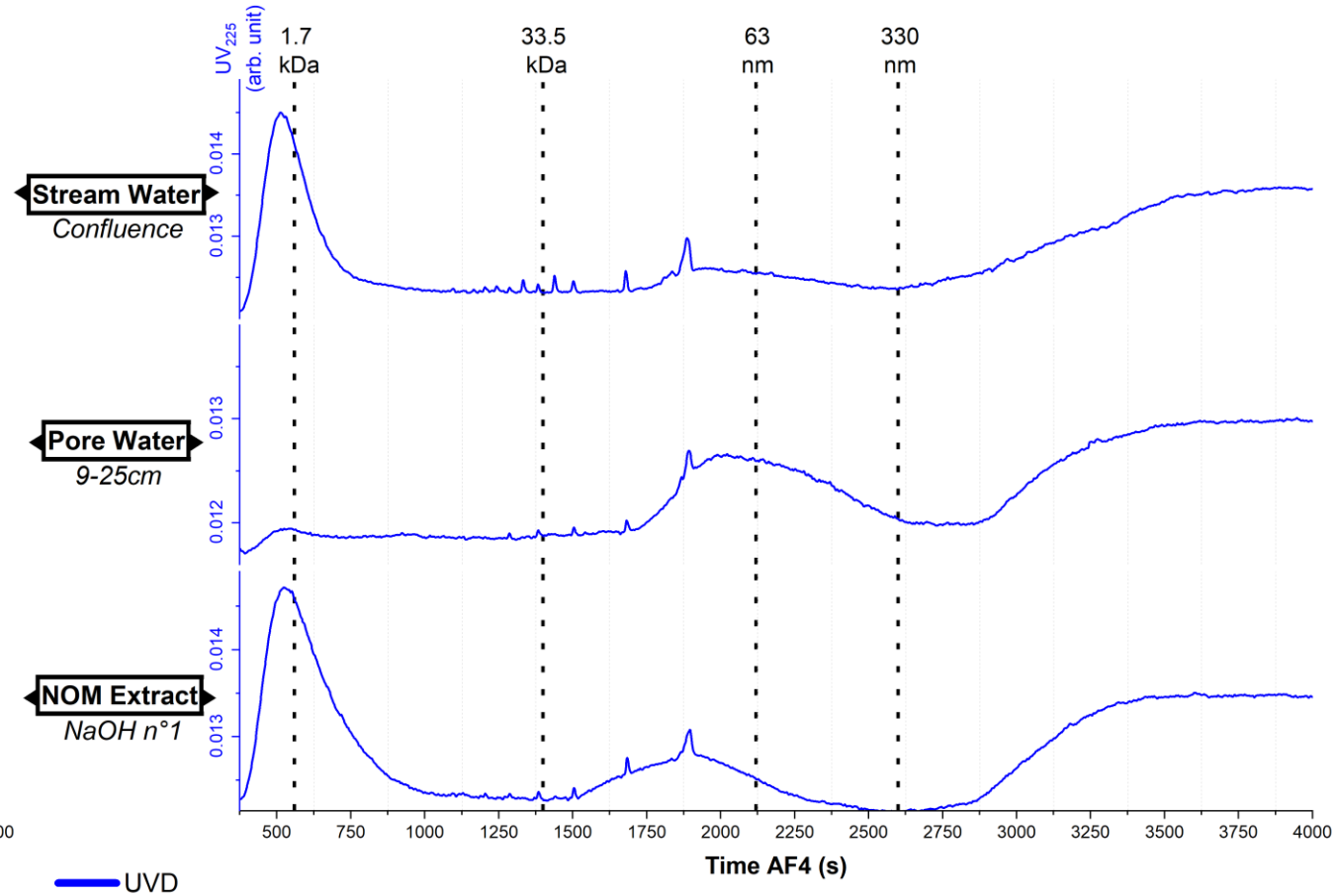

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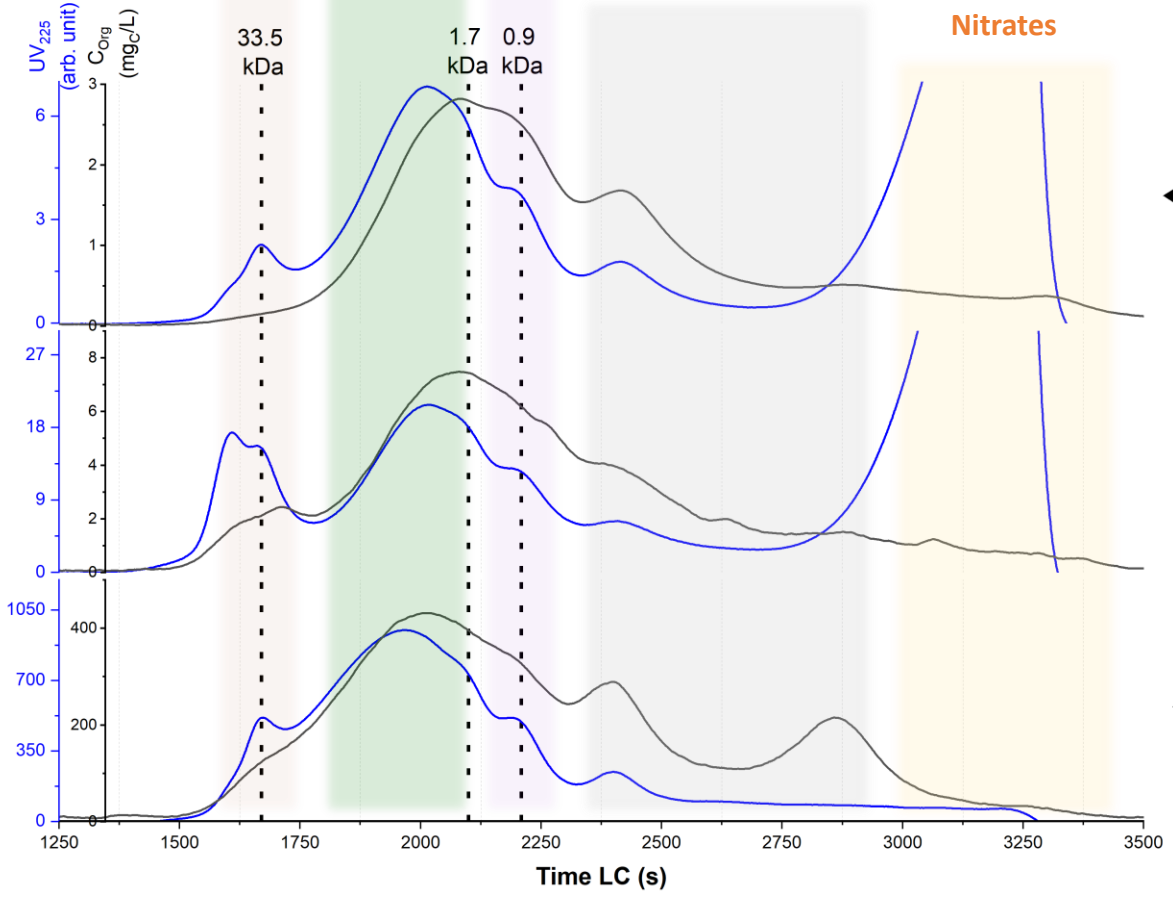
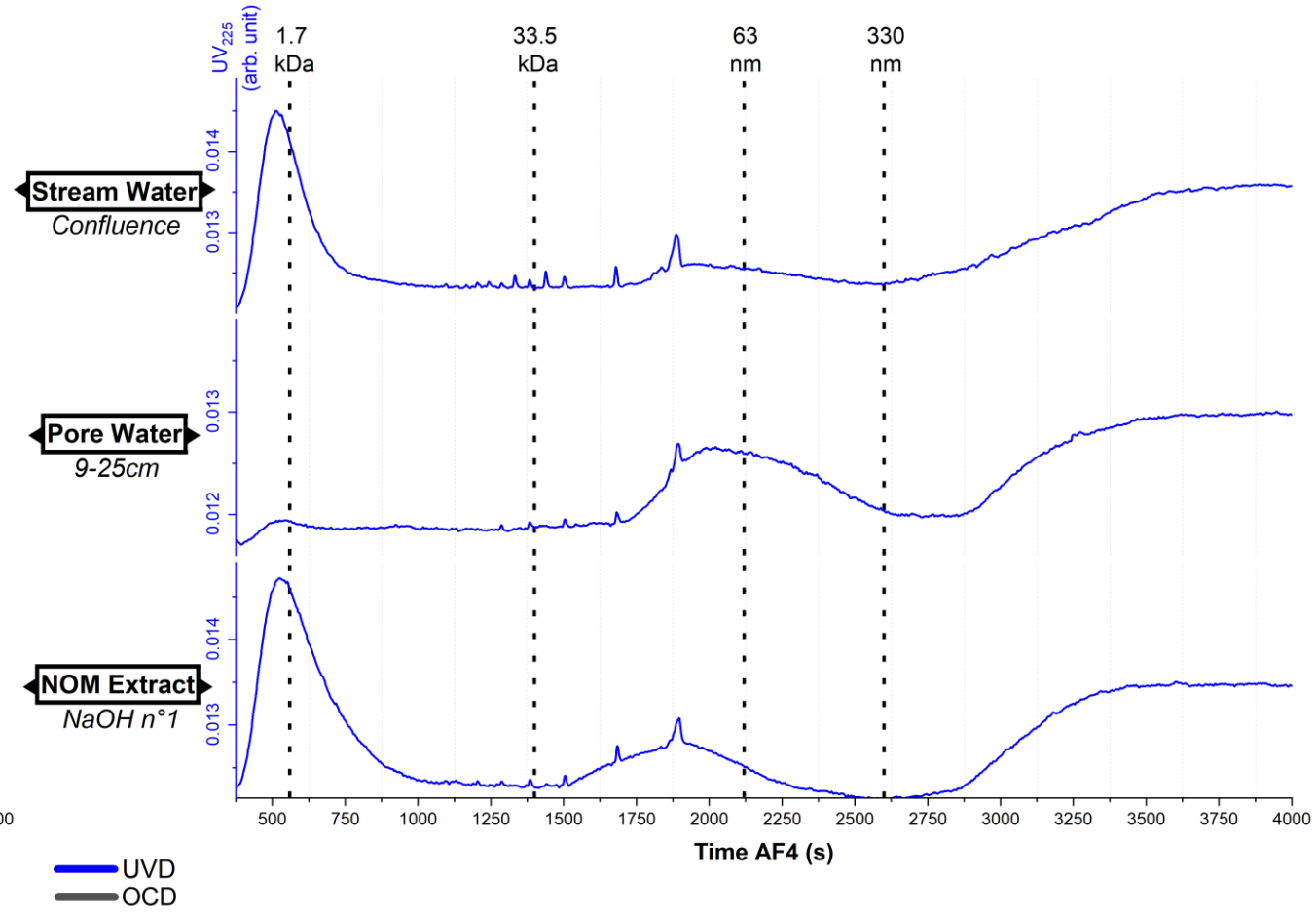
Inorganic Colloids

Building Blocks = Breakdown products of HS

Low Molecular Weight compounds

Nitrates





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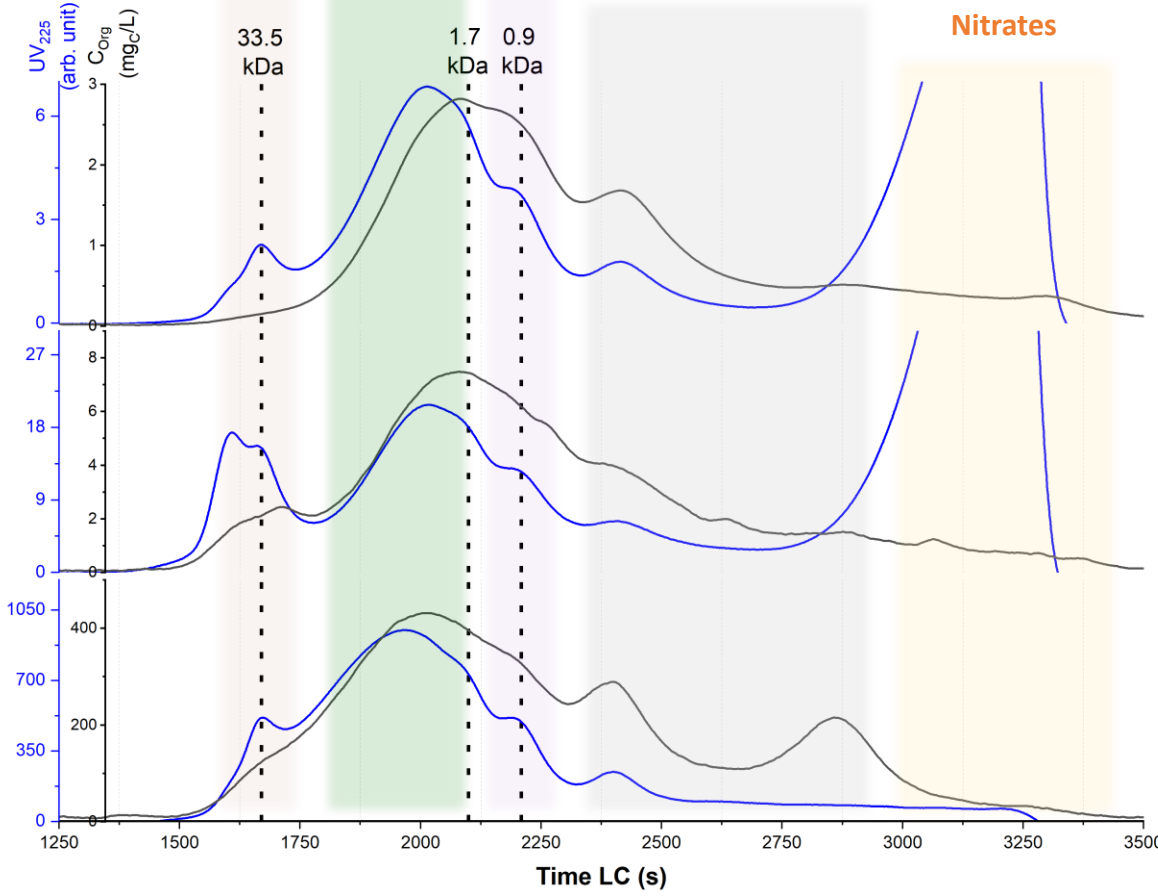
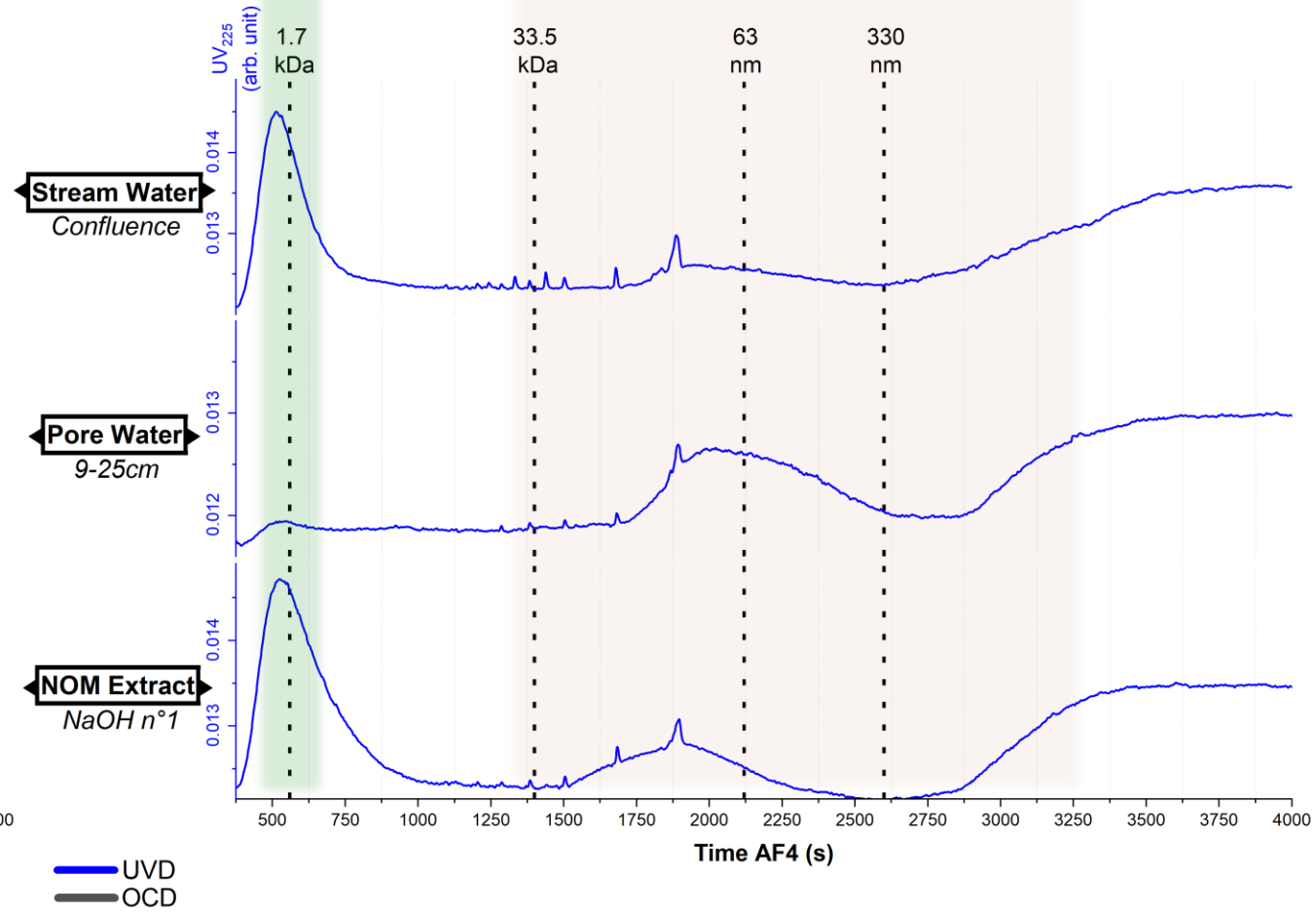


Humic-like Substances

Inorganic Colloids



- Size of detected inorganic colloids range from 20 to 60 nm
- Bigger inorganic colloids are found in Pore Waters

Pb Speciation

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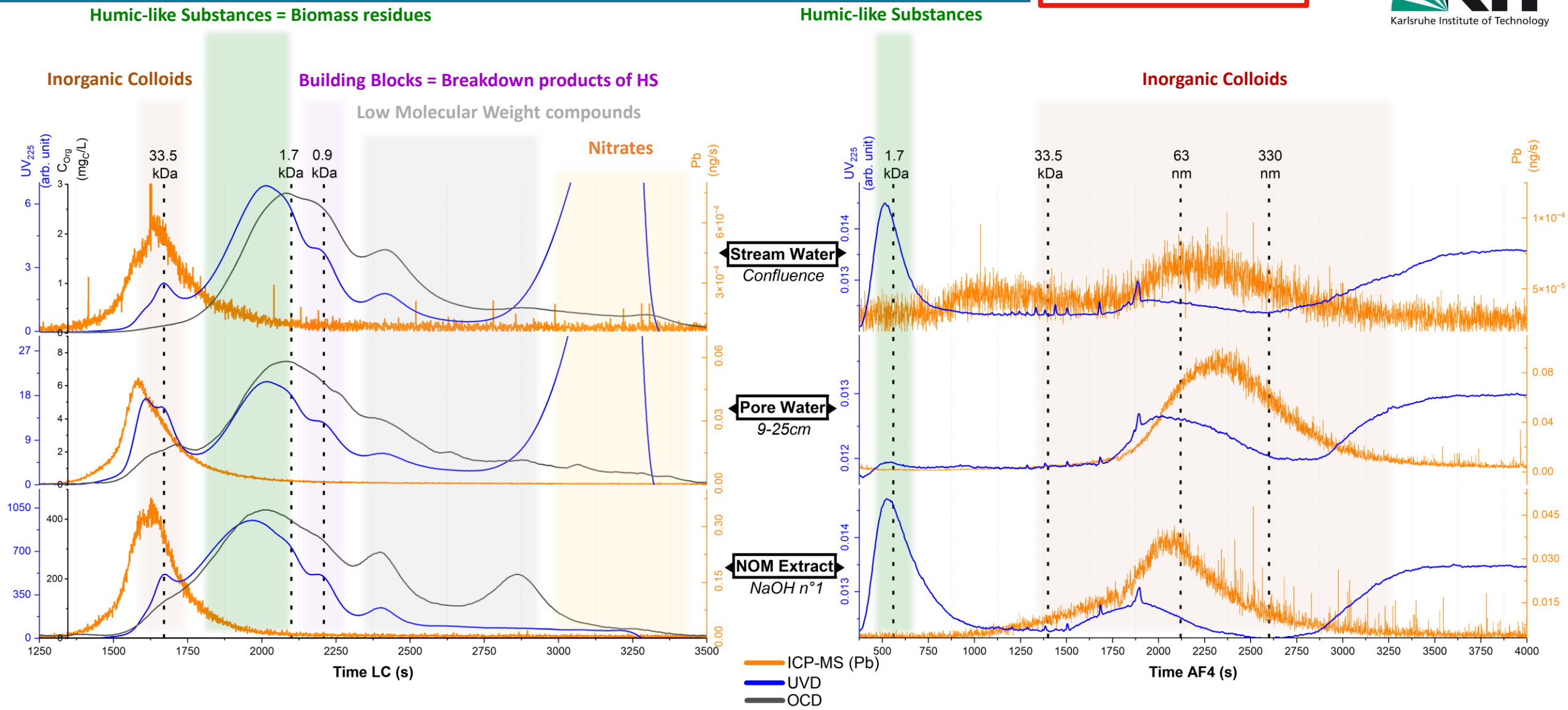

- Pb mainly eluting with inorganic colloids
- Consistent with peak attribution from OCD and UVD

Th Speciation

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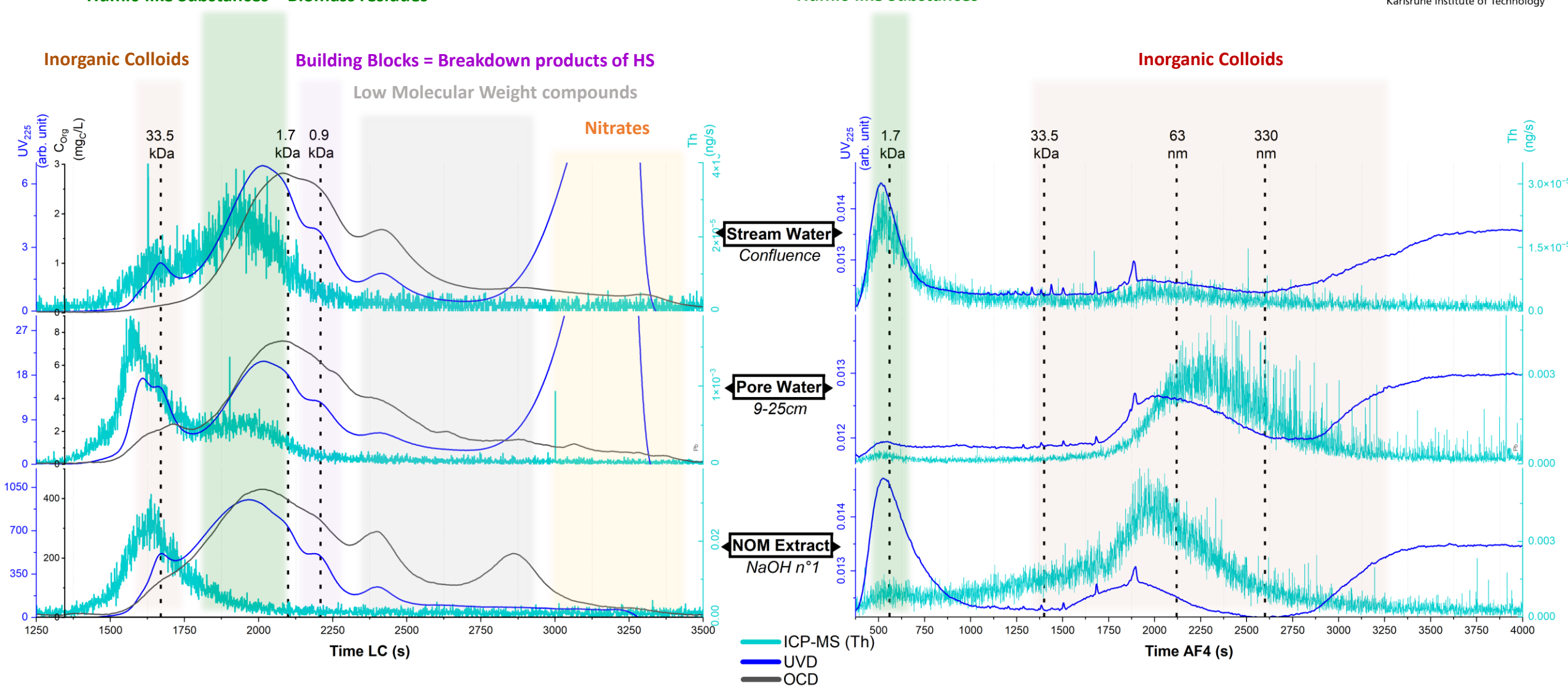

- Th mainly eluting with organic colloids (Stream Water) or with inorganic colloids (Pore Water/SOM Extract)
- Consistent with peak attribution from OCD and UVD

U Speciation

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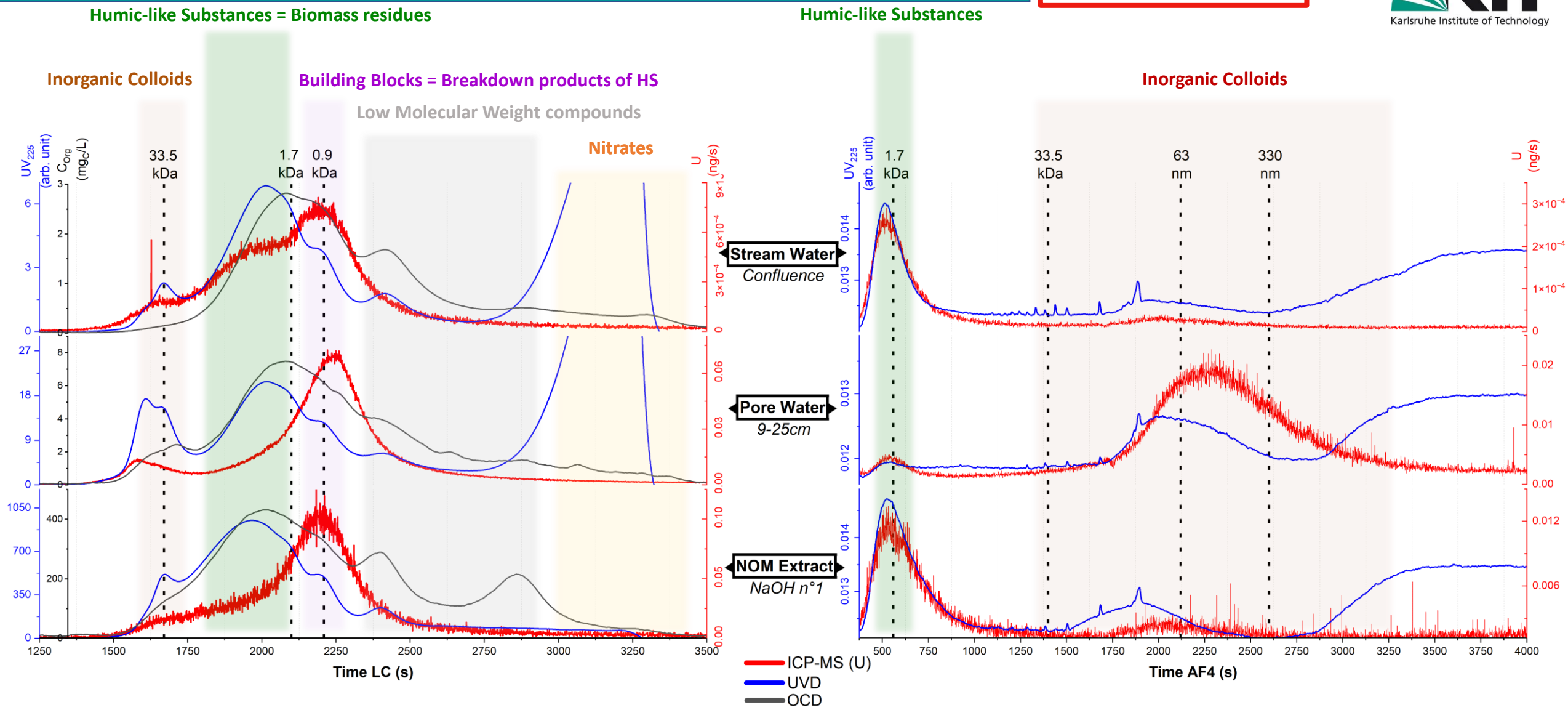
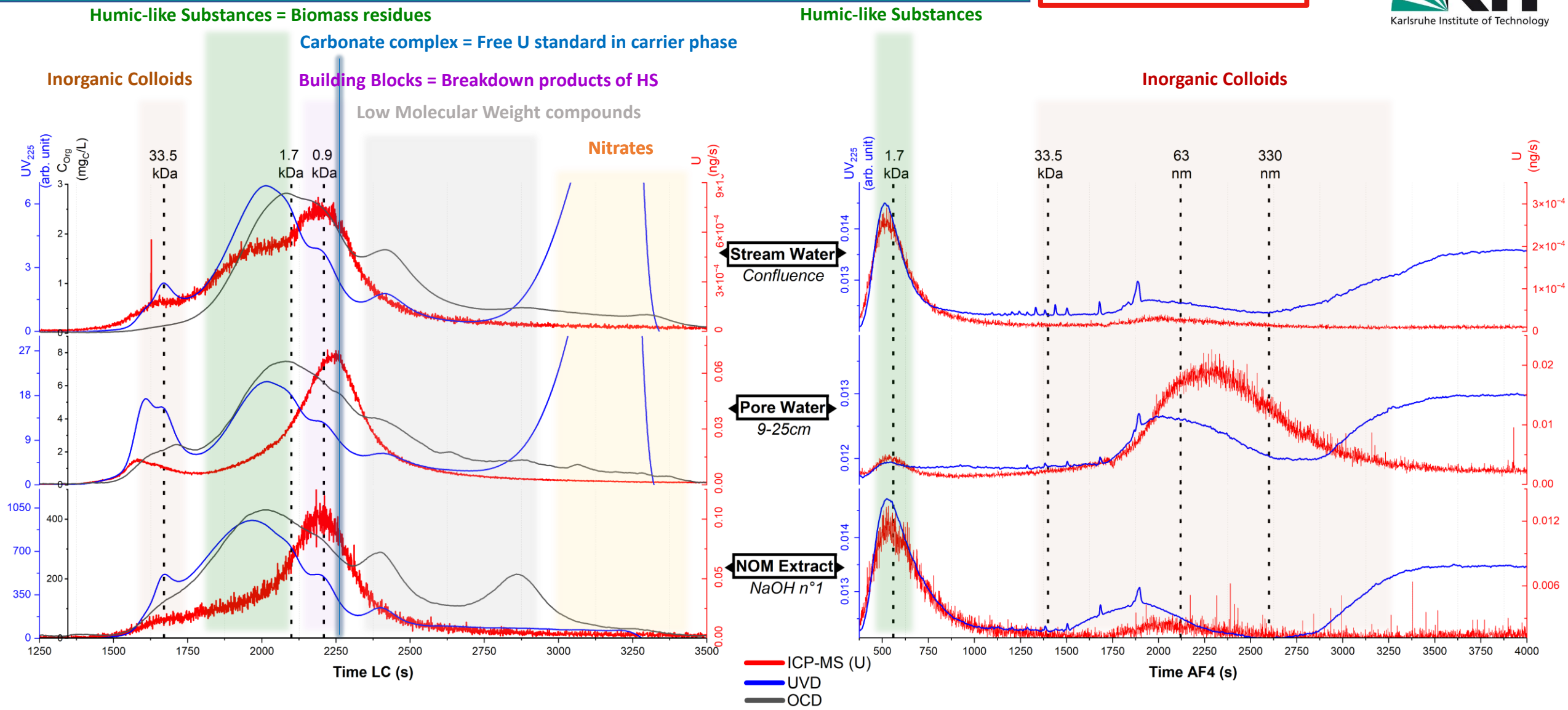


- Dissolved fraction (<1kDa/1nm) is not visible in AF4
- ICP-MS detection is semi-quantitative for both LC and AF4

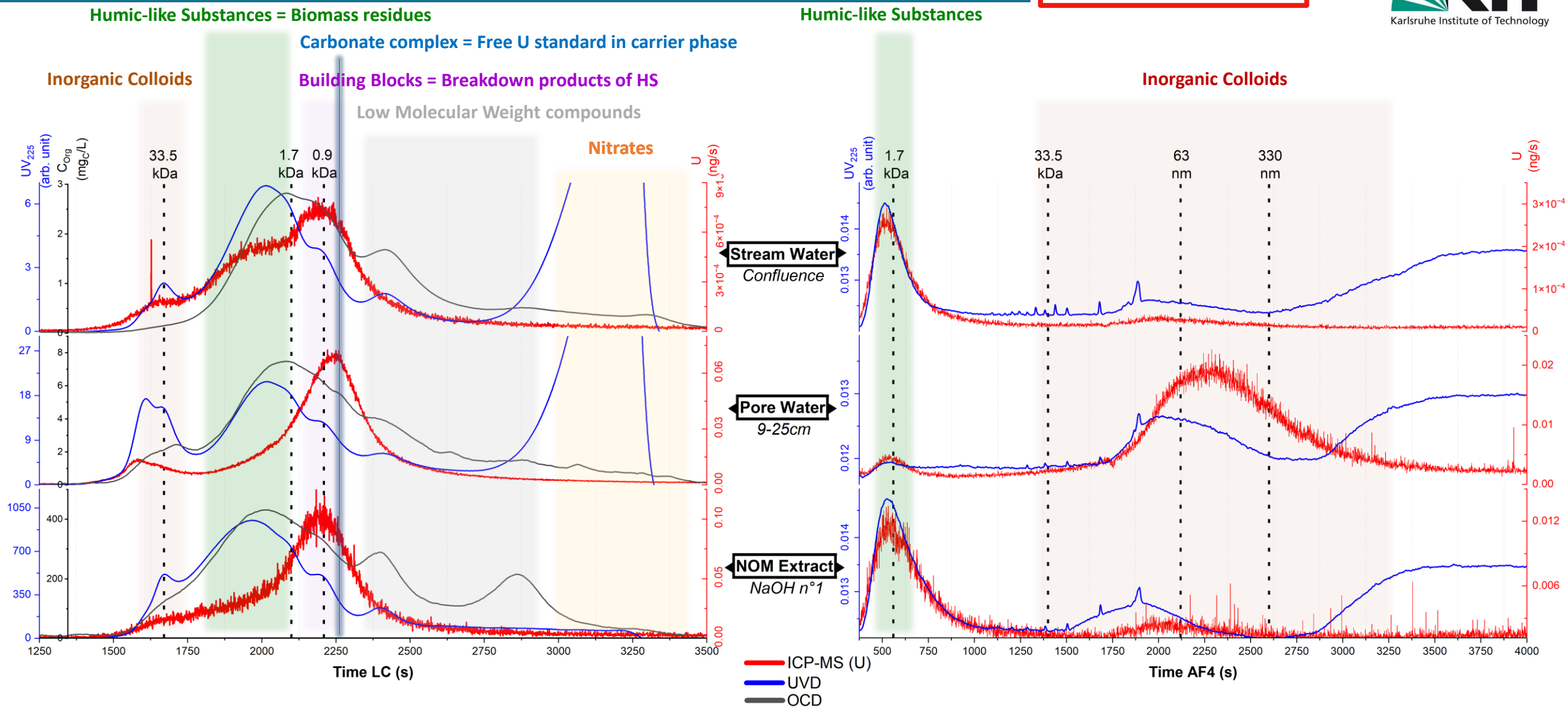
U Speciation

Karlsruhe Institute of Technology



U Speciation

Karlsruhe Institute of Technology



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U Speciation

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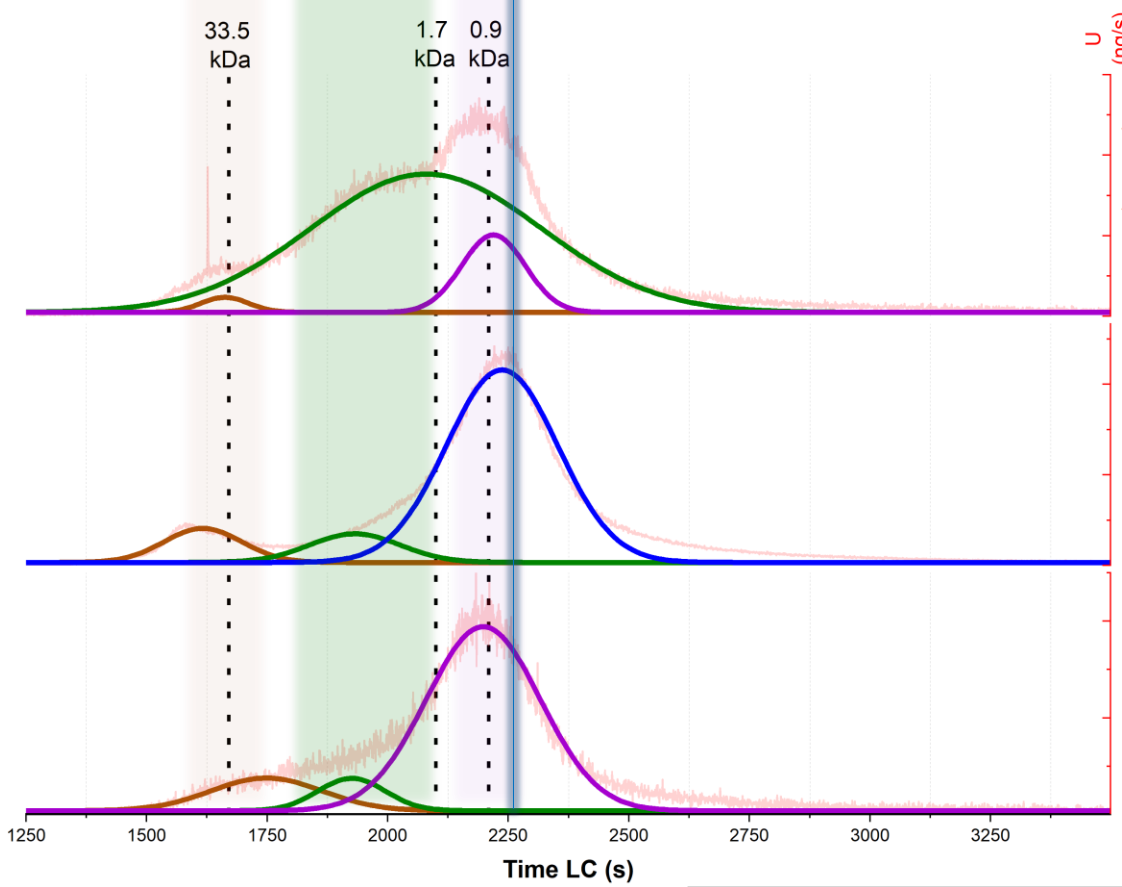
Humic-like Substances = Biomass residues

Carbonate complex = Free U standard in carrier phase

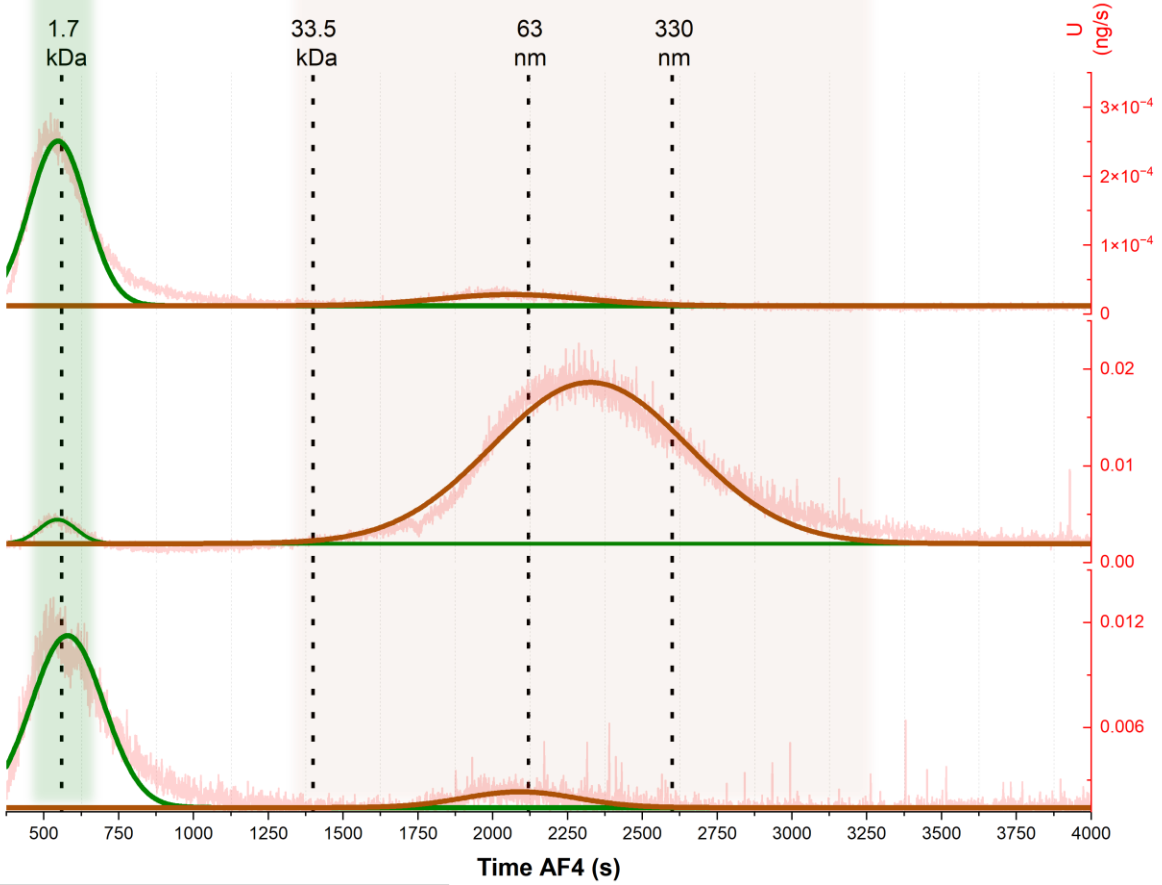
Inorganic Colloids

Building Blocks = Breakdown products of HS



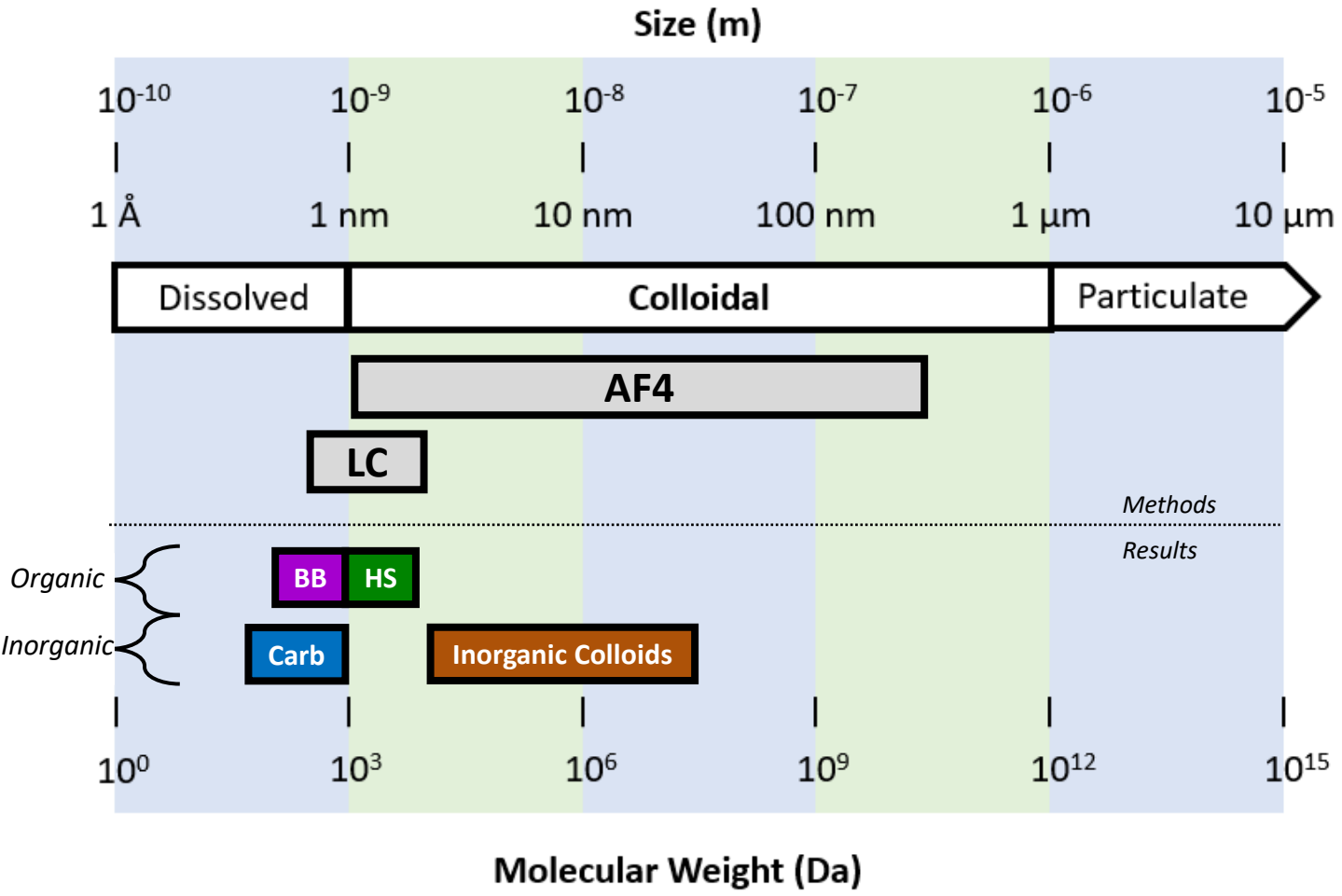
Humic-like Substances

Inorganic Colloids



Stream Water	Humic-like Substances
Pore Water	Carbonates + Inorganic Colloids
NOM Extraction	Humic-like Substances + Building Blocks

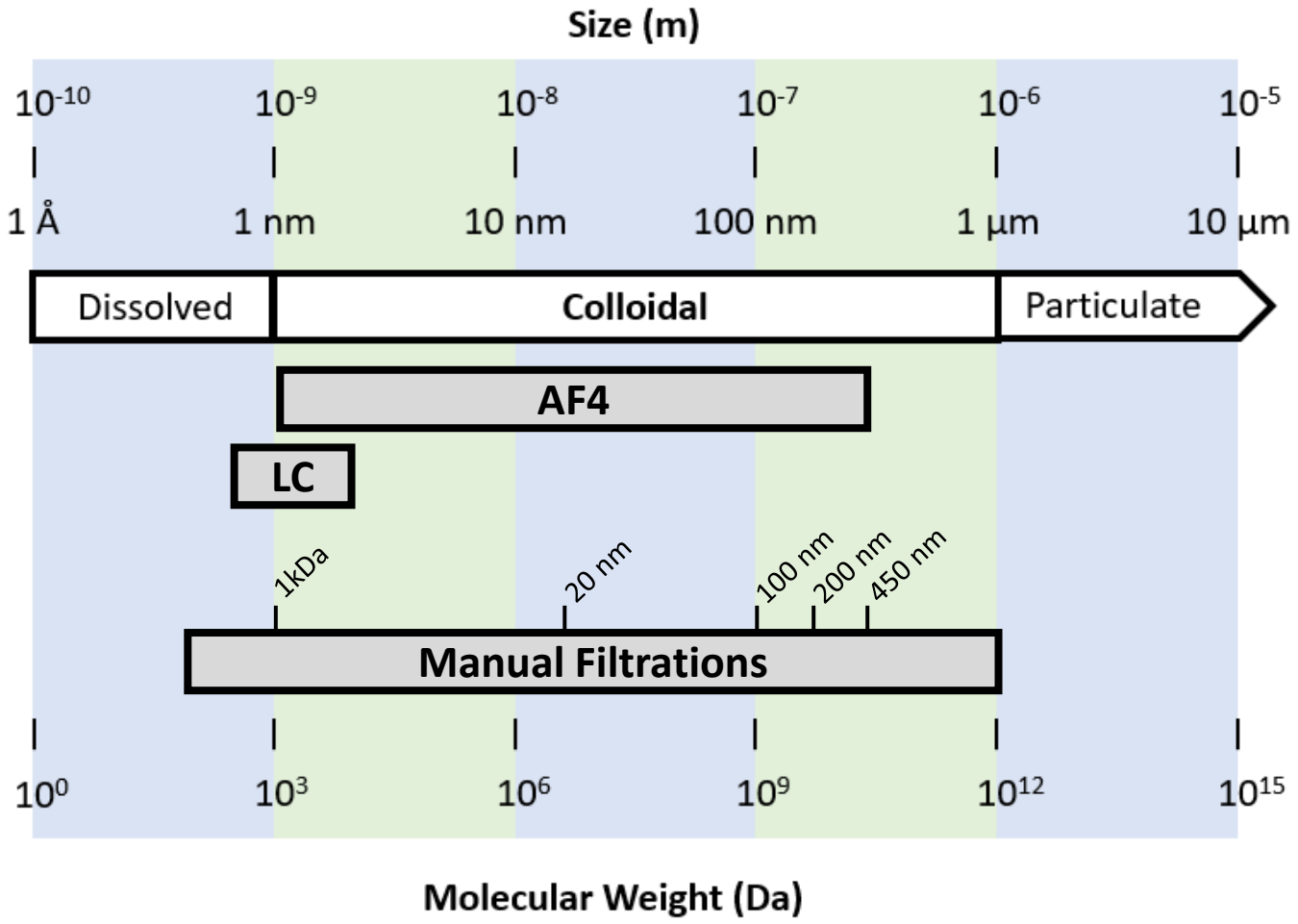
Predominant U-bearing particles, based on signal deconvolutions



Stream Water	Humic-like Substances
Pore Water	Carbonates + Inorganic Colloids
NOM Extraction	Humic-like Substances + Building Blocks

Predominant U-bearing particles

- LC-OCD-UVD and AF4-UVD systems allowed characterization of organic and inorganic colloids
- Coupling with ICP-MS evidenced differences in U speciation across aqueous environments of Rophin wetland
- Significant proximity between natural samples and SOM Extraction was observed



Completing colloids characterization

- SAXS analysis (Inorganic)
- ESI-MS analysis (Organic)

Completing Uranium speciation

- Manual filtrations + ICP-MS analysis
- Modelling calculation (PhreeQC/Vminteq)

Starting U/Ra – NOM reactivity experiments

- Purification of Extracted NOM
- Experimental complexation constant

Thank you for your attention !

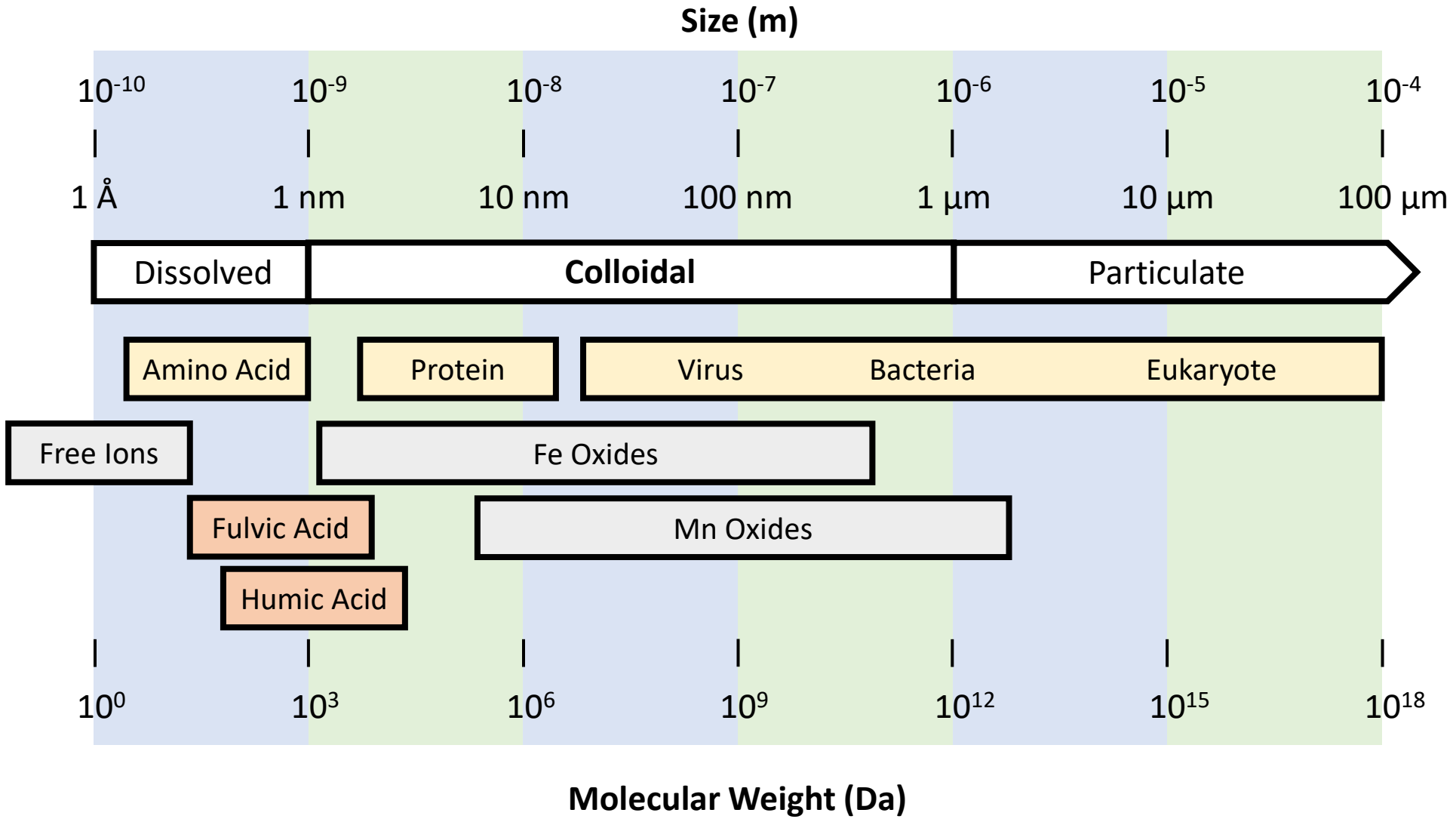
Karlsruher Institut für Technologie - Institut für Nukleare Entsorgung

Bouby Muriel, Geyer Frank, Müller Natalia

Subatech - Radiochemistry

Nivesse Anne-Laure, Lebault Catherine, Colin Travis, Benalcazar Soraya, Landesman Catherine, Montavon Gilles

Backups Slides : Colloidal Range – Typical molecules in natural systems



Backups Slides : Global parameters across Rophin wetland

I - Global parameters

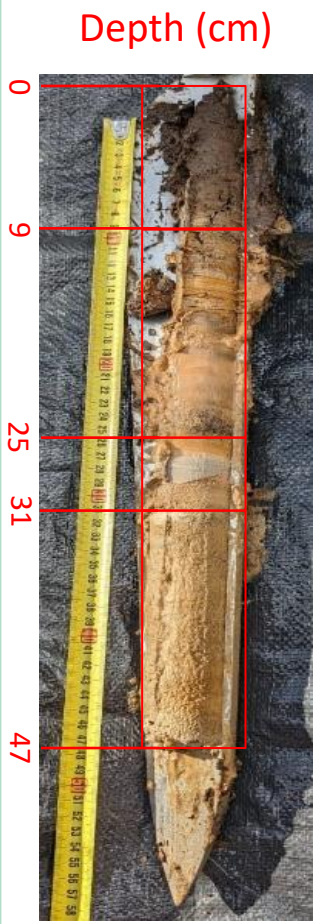
Sample	$NPOC_{tot}$ (mg_C/L)	U_{tot} ($\mu g_U/L$)
Upstream	3.2 ± 0.1	0.8 ± 0.1
Confluence	4.5 ± 0.2	2.8 ± 0.1
Exort	4.6 ± 0.2	4.4 ± 0.1
Downstream	4.7 ± 0.3	3.5 ± 0.1
0-9 cm	9.9 ± 0.5	166 ± 2
9-25 cm	21.1 ± 0.7	1400 ± 100
25-31 cm	12.0 ± 0.9	92 ± 7
31-47 cm	16.2 ± 0.7	54 ± 1
Extr. 1	800 ± 30	154 ± 2
Extr. 2	220 ± 10	41 ± 1
Extr. 3	80 ± 10	17 ± 1

- $[NPOC_{tot}]_{Upstream} < [NPOC_{tot}]_{Confluence, Exort, Downstream}$
  → Part of the NOM comes from the mine/the wetland.

- **$[U_{tot}]$ in *stream waters:***
  - $[U_{tot}]_{Exort} > [U_{tot}]_{Upstream}$ → **Storage site = primary source of U in the stream**, as observed in [2].
  - $[U_{tot}]_{Confluence} < [U_{tot}]_{Downstream}$ → **Stream recharged in U through the wetland**, as observed in [2].

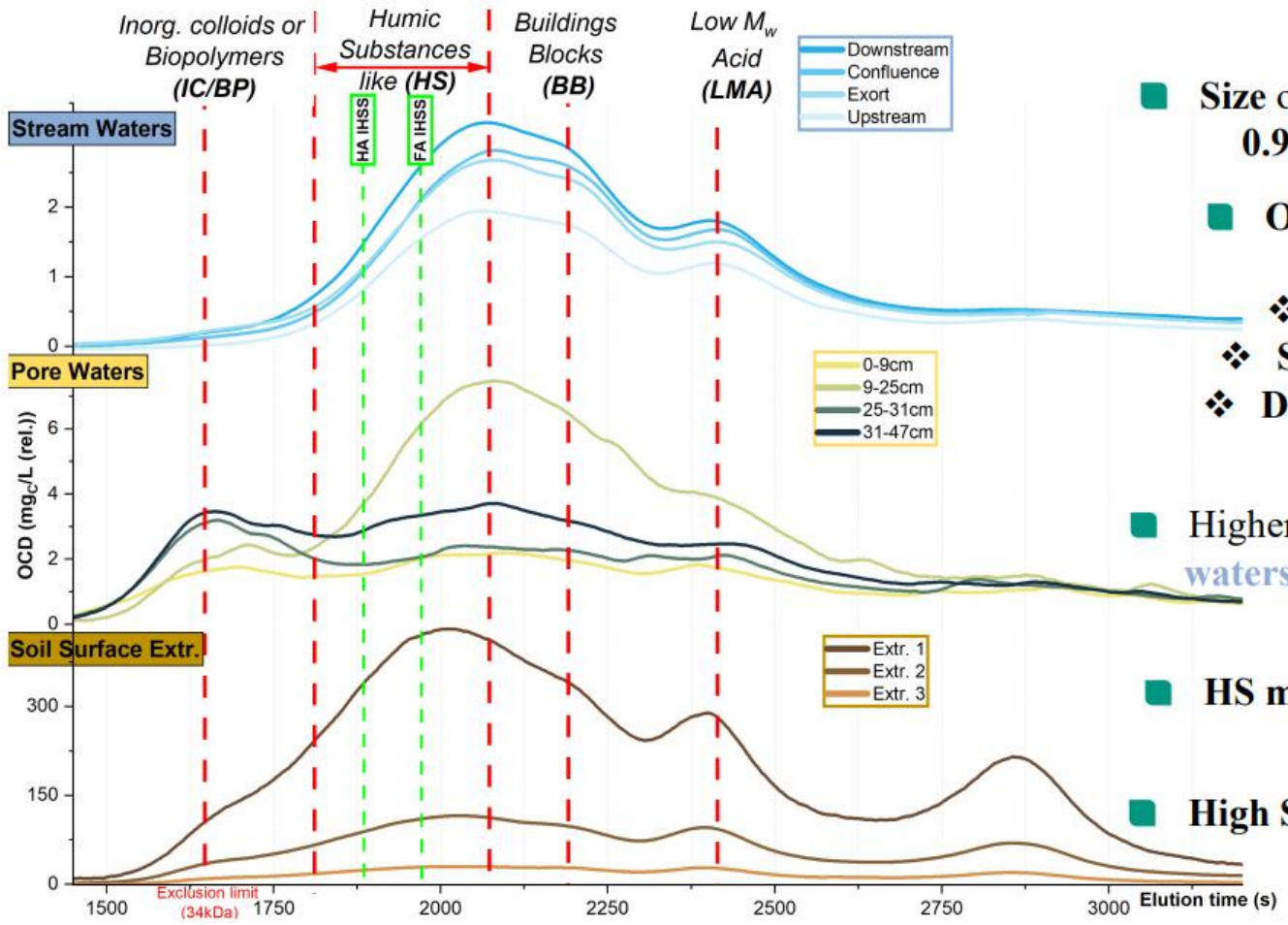
- **$[U_{tot}]$ in *pore waters:***
  - Very high in the layer at 9-25cm → **Pollution** resulting **from past U mining activities**, as discussed in [1].
  - Not correlated with $[NPOC_{tot}]$ → Supports **U-carbonate species presence** *(see III)*.

- **$[NPOC_{tot}]$ in *soil surface extracts:***
  - Decreasing with successive extractions but C/N ratio is constant → **same NOM**.
  - Correlated with $[U_{tot}]$ → Supports **U-BB species presence** *(see III)*.



Backups Slides : Detailed Organic Colloids Characterization (LC-OCD)

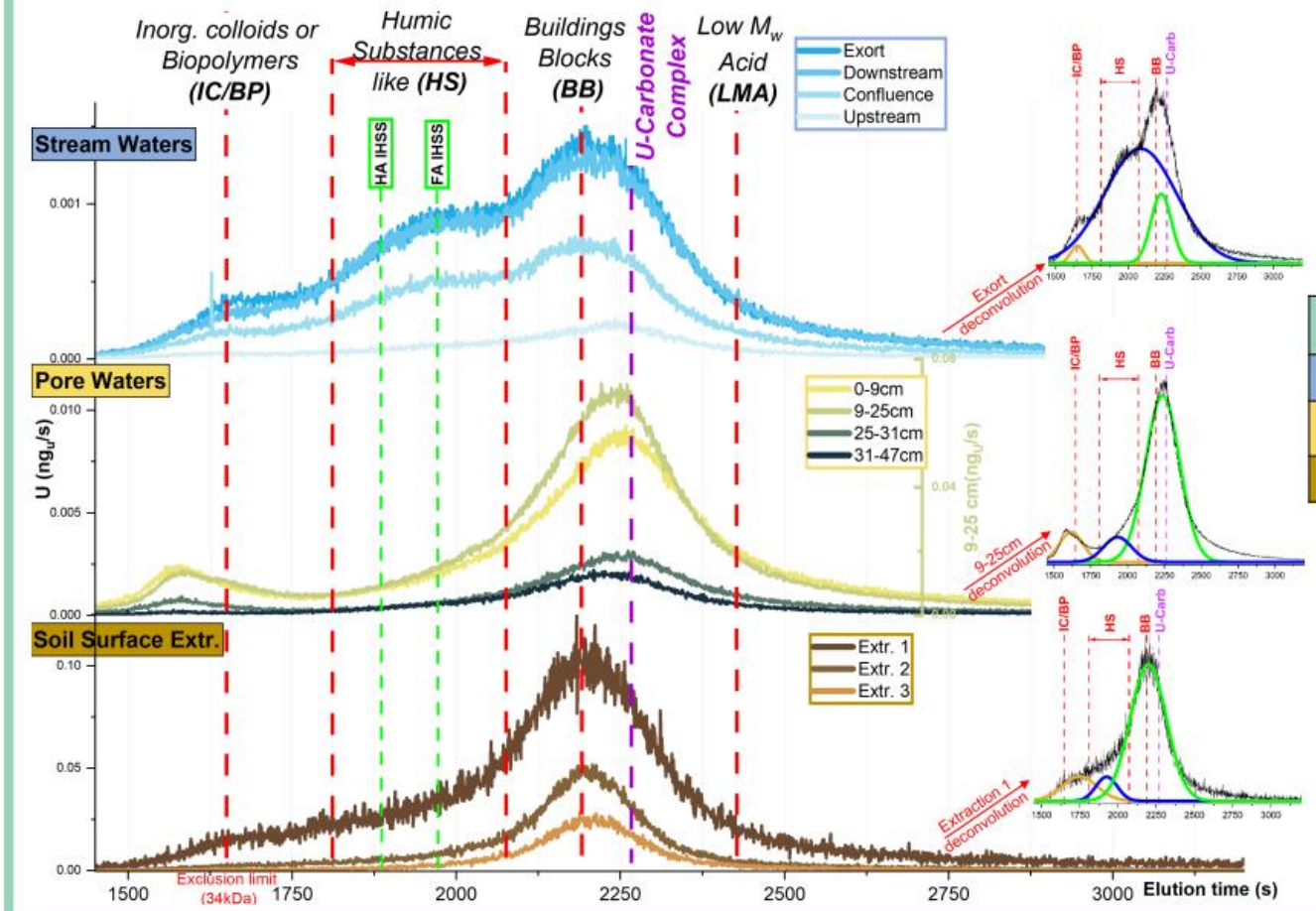
II - Organic Colloids characterization



- **NOM found in all samples**. Fraction identification acc.to [3].
- **Size** of detected **organic colloids** range from **0.9 to 6.4 kDa** (*acc. to Na-PSS calibration).*
- **Organic colloids size/apparent M_w** distribution is:
  - ❖ **Similar** for the 4 stream waters
  - ❖ **Similar** for the 3 **soil surface extracts**
  - ❖ **Different** for the 4 pore waters (amount and fraction abundances variations)
- Higher M_w fraction is less abundant in stream waters than in **soil surface extracts** → natural filtration process.
- **HS most abundant fraction** for all samples (~50% of [$NPOC_{tot}$])
- **High $SUVA_{225}$** for all the samples → presence of **aromatic compounds.**

Backups Slides : Detailed Uranium Distribution (LC-ICP)

III - Uranium Distribution



- Elution of a **U-carbonate complex** at 2270s.

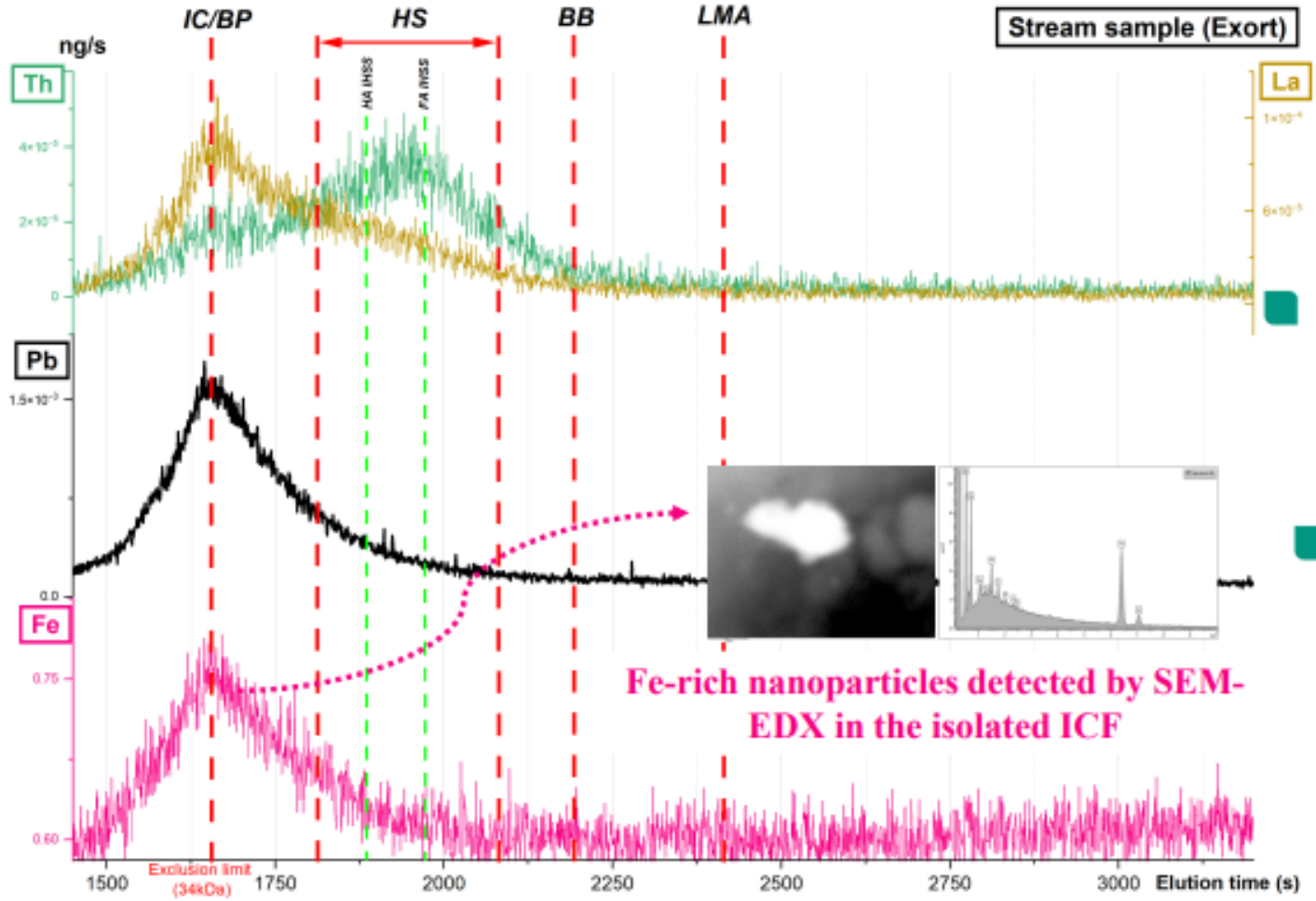
Sample	Main U-bearing specie*
Stream Waters	HS
Pore Waters	Carbonates/BB
Soil Surface Extracts	BB

* : >80% of detected U, based on deconvolutions

- U also co-elutes with an **inorganic colloidal fraction** in all the samples, but in **smaller proportion** (<10%).

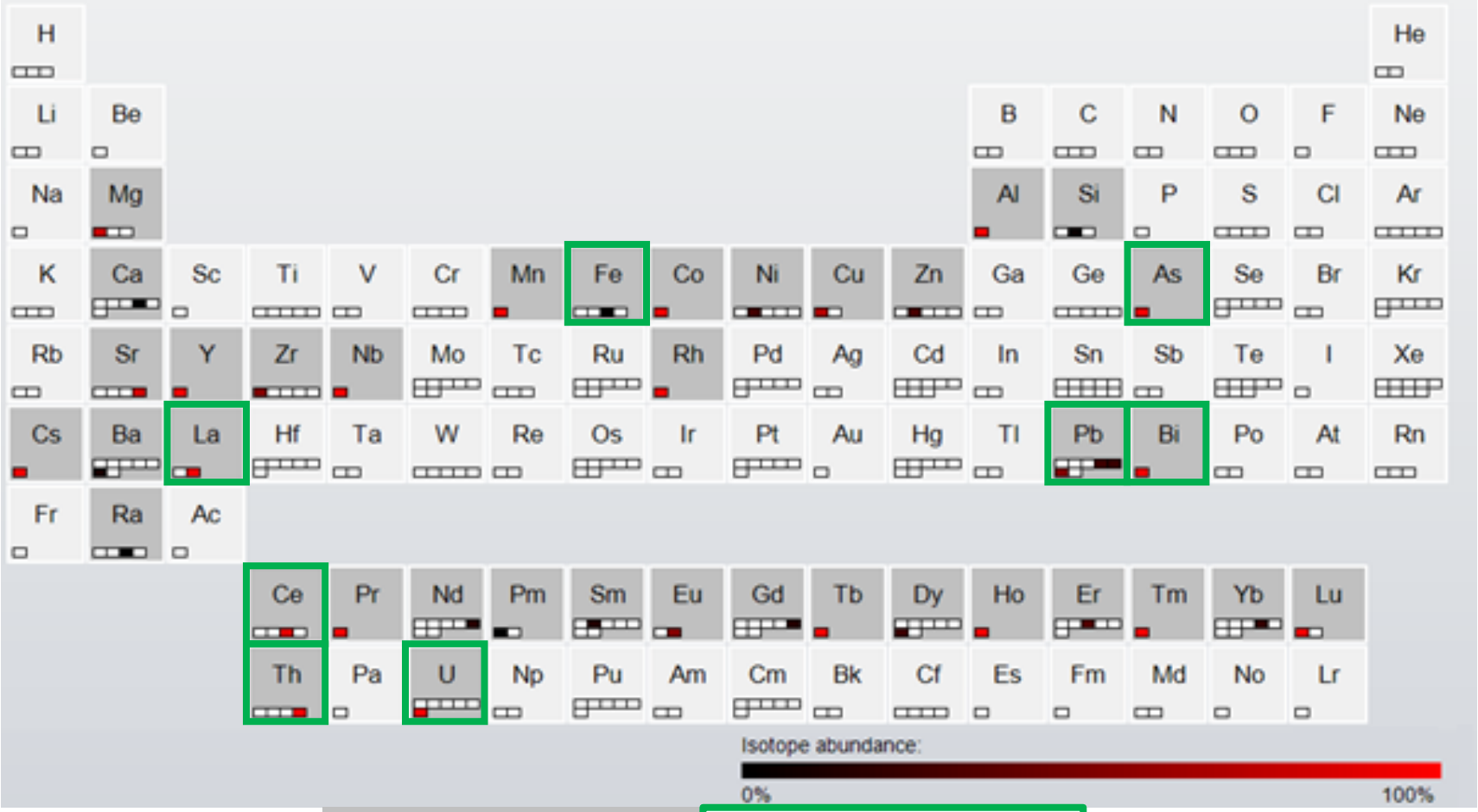
Backups Slides : LC/AF4- ICPMS : Other analyzed elements (LC-ICP)

IV - Inorganic colloidal fraction (ICF) composition and other elements co-elution



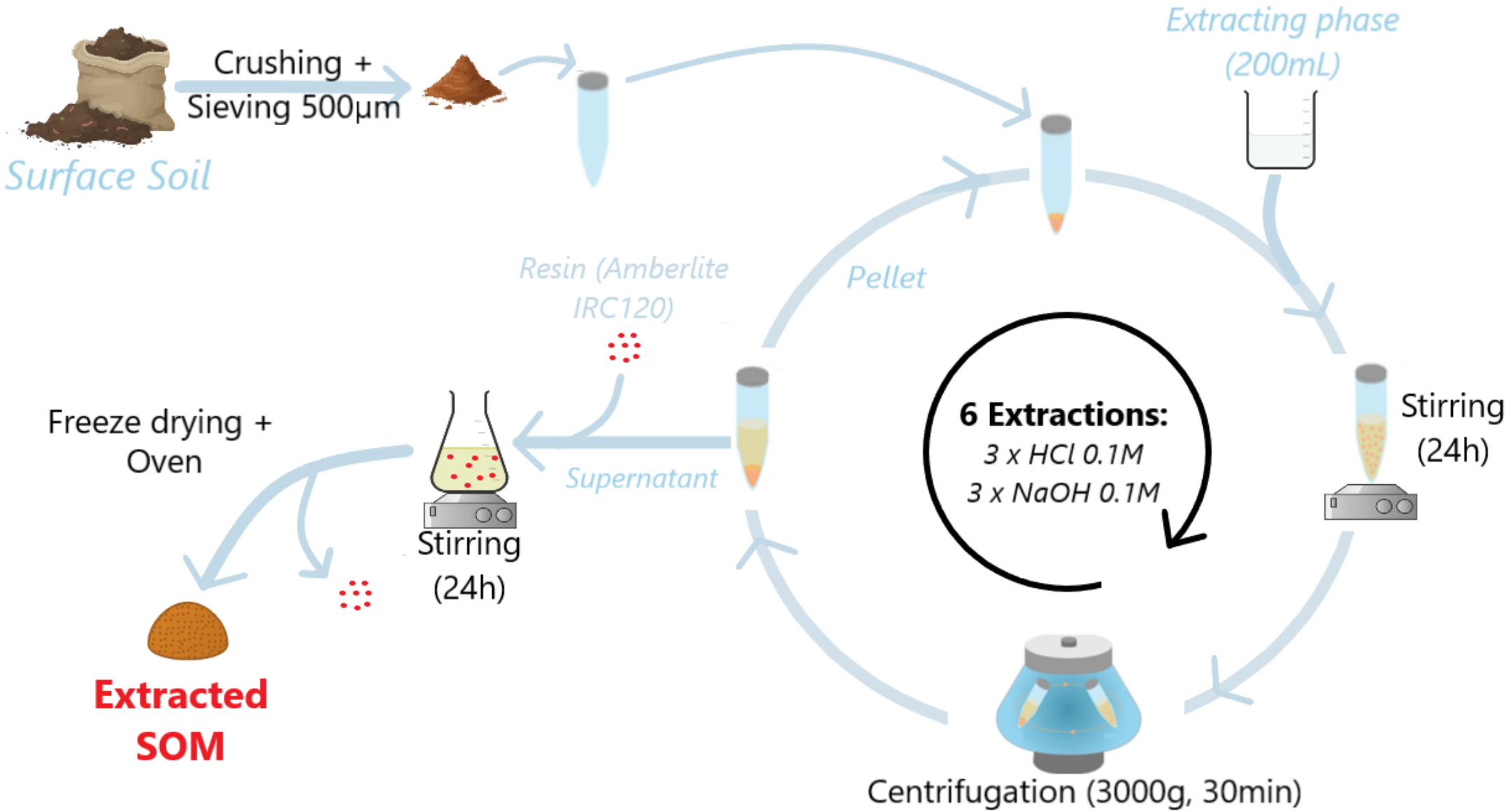
- Detection of ICF confirmed by UVD signal recorded.
- ICF mainly **composed of Fe** and traces of **Pb**.
- **Th** and **La** (and the **lanthanides in general**) co-elute with ICF and **higher M_w NOM** fraction.

Backups Slides : LC/AF4- ICPMS : Other analyzed elements (ICP)



Elements analyzed | *Relevant signal*

Backups Slides : SOM Extraction Process



Backups Slides : Size-based fractionation principles (LC and AF4)

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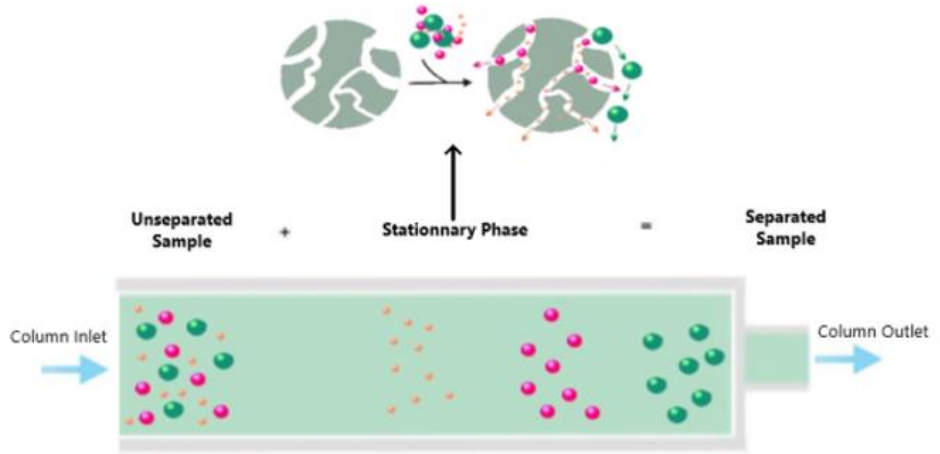
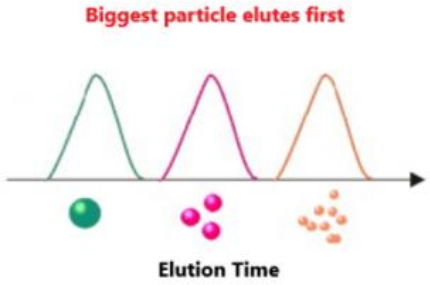
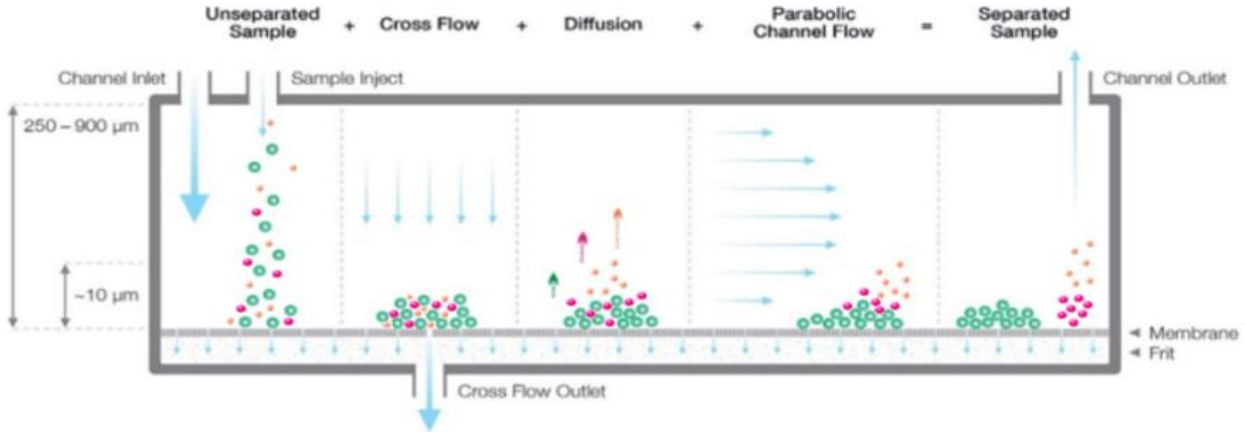
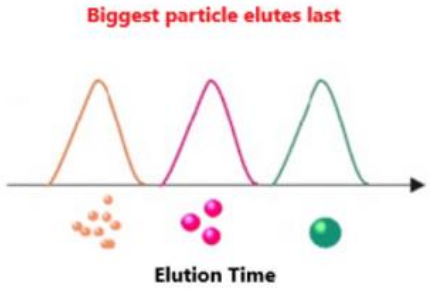
Liquid Chromatography = Size Exclusion Chromatography





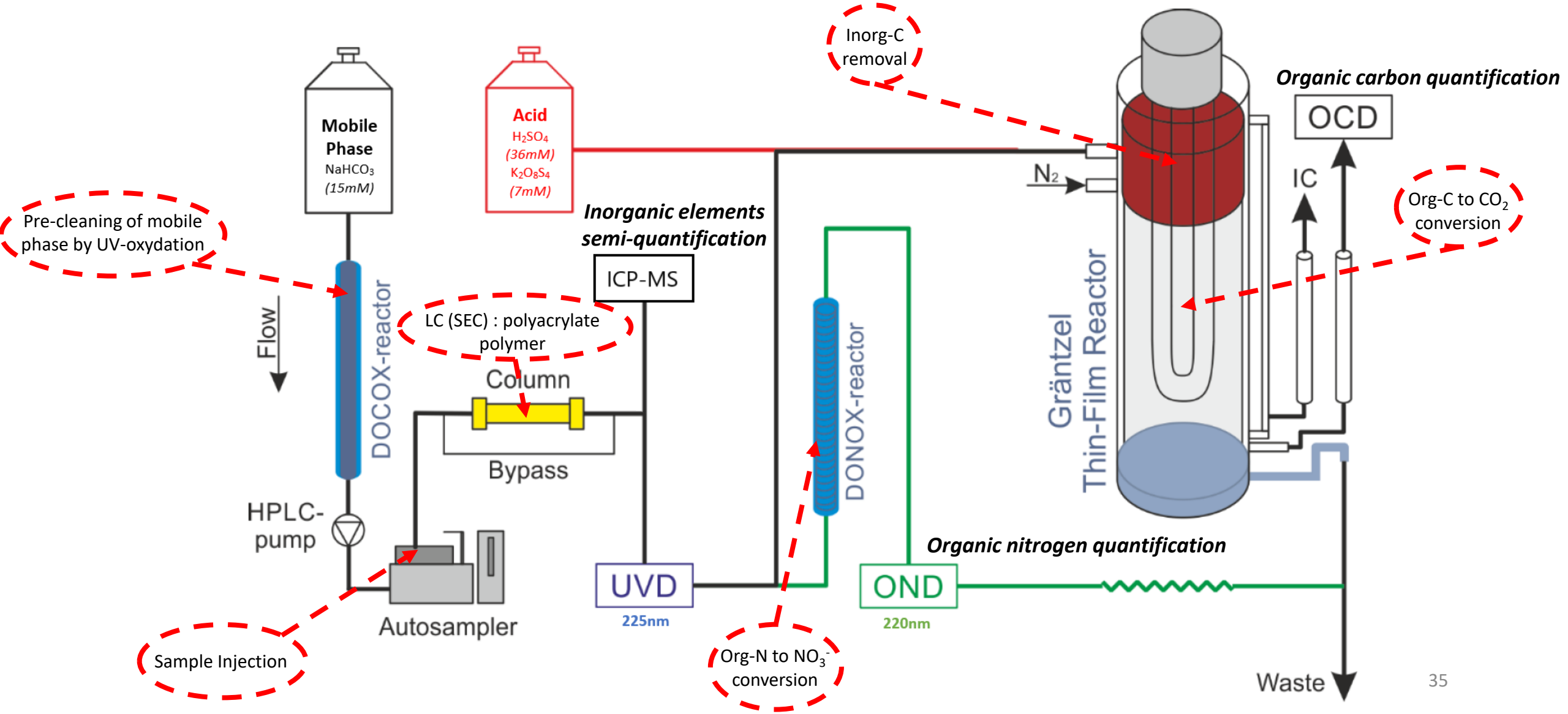
Asymmetric Flow Field-Flow Fractionation



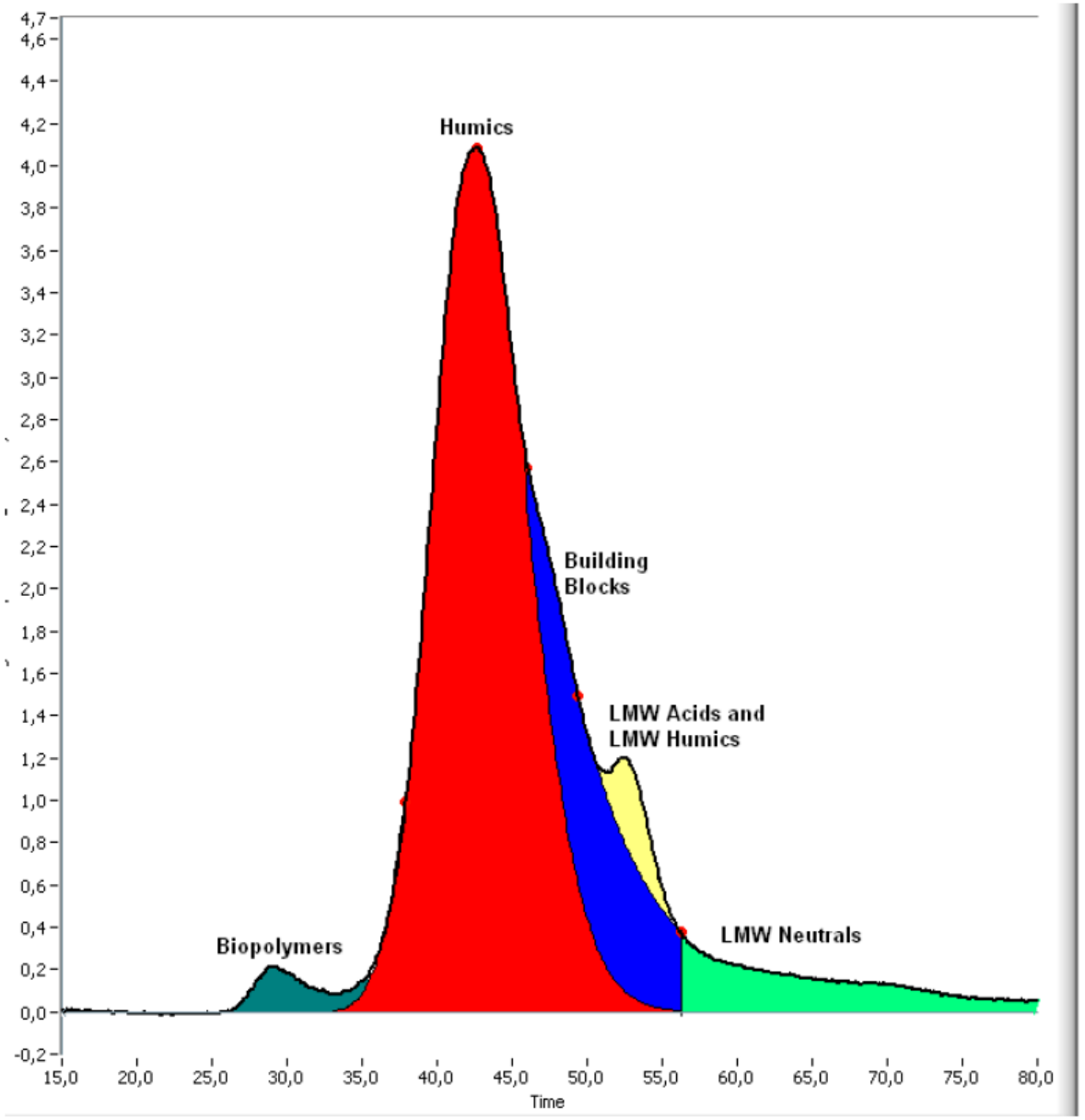


Backups Slides : LC-OCD-OND-UVD-ICP-MS Flowchart

LC-OCD-OND-UVD / ICP-MS system

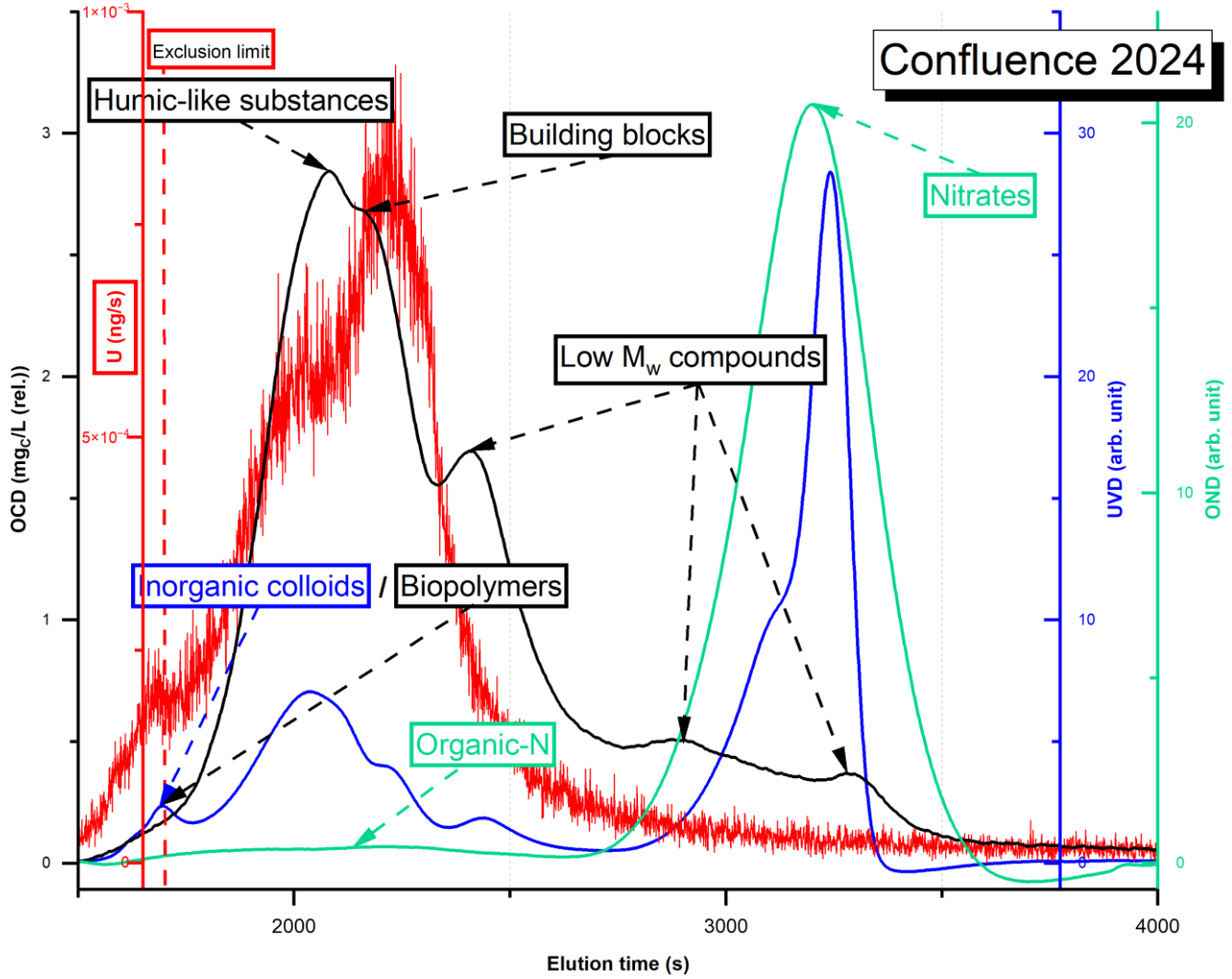


Backups Slides : LC-OCD-OND-UVD characteristics signal peaks



Backups Slides : LC-OCD-OND-UVD characteristics signal peaks

Peak name	Description	Eluting time (s)
Inorganic colloids/biopolymers (IC/BP)	Particles with M_w > 33.5kDa	1700 (Exclusion limit)
Humic-like substances (HS)	Biomass residues, major part of dissolved organic carbon in environmental matrixes	2100
Building Blocks (BB)	Breakdown products of humic substances	2200
Low M_w compounds (LMW)	Small organic acids and neutrals compounds	2400-3300
Nitrates (N)		3200



Main Objective :

Better understanding of colloids role in U/Ra migration for the ZATU sites

I

Implementing innovative methodologies for the **characterization** of field colloids and their associations with U (1st year)

- Action I.1 : Colloids characterization
- Action I.2 : U distribution amongst colloidal range

Main Objective :

Better understanding of colloids role in U/Ra migration for the ZATU sites

I Implementing innovative methodologies for the **characterization** of field colloids and their associations with U (1st year)

II Describing the **reactivity** of U and Ra with respect to colloids through laboratory experiments on model colloids (2nd year)

III Bioavailability of U and transfer to microorganisms (3rd year)

Backups Slides :