Chemistry of ^{226}Ra and other contaminants in a historically contaminated river bank:

Lessons learned on Kd and importance to check precipitation reactions

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Remplex 2023 Summit

Emerging Remediation Technologies Technical Session

sck cen

Belgian Nuclear Research Centre

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Mirroring societal needs

- Climate change
- Circular economy
- Fight against cancer

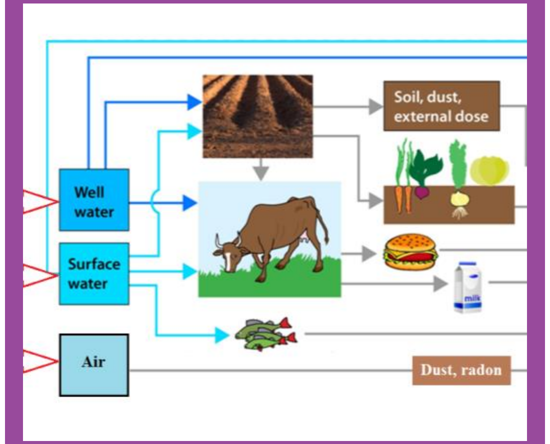
Site Remediation activities at SCK CEN

Site characterisation

Monitoring

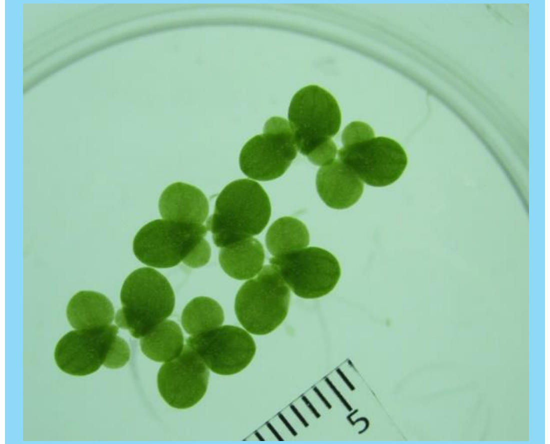
Transfer experiments and models

Impact human and non-human biota



New scenarios ask for new models

Remediation strategies



Chemical and biological solutions for remediation

Decision support models

Site management (site health)

Radioecology

Multicriterial decision support

Stakeholder involvement

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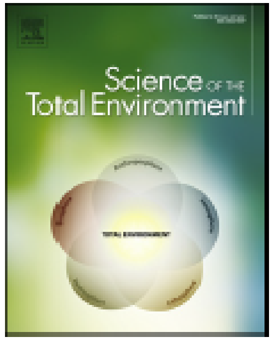

In-depth understanding of local soil chemistry reveals that addition of Ca may counteract the mobilisation of ^{226}Ra and other pollutants before wetland creation on the Grote Nete river banks

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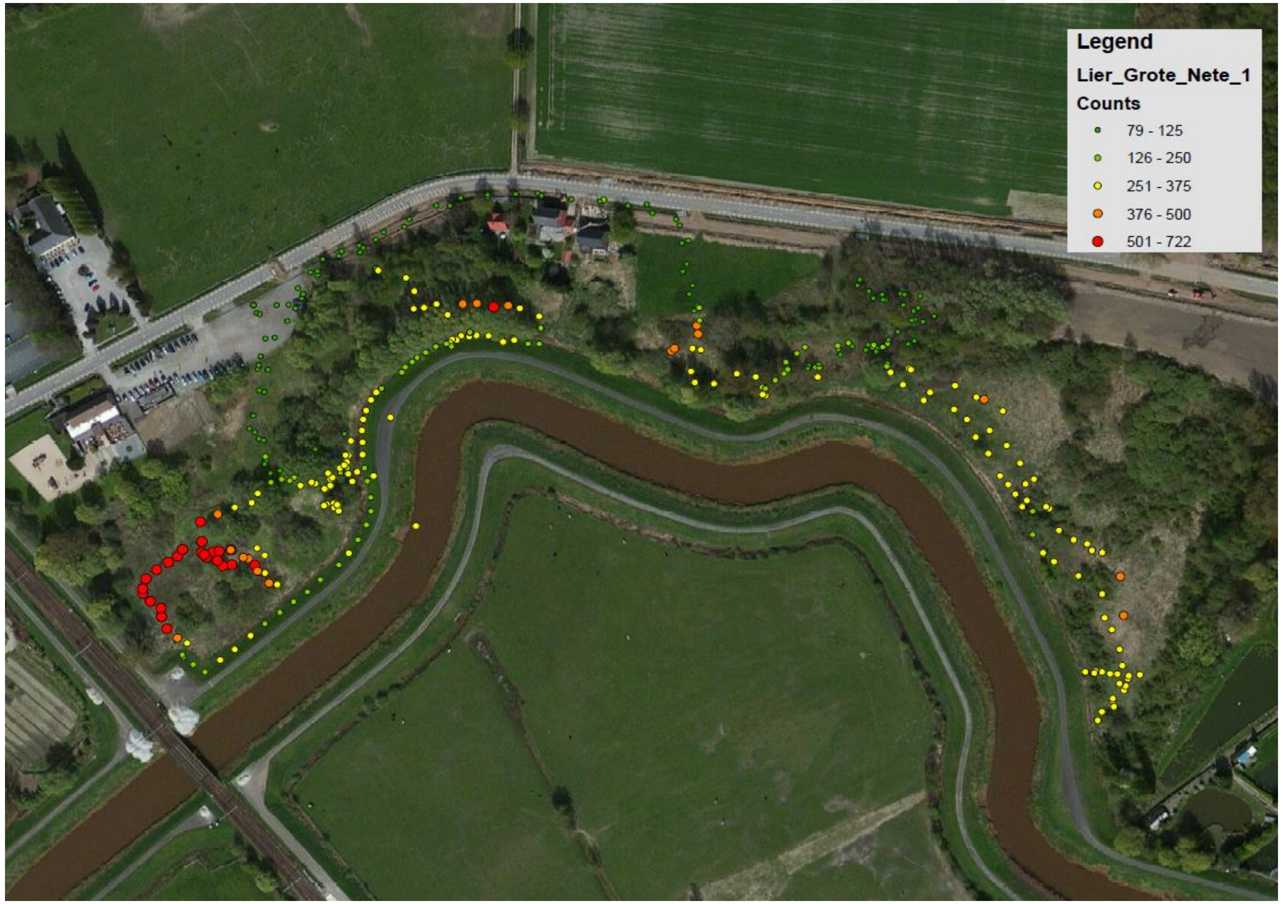
Ra-226 at the Grote Nete riverbank

“**Sigma plan**” aims to create inundation zones along the Grote Nete to prevent Antwerp from flooding in case of extreme weather conditions

The riverbanks of the Grote Nete are at some **hotspots historically contaminated** by the phosphate industry (TE-NORM), the nuclear industry (artificial radionuclides), and others (heavy metals and (poly)aromatic hydrocarbons)

Ra-226 is one of the most important radionuclides present due to its radiotoxicity, half-life and concentrations.

Assess **transport or immobilisation** of Ra-226 if the Sigma plan is implemented.

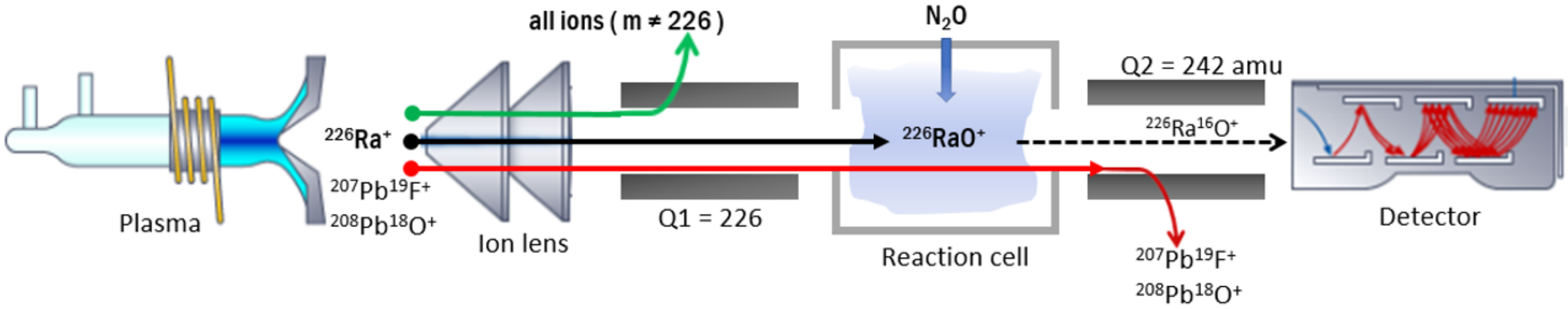


Quick Ra analysis down to drinking water limits by QQQ ICPMS

N_2O as reaction gas for ^{226}Ra

- Ra is in group two, and will react efficiently with N_2O. The interferences will not.

Parameter	Setting
Scan type	MS/MS
Monitored mass pairs (Q1 → Q2):	169 → 185 ($^{169}Tm^+ \rightarrow {}^{169}Tm^{16}O^+$) 226 → 242 ($^{226}Ra^+ \rightarrow {}^{226}Ra^{16}O^+$)
Integration time	10 s for Ra; 0.25 s for Tm
Replicates	5
RF Power	1600 W
Sample depth plasma	7.5 mm
Nebulizer gas flow	0.75 L min^{-1}
Spray chamber temperature	2 °C
Makeup gas flow	0.32 – 0.38 L min^{-1}
Collision-reaction cell:	
N_2O flow rate	0.45 mL min^{-1}
Octopole bias	-3.0 V
Axial acceleration	1 V
Energy discrimination	-7.0 V
Deflect lens	5.0 – 5.4 V



Ra analysis down to drinking water limits by QQQ ICPMS

Interferences on ^{226}Ra

- $^{88}Sr^{138}Ba^{+}$
- $^{186}W^{40}Ar^{+}$
- $^{208}Pb^{18}O^{+}$
- $^{207}Pb^{19}F^{+}$, $^{208}Pb^{18}O^{+}$

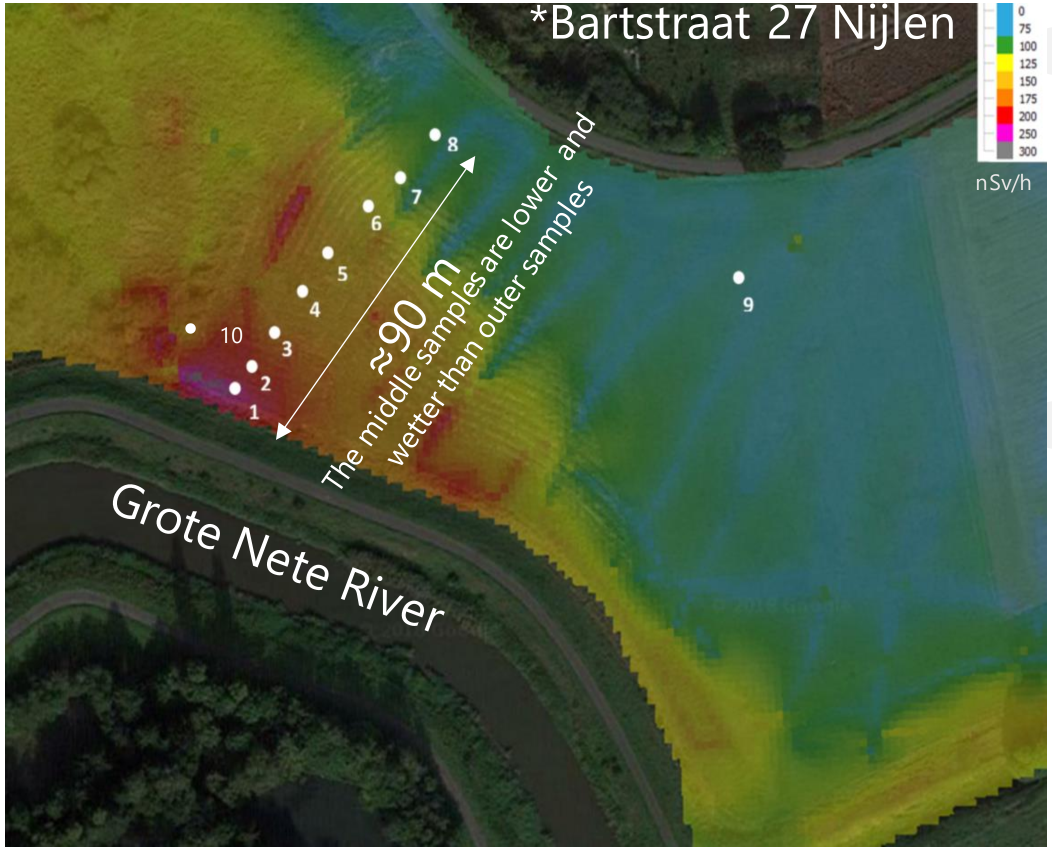
Test solution	Suspected interferences	BEC (pg L^{-1} ^{226}Ra)				
		No gas		He		N_2O
		MS	MS/MS	MS	MS/MS	MS/MS
100 mg L^{-1} Sr 100 mg L^{-1} Ba	$^{88}Sr^{138}Ba^{+}$	< LOD	< LOD	< LOD	< LOD	< LOD
10 mg L^{-1} W	$^{186}W^{40}Ar^{+}$	520	4	4	< LOD	< LOD
10 mg L^{-1} Pb	$^{208}Pb^{18}O^{+}$	89	62	51	22	< LOD
10 mg L^{-1} Pb w/ 0.1 % HF	$^{207}Pb^{19}F^{+}$, $^{208}Pb^{18}O^{+}$	130	81	99	49	< LOD
200 µg L^{-1} of 61 elements	Above-mentioned, $^{40}Ar_2{}^{146}Nd^{+}$, $^{87}Sr^{139}La^{+}$, $^{86}Sr^{140}Ce^{+}$, $^{209}Bi^{16}O^{1}H^{+}$, $^{92+n}Mo^{134-n}Xe^{+}$ and more	18	7	6	< LOD	< LOD

Some polyatomic interferences are not formed in the plasma!

Ra-226 and γ-heatmap in potential inundation zone

Sample N°	Ra-226 in soil (Bq/kg)
1	368
2	665
3	1130
4	2500
5	3630
6	960
7	142
8	73
9	19
10	2349

Heat map of γ radiation; Sampling positions

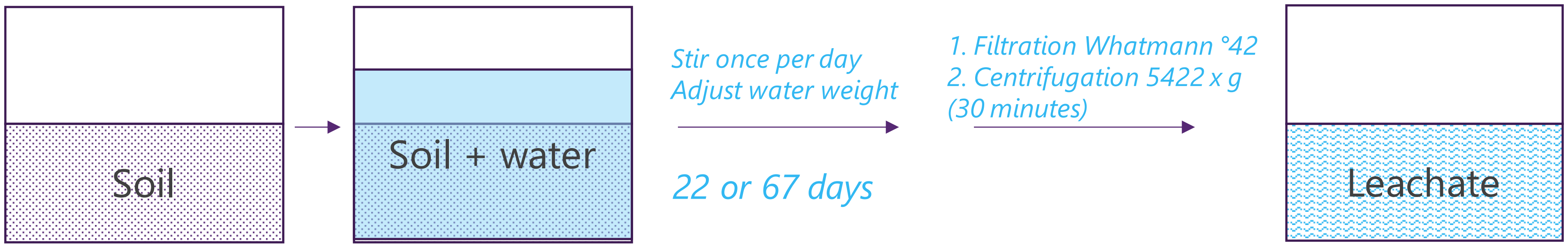


Ra-226 exemption limits in Belgian legislation = 500 Bq/kg

Half-life 1600 years, α-γ radiation

Heatmap reference: Paridaens, J., Olyslaegers, G., and Gueibe, C. (2016) Results of the Belgian Aerial Gamma Survay (AGS) Campaign Organized During the Spring of 2016. **SCK•CEN-ER-0343**
Sample location 1-9: Rogiers et al. 2021

Experimental setup: batch and kinetic experiments



Soil dried at 40°C

Add H_2O to FC150% or FC1000%

Sample No	gram H_2O /100g soil @150% FC
1	38
2	34
3	34
4	42
5	56
6	46
7	28
8	31

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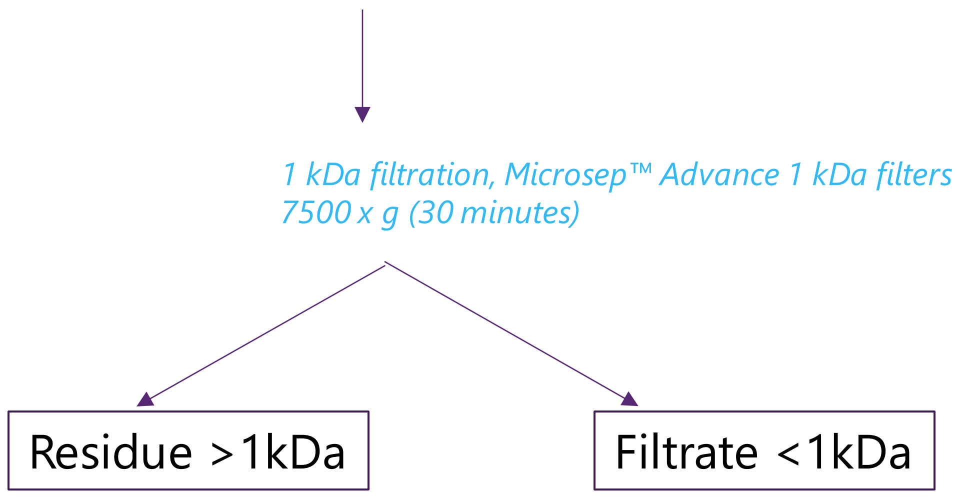
Sample 10	gram H_2O/100g soil
FC 150%	82
FC 1000%	547



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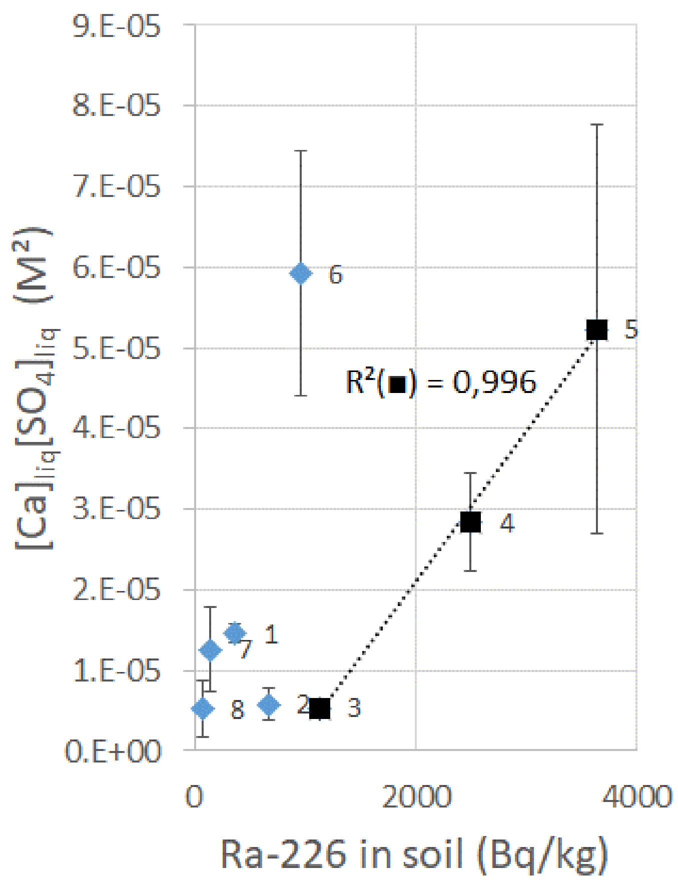
Soil sample analysis

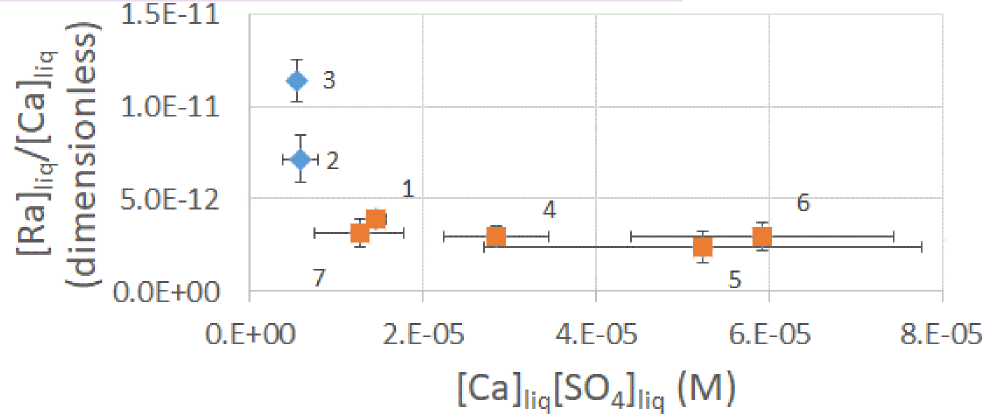
Sample	^{226}Ra in soil	CEC clay minerals	$[Ca]_{liq}$	$[SO_4]_{liq}$	$[Ca]_{liq}*[SO_4]_{liq}$	$[Ca]_{liq}:[SO_4]_{liq}$	$[Ra]_{liq}$	$[Ra]_{liq}$
N°	Bq/kg DW*	cmol e^- /kg DW*	M	M	M^2	Dimensionless	pg/L	pg/L
	Soil		Soil solution FC150 22d pre-filtration					Post filtration <1kDa
1	368	14	1.2E-02	1.3E-03	1.5E-05	9.2	10.3	10.7
2	665	14	8.9E-03	6.5E-04	5.8E-06	13.6	14.3	14.3
3	1130	**19**	7.8E-03	6.8E-04	5.3E-06	11.5	**20.2**	**20.8**
4	2500	14	1.5E-02	1.9E-03	2.8E-05	8.2	10.4	10.5
5	**3630**	13	**1.7E-02**	3.0E-03	5.2E-05	5.7	9.4	9.2
6	960	14	1.3E-02	**4.7E-03**	**5.9E-05**	**2.7**	8.5	9.9
7	142	10	9.0E-03	1.4E-03	1.3E-05	6.4	6.4	7.1
8	73	8	3.0E-03	1.8E-03	5.3E-06	1.7	NA*	NA*

Role of saturation of $CaSO_4.2H_2O$

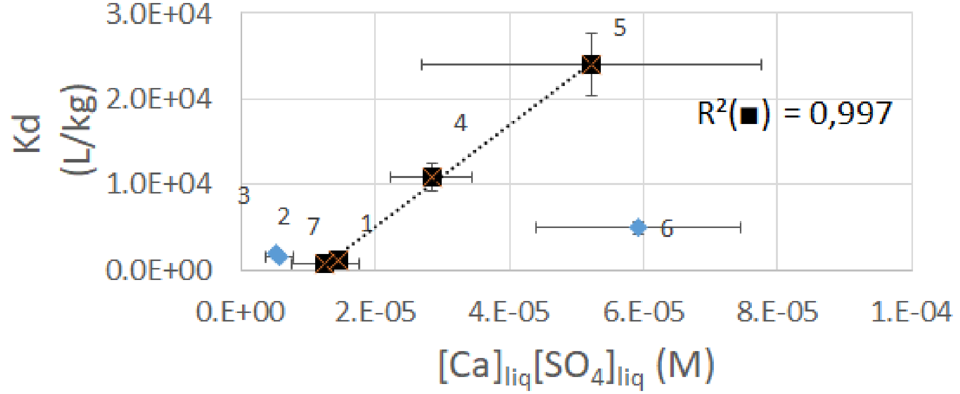
High correlation if $CaSO_4$ present



Constant ratio if $CaSO_4$ present



Linear increase of Kd if $CaSO_4$ present



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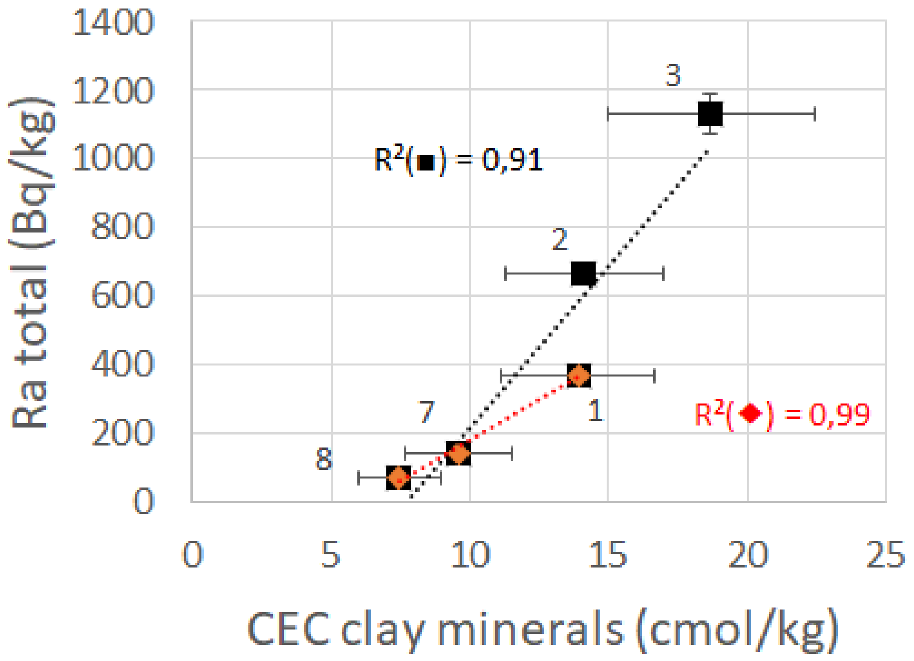
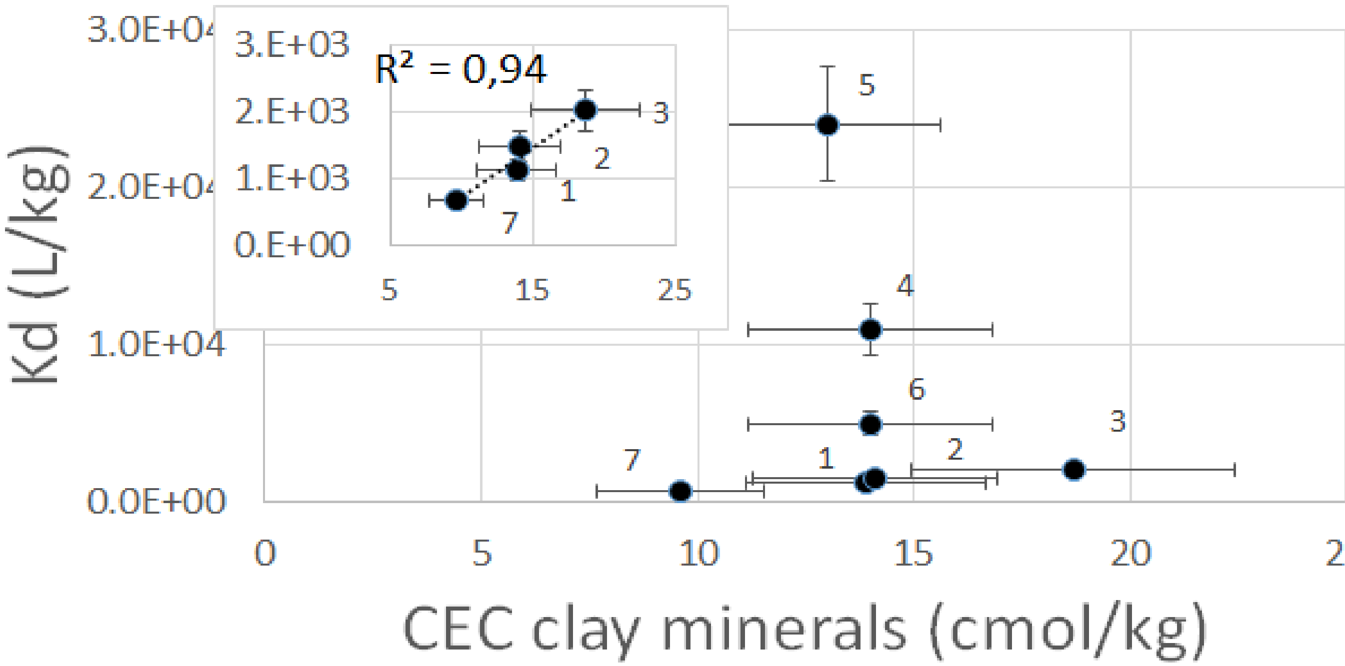
Role of Cation Exchange Capacity of Clay Minerals *(omitting samples with $CaSO_4.2H_2O$ saturation)*

Highest correlation if Ra< 400 Bq/g

→ Clay minerals may have carried fractrion of Ra to the river bank



CEC Clay minerals govern Kd if Ra<400 Bq/g



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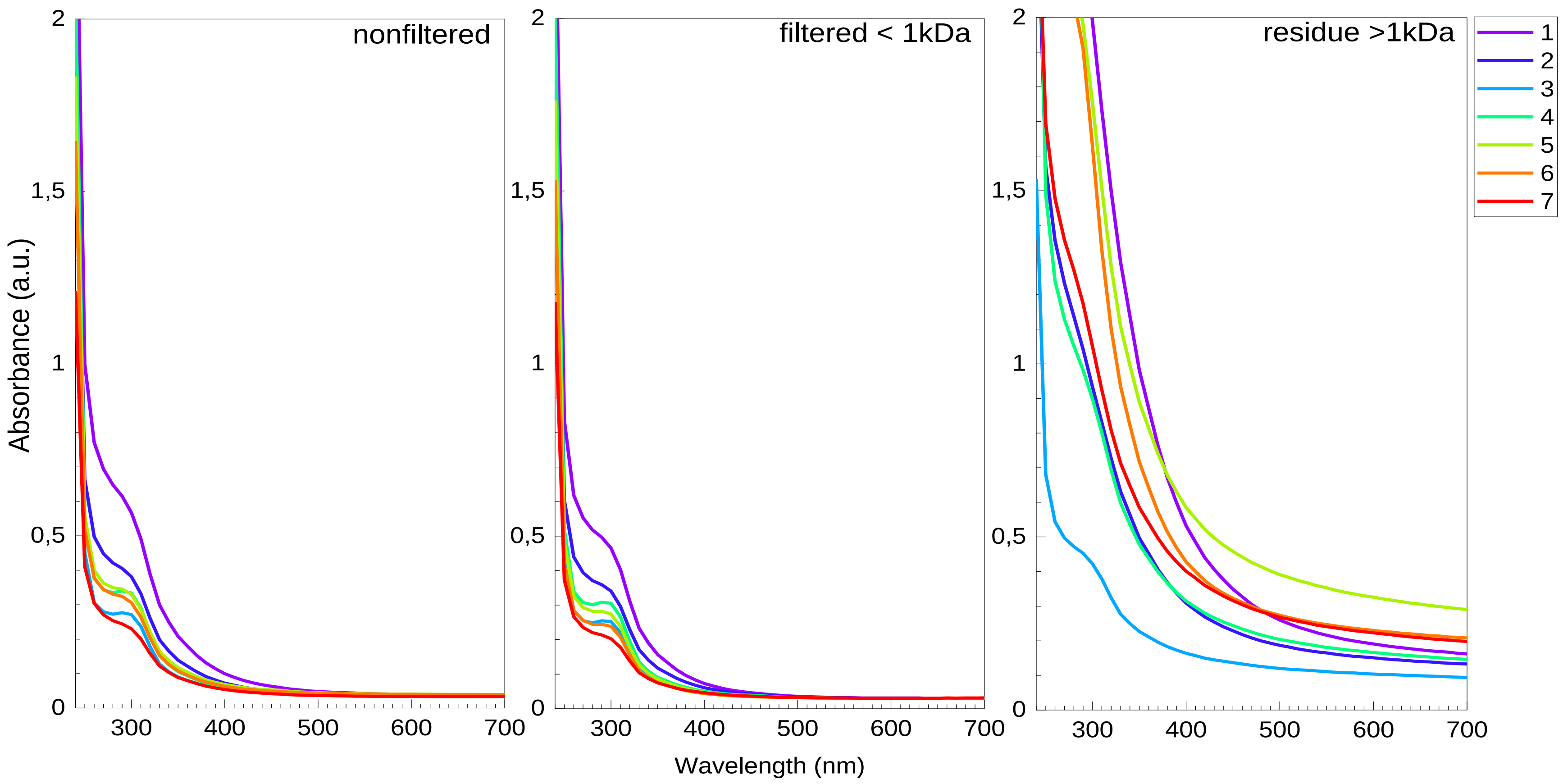
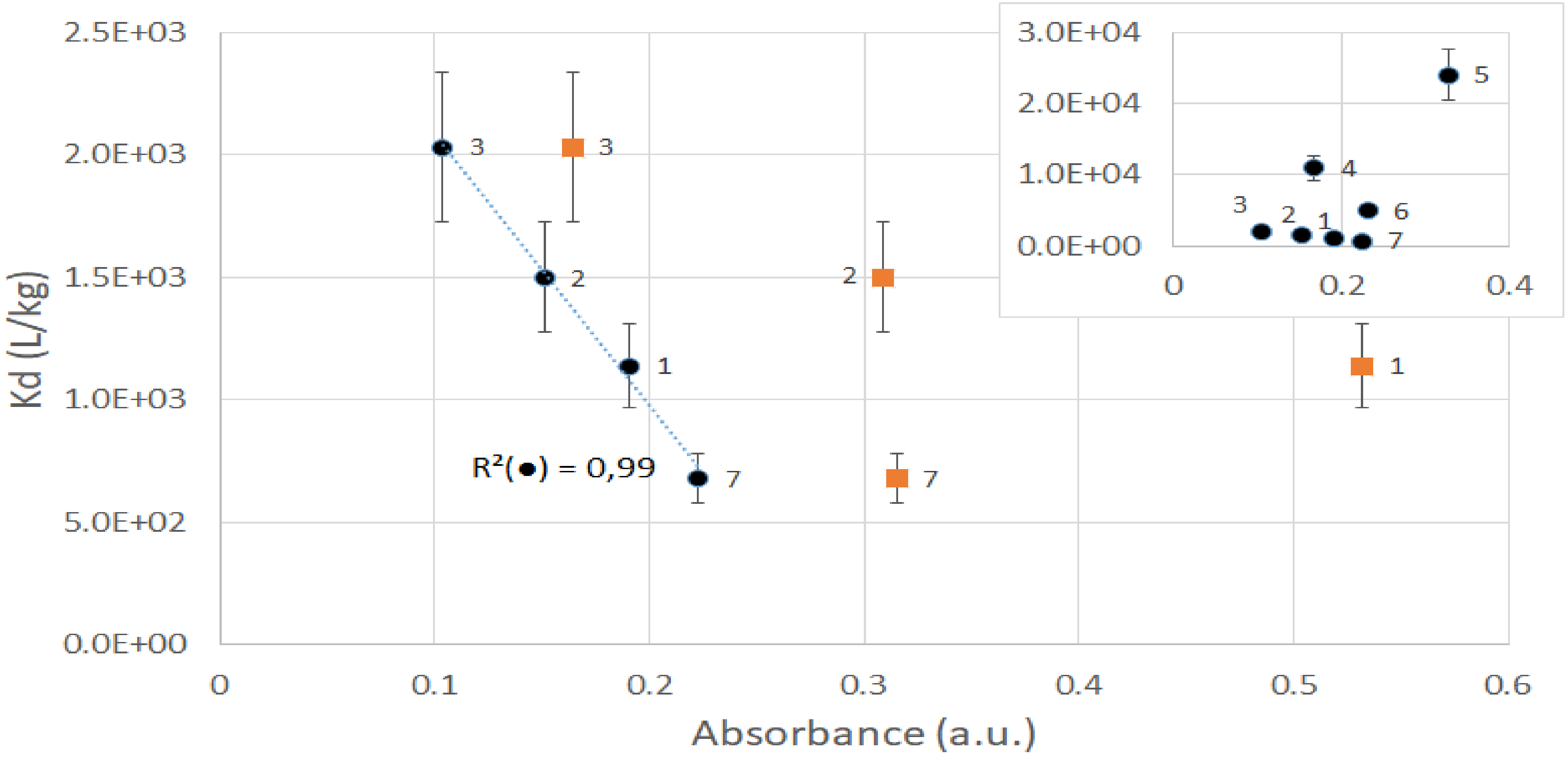
Role of Humic/ fulvic acids
(omitting samples with $CaSO_4.2H_2O$ saturation)



400 nm: inter-intra donor acceptor between HA/FA
600 nm: donor-acceptor of metal-HA/FA

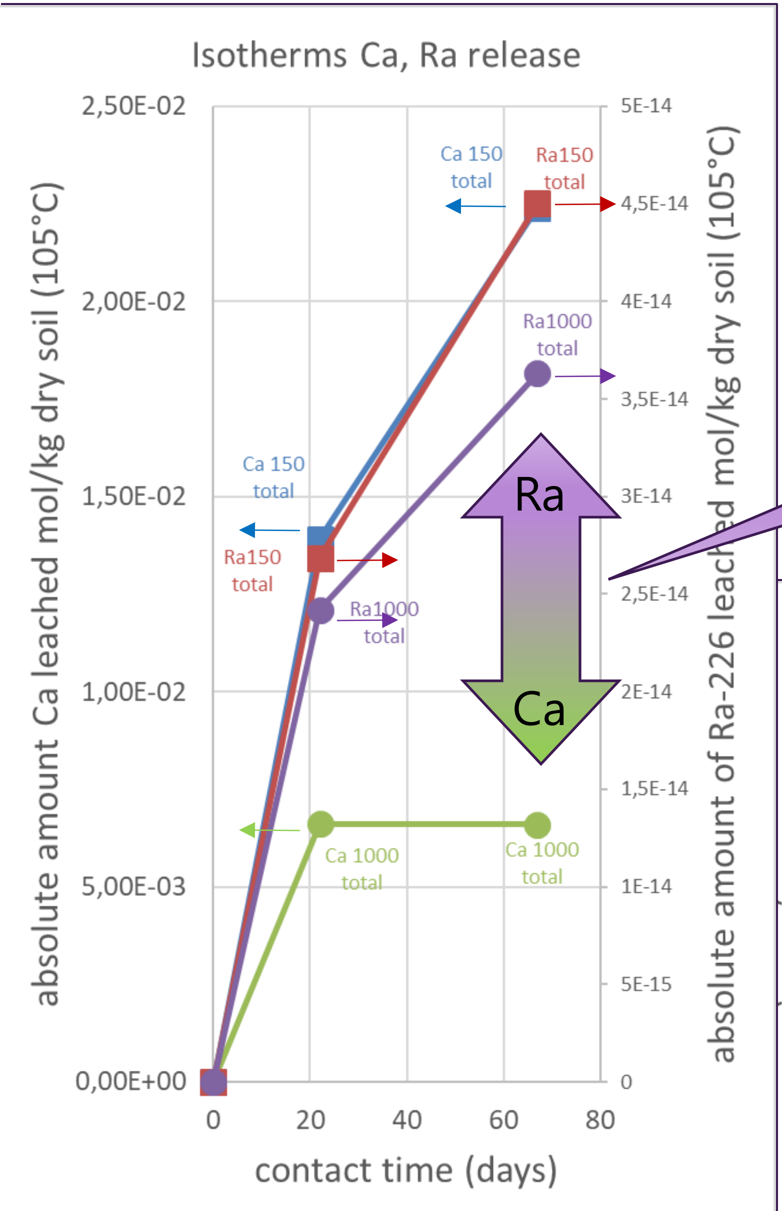
Humic / fulvic acids strongly correlate with Kd Ra



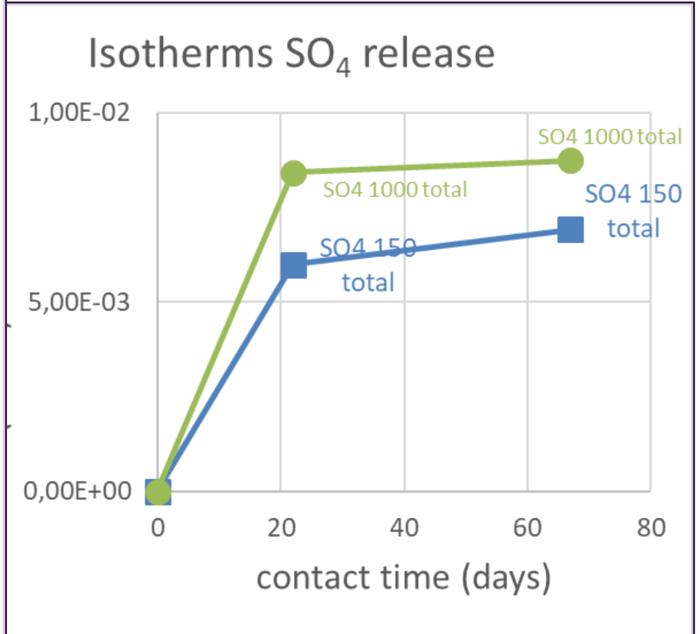
Orange: 400 nm: inter-intra donor acceptor between HA/FA
Black: 600 nm: donor-acceptor of metal-HA/FA

Ca, Ra and SO_4 release

FC experiments 150% FC, 22d + 67d
FC experiments 1000% FC, 22d + 67d

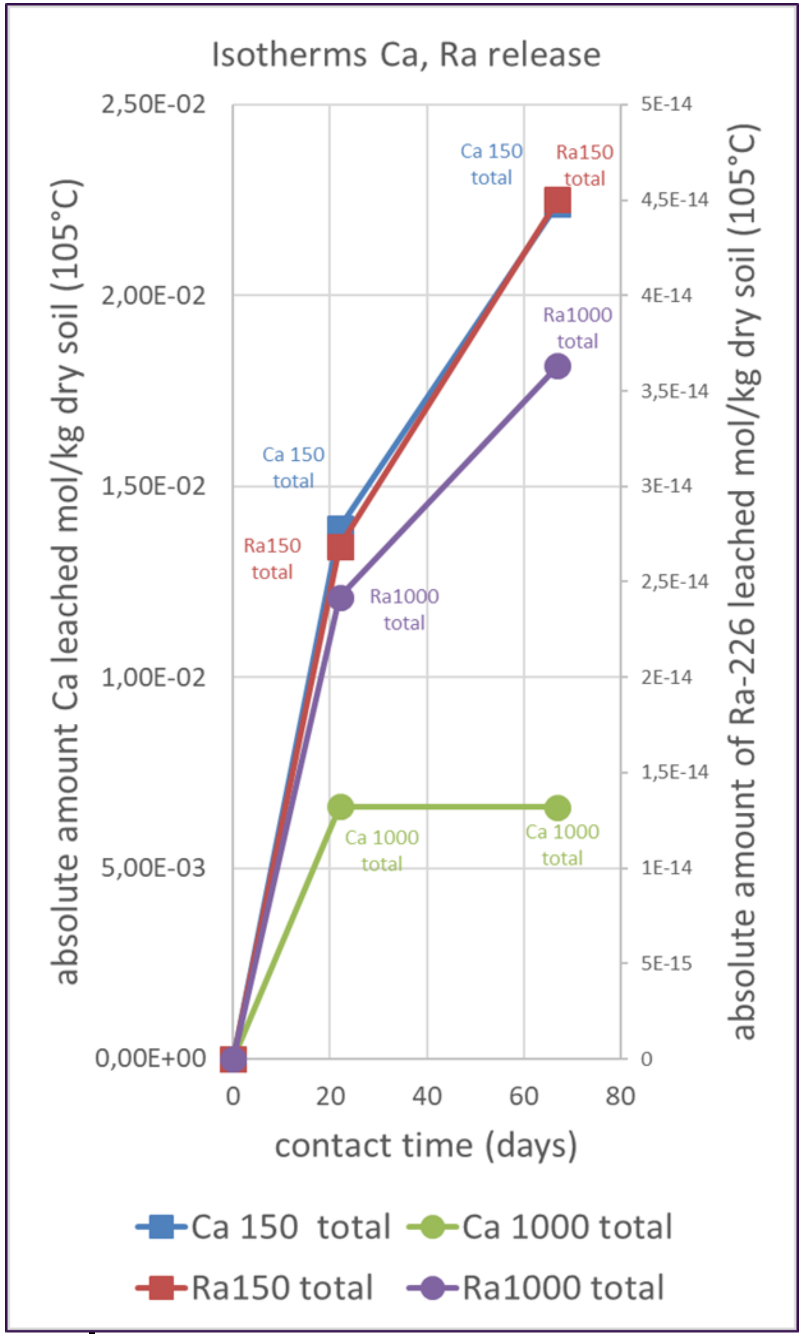


Which mechanisms induce different behaviour of Ra vs Ca?

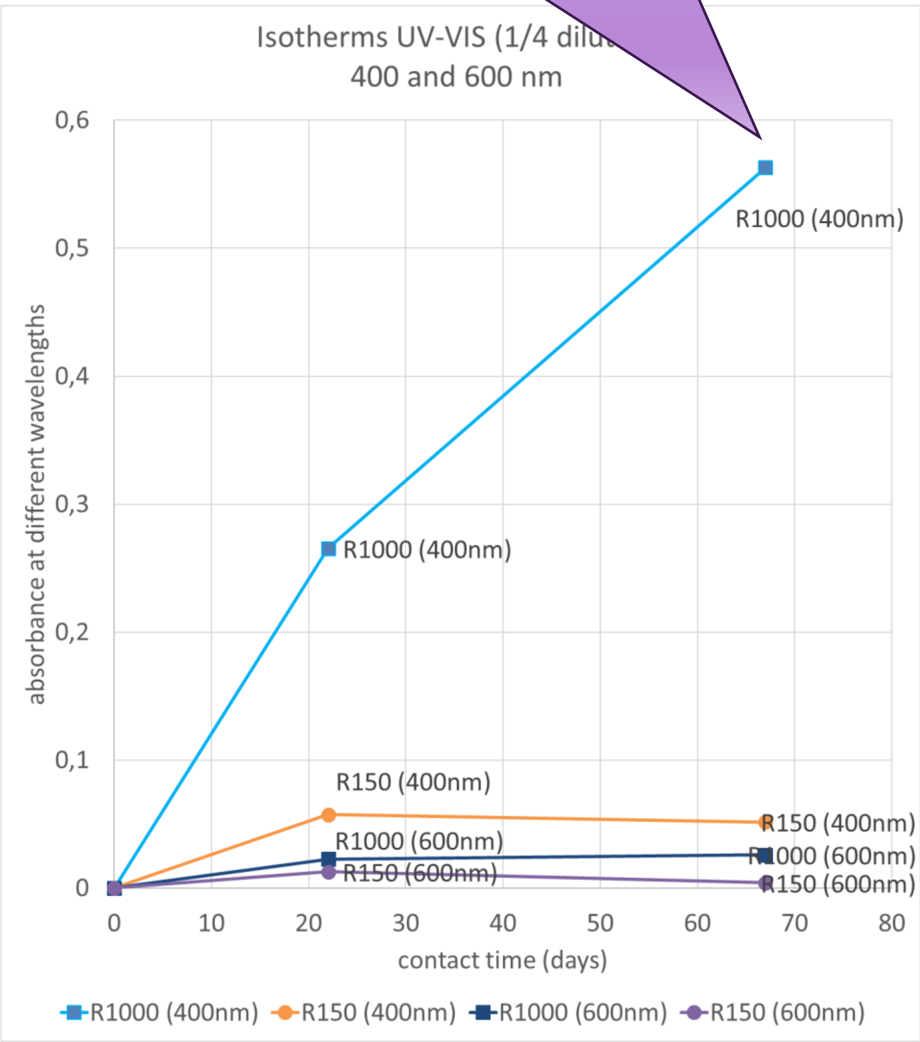


At FC=1000, **Ca and Ra behave differently** , leaching of Ca and SO_4 in same range, but Ca<SO_4

At FC=150, **Ca and Ra behave similarly** but much more Ca release than SO_4



Ra and 400 nm
in >1 kDa fraction
behave similarly!



FC150:
Ca and Ra: **similar behaviour, no equilibrium**

FC1000:
Radium: no equilibrium at 22d
Ra_{liq}↑
400nm absorbance↑
Also 270, 300 nm ↑ (not shown for clarity)
1 kDa fraction weight↓

→ Ra^{2+} chelates with HA/FA 270-400nm

Calcium: apparent equilibrium at 22d

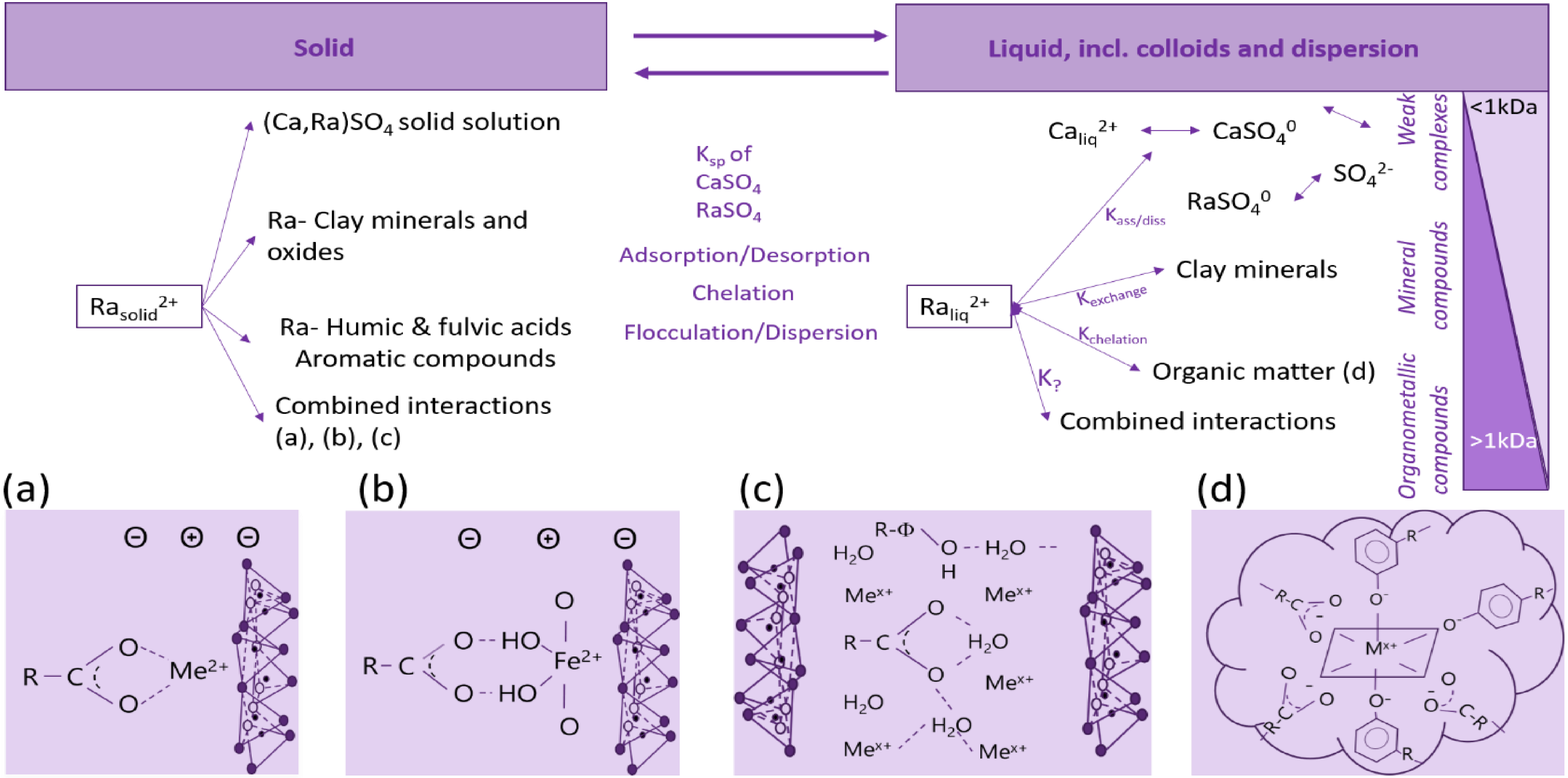
1kDa 600 nm conc constant but total mass↓ (= condensation of structures ?)
→migration of of largest molecules to solid phase?

→ Ca^{2+} induces aggregation

Supported by Durce 2016: *"Ca^{2+} is a "hard" ion compared to Ra and tends to promote aggregation"*

Hydrophilic groups directed to Ca, hydrophobic at outer phase → induce precipitation

Summary behaviour of Radium in river bank



Calcium as a potential key in Radium immobilisation / site remediation

$$\frac{\{Ra\}_{surface}}{\{Ba\}_{surface}} = \lambda \frac{[Ra]_{solution}}{[Ba]_{solution}}$$

1. **$CaSO_4$** : if liquid phase is saturated with $CaSO_4$
   - Predict $[Ra_{liq}]$ from $[Ca_{liq}]$ if $[Ca][SO_4] \geq Ksp$
   - If we can increase the Ca content at the solid solution, less Ra will be released
2. **Clay minerals**: only weak interactions / low selectivity for Ra; but Ca may induce "cementation" between clay minerals and humic/fulvic acids
3. **Humic /fulvic acids**:
   1. Stronger correlation with variation of Kd_{Ra} than clay minerals,
   2. Ra-chelation with 400 nm species >1kDa
   3. Dilution results in aggregation/flocculation of 600 nm species by Ca
   4. Addition of extra Ca might result in immobilisation of the Ra-chelates

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Summary Kd $_{Ra}$ and other pollutants in river bank

Kd_{Ra} before and after wetland construction

H_2O<Saturated Paste

$CaSO_4.2H_2O$ oversaturation

$Kd_{Ra} \sim [Ca][SO_4]_{liq}$

>

Inundation

No $CaSO_4.2H_2O$ saturation

$Kd_{Ra} \sim \frac{CEC_{\text{clay minerals}}}{HA\&FA_{liq}}$

<

+ Ca before wetland creation

$Kd_{Ra} \sim \frac{CEC_{\text{clay minerals}}\text{; cementation}}{HA\&FA_{liq}}$

Other pollutants @ H_2O < Saturate Paste Conditions

$PbSO_4$↓ **Cd, Zn Arsenates ↓** **Zn^{2+}**

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Thank you

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