Chemically Enhanced Biodegradation of cis-1,2 DCE in a Limestone Aquifer

Remediation using iron sulphide and microbes through batch testing

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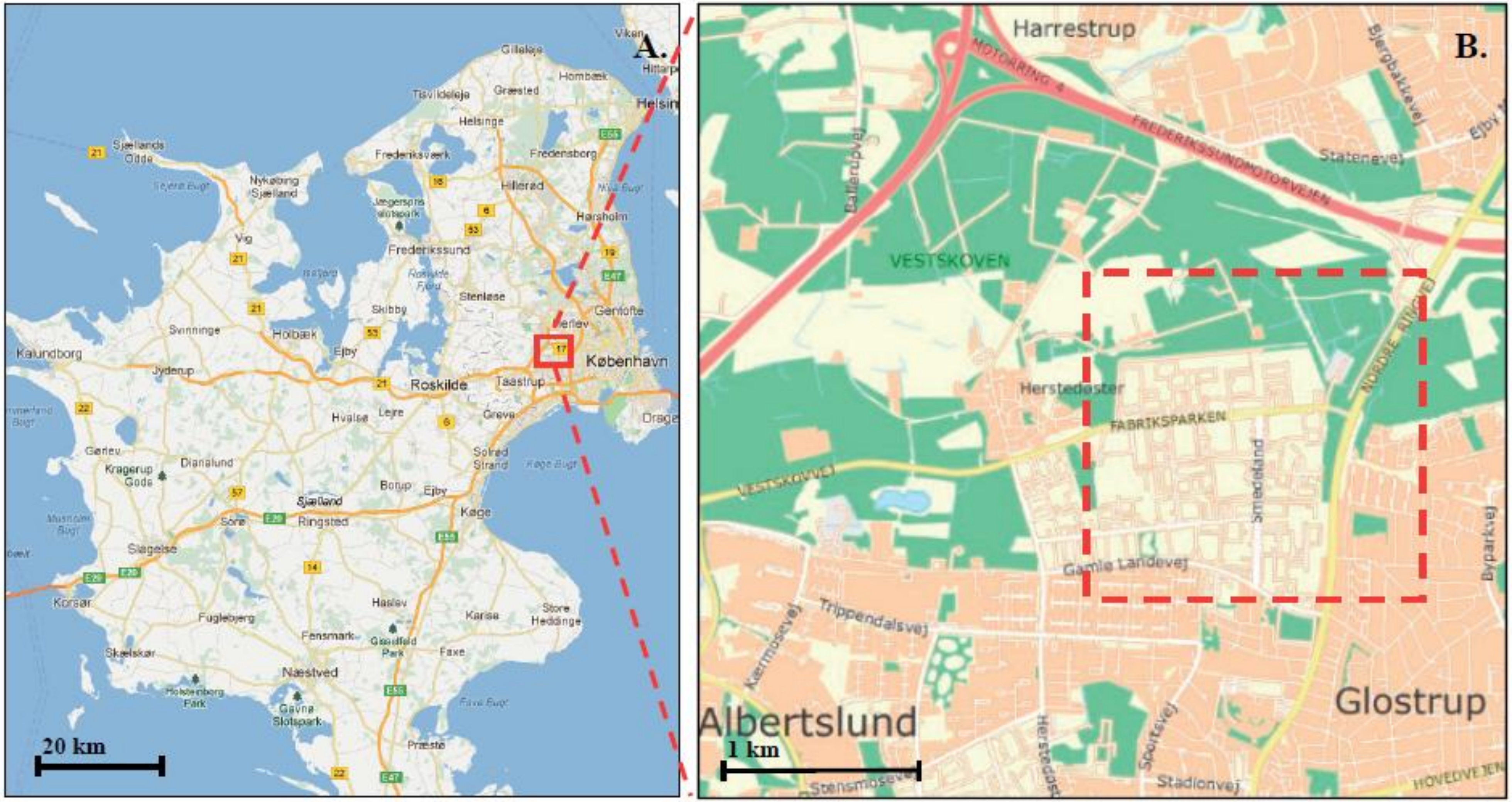
DTU Sustain

Department of Environmental and Resource Engineering

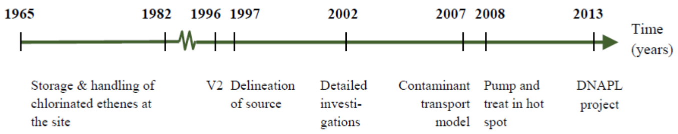
Motivation: Site location



Naverland is located in Glostrup municipality, near the border to Albertslund municipality and near Vestskoven [Hemdorff 2013]

Motivation

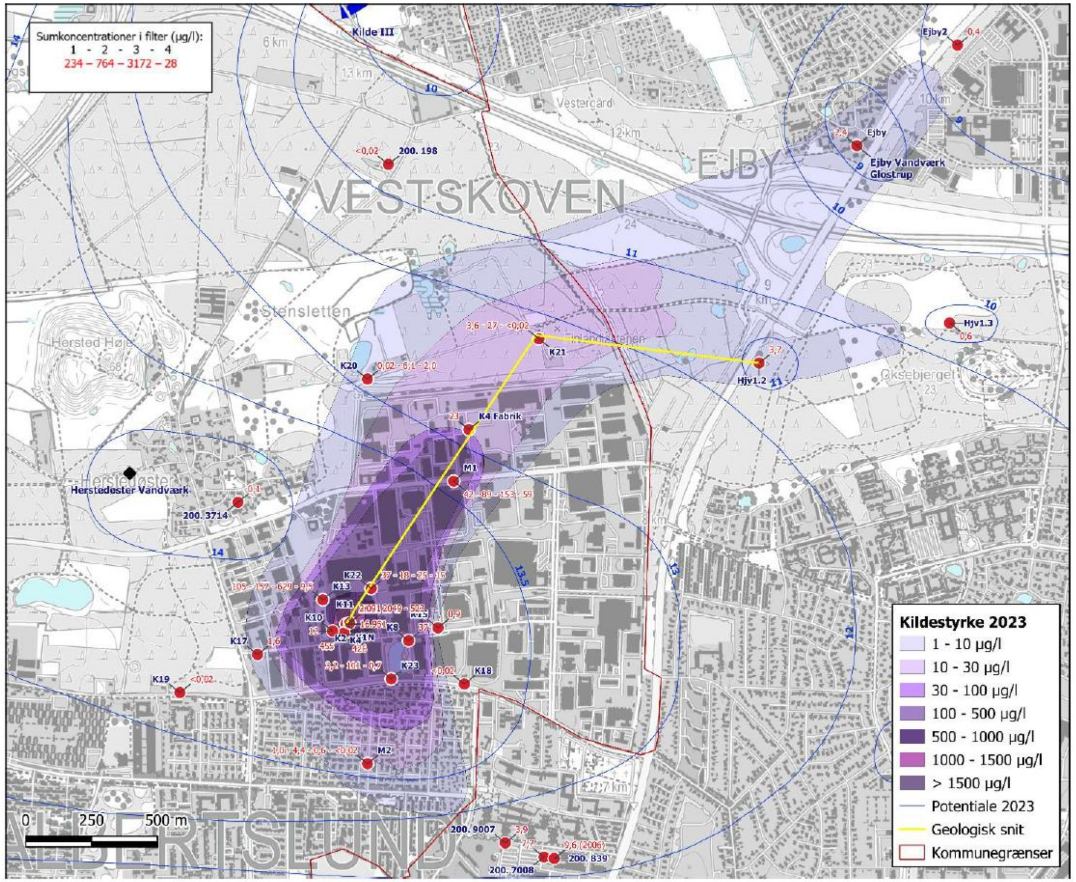
- Ingolf Jacobsen resold chlorinated solvents
- 1965 - 1982
- ~5000 ton PCE
- ~1500 ton TCE



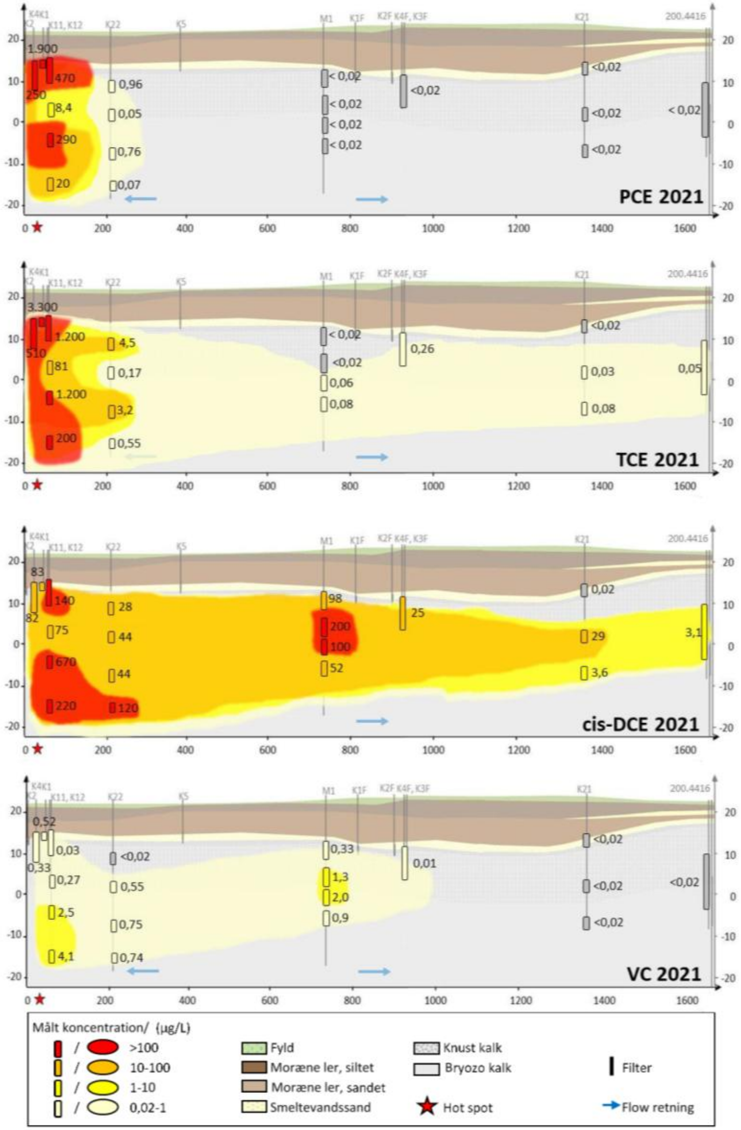
- Chlorinated solvents are over the groundwater quality criterion
- Plume is mainly cDCE

Table 3.2: *Soil and groundwater quality criteria in Denmark*

CE	Soil quality criterion [mg/kg]	Groundwater quality criteria [$\mu g/L$]
TCE	5	1
DCE	85	1
VC	0.4	0.2



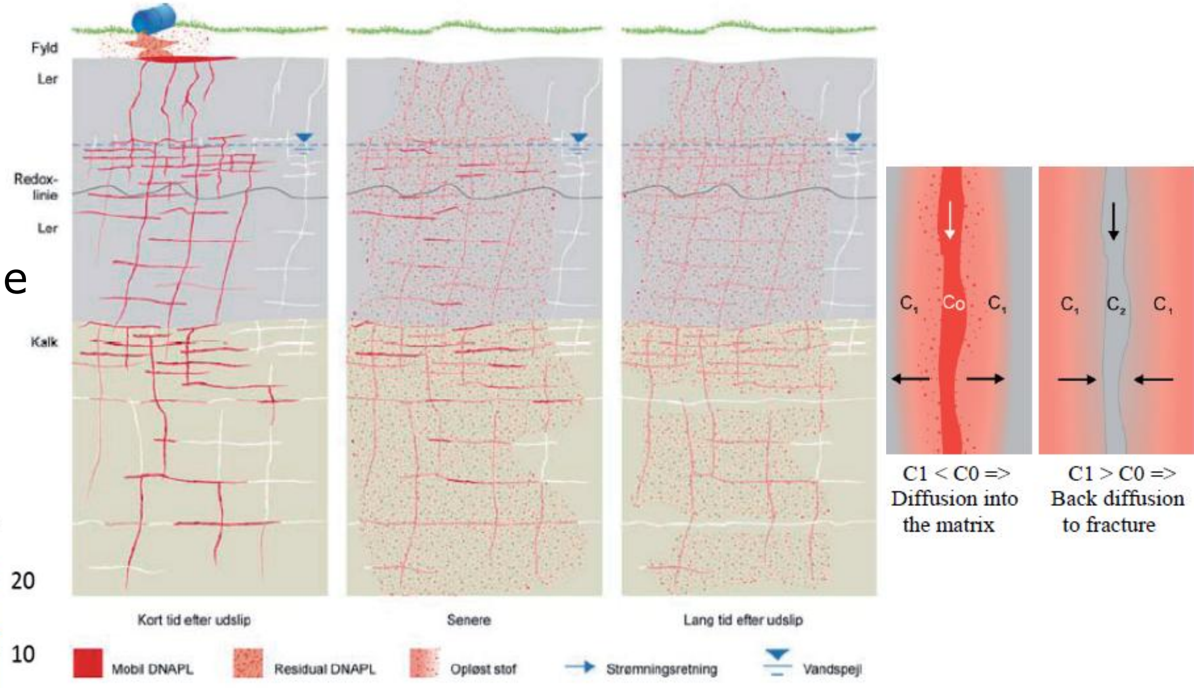
Monitoring of the pollution spread in 2023 is shown as the sum concentrations of all chlorinated solvents (in µg/l) [Sø, 2023]



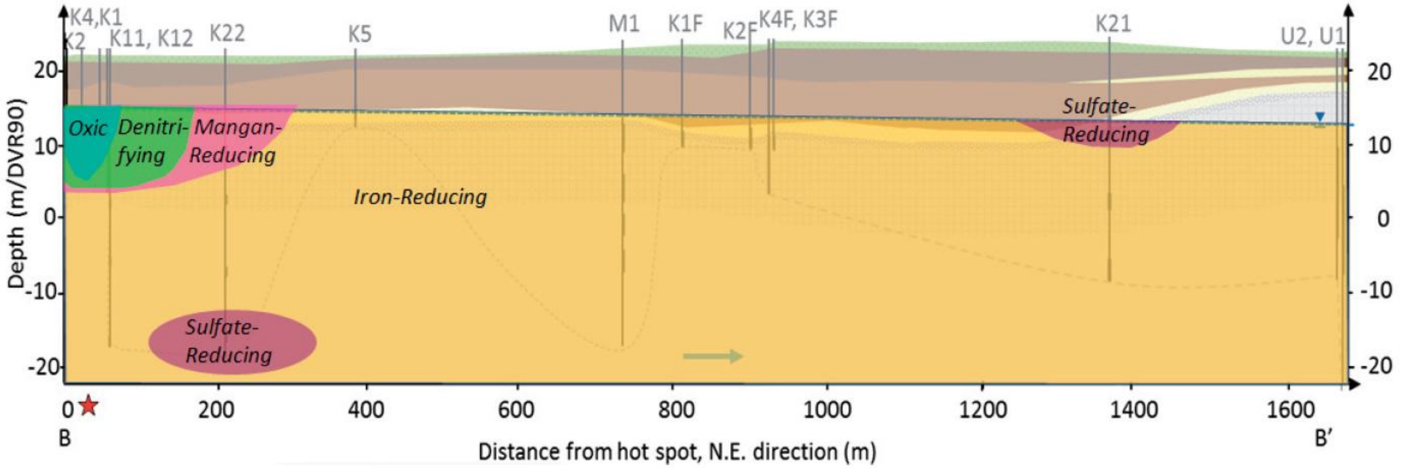
Measured concentrations (in µg/l) from the source area at Naverland 26 and out to Glostrup's well 200.4416.

Motivation and site conditions

- Limestone aquifers
  - more vulnerable due to their dual porosity
- Deep aquifer
  - Remedial methods cannot include trenching
  - Amendments should therefore be injectable and mobile
- Anaerobic conditions in the plume
  - Therefore, reductive remediation methods



Vulnerability of limestone aquifers [Hemdorff 2013]



Redox conditions of Naverland [Hemdorff 2013]

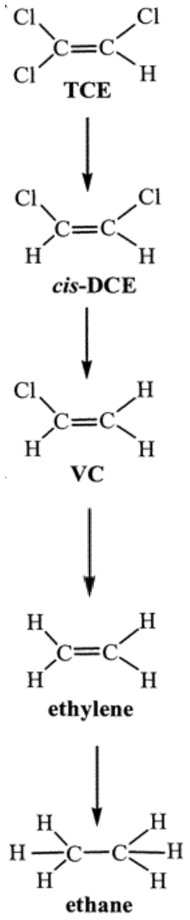
Aim

- Developing and performing batch tests to assess the feasibility of using reductive dechlorination to remediate limestone aquifers contaminated with cDCE.

- Analyse the results of the batch experiments in relation to existing literature

- Evaluate the effectiveness of BiRD and ERD and reflect on a pilot field project for the implementation of the most promising approach.

Enhanced Reductive Dechlorination (ERD)



Biotic pathway for the enhanced reductive dechlorination of chlorinated ethenes by *Dehalococcoides* [Ottosen, 2020]

Hydrogenolysis

Few bacterial genera:
Dehalococcoides
Dehalogenimonas

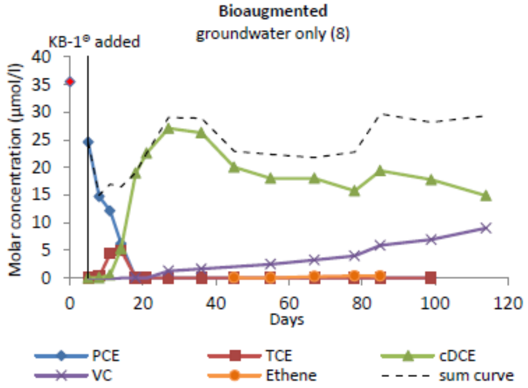


Figure 21: Development of chlorinated ethenes at 15 mbs. Groundwater-only sample. Stimulated at day 0, bioaugmented at day 5. No analysis was made until day 5, the red dot represents the average concentration in the rest of the samples (35µmol/l).

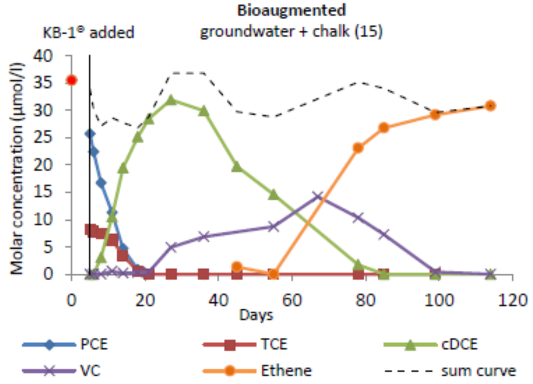
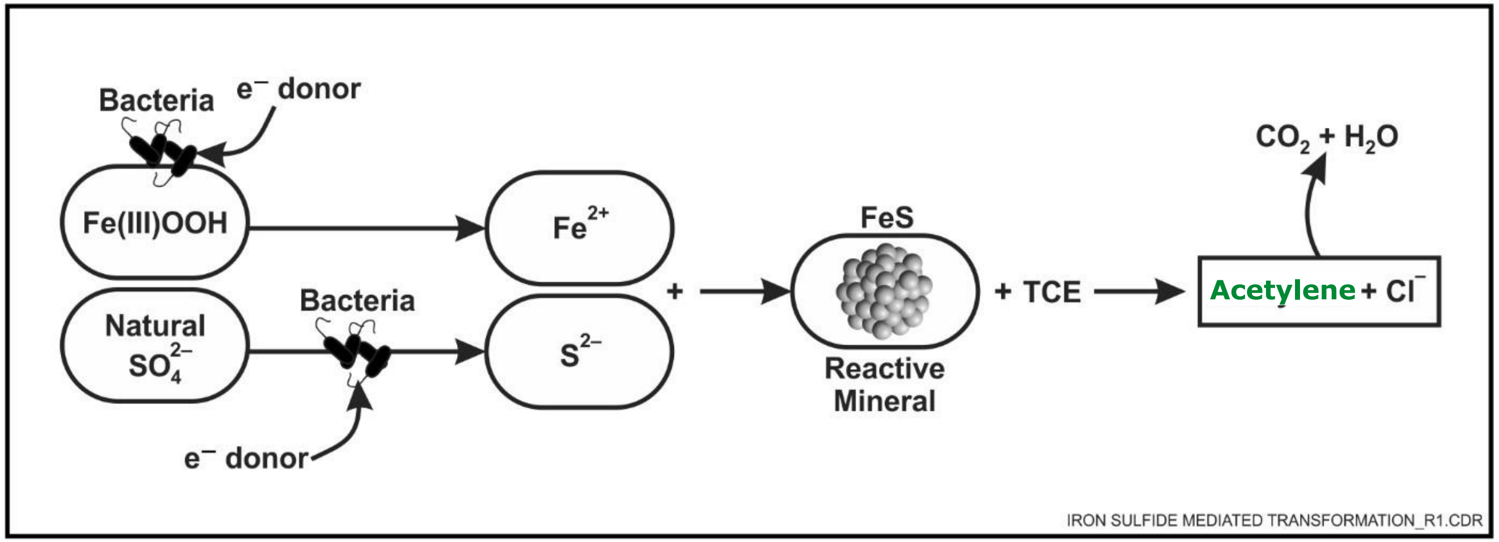


Figure 20: Development of chlorinated ethenes at 15 mbs. Chalk-containing sample. Stimulated at day 0, bioaugmented at day 5. No analysis was made until day 5, the red dot represents the average concentration in the rest of the samples (35µmol/l).

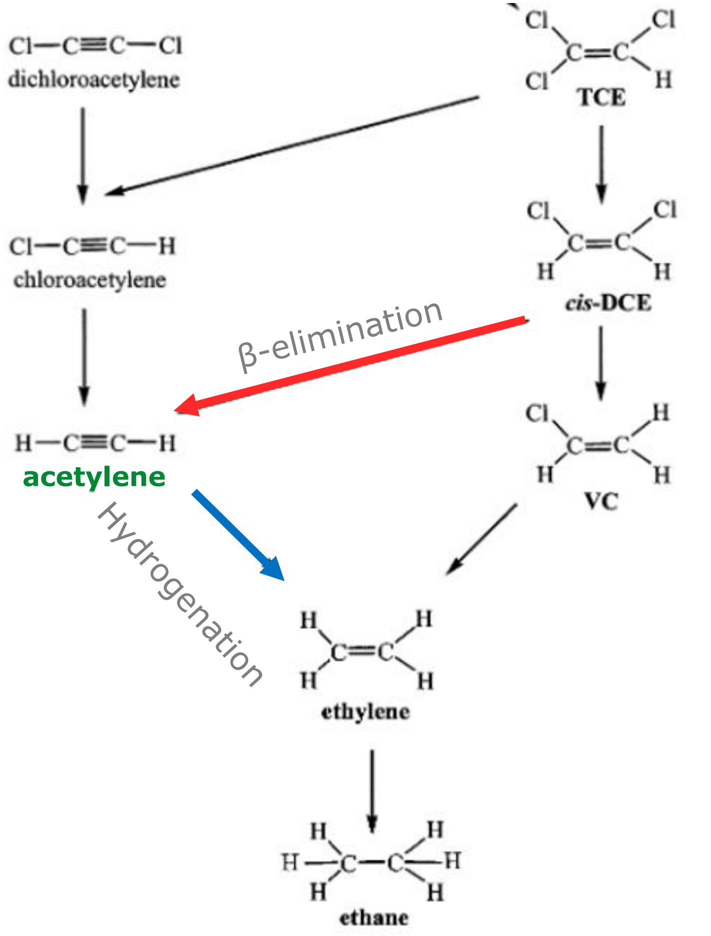
ERD done by [Sørensen 2013] from **source** at Naverland

- Bioaugmentation required
- KB-1 used
- Inclusion of chalk improved the dechlorination rate

Biogeochemical Reductive Dechlorination (BiRD)



BiRD process schematic https://frtr.gov/matrix/Biogeochemical-Transformation/



pathways for the reductive dechlorination of chlorinated ethenes by iron sulphides adopted from [Lee et al., 2002]

Mackinawite, pyrite, magnetite, goethite, green rust, phyllosilicate clay

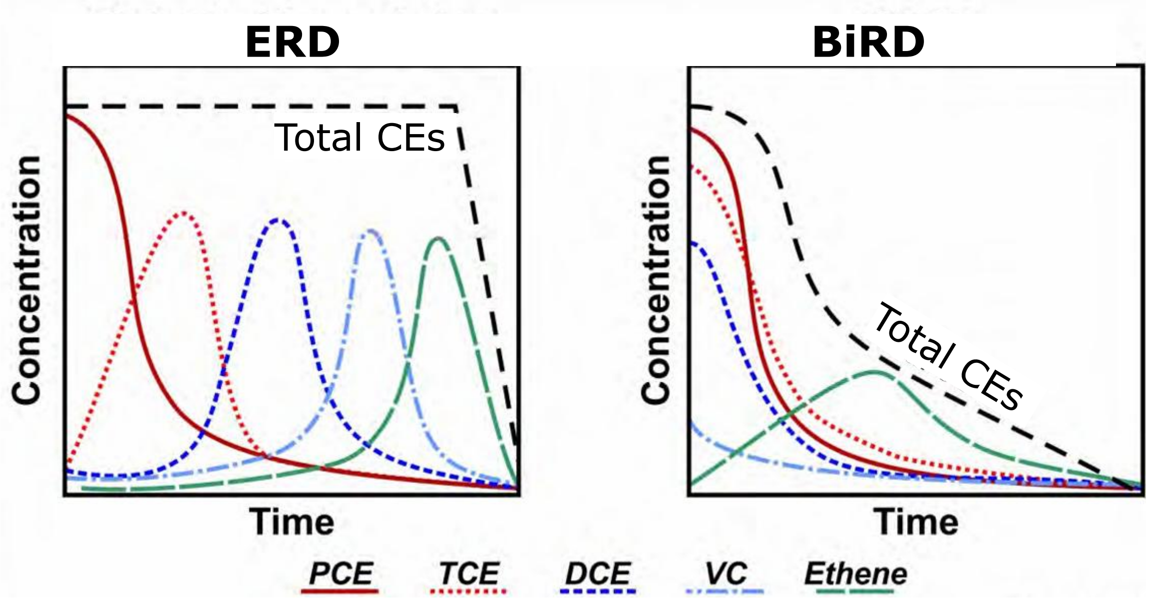
Freeze-drying processes → unreactive

No VC formation

Combination

• FeS Enhances *Dehalococcoides* at 0.2 mM
25.46 ± 1.15 to 37.84 $\mu mol \cdot L{-1} \cdot day{-1}$ rate increase
FeS Inhibits *Dehalococcoides* at high concentrations (0.6mM)

• PCE →DCE greater percentages of acetylene than abiotic controls, OHRB-mediated dechlorination may help FeS-mediated acetylene synthesis by supplying intermediates (2.5g/L in soil)
FeS Inhibits *Dehalococcoides* (at 25g/L in soil)



Degradation pattern for CE; biotic vs abiotic [Darlington and Rectanus, 2015]

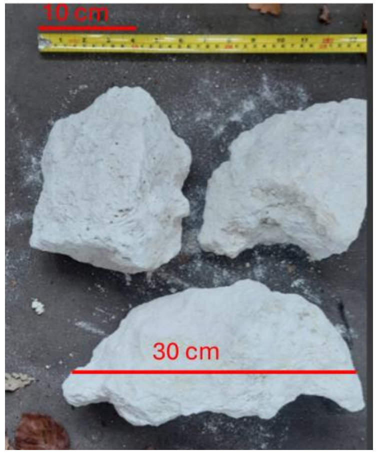
Activities

Limestone collection

Limestone crushing

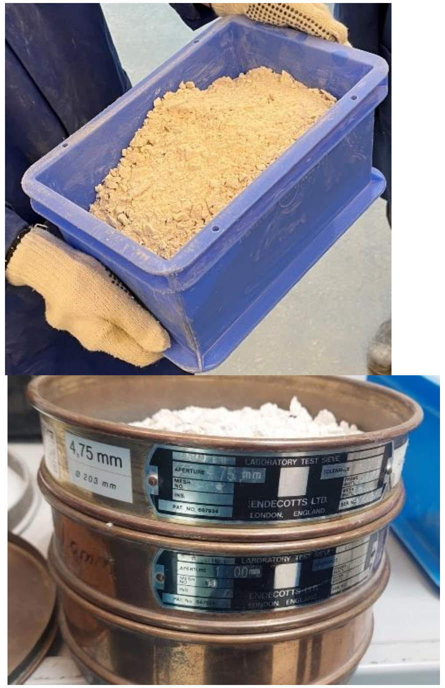
Groundwater abstraction

Microcosm design and set up



Faxe Kalkbrud
Bryozoan limestone
Danian period

Lab Jaw Crusher Pulverisette



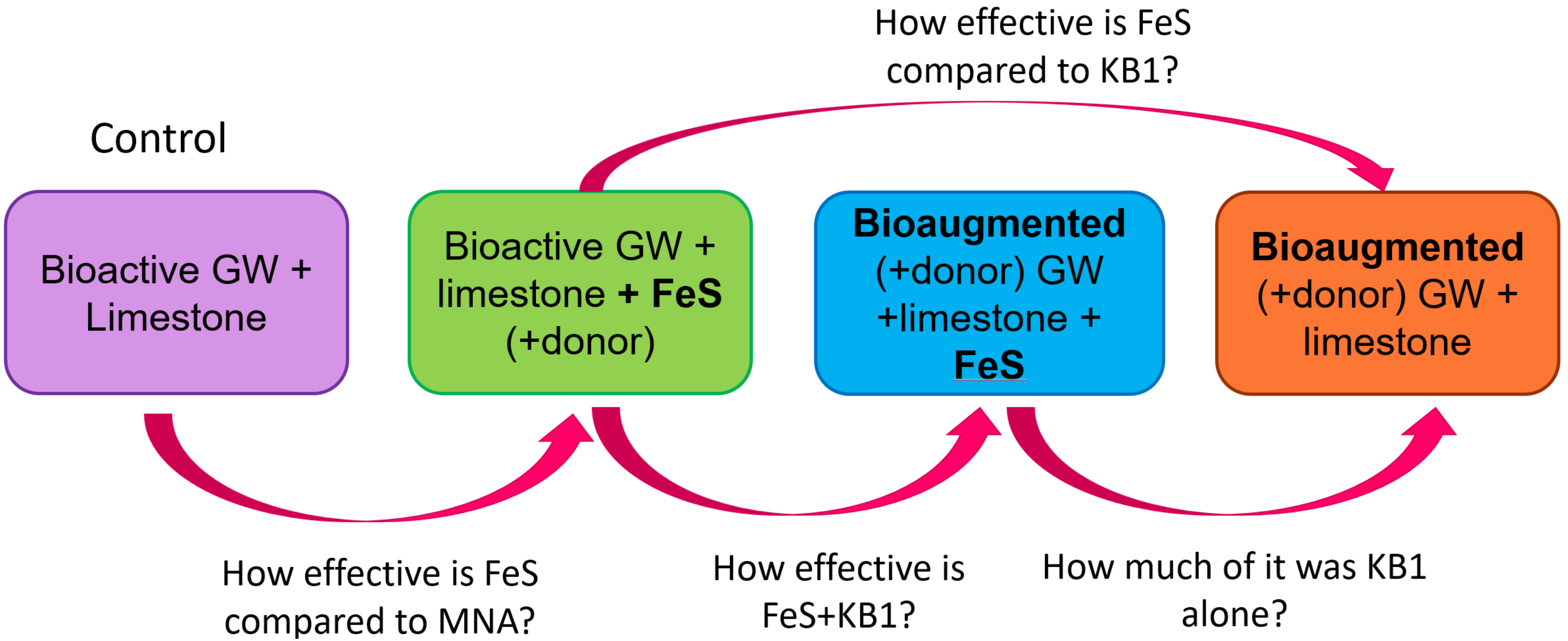
Sieving: grain size 1 – 5 mm

Groundwater abstraction from M1 well

Batch bottles

Filtering sample

Batch test design



FeS containing batches set up

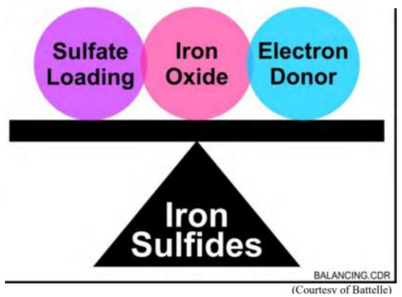
Bioactive GW + Limestone

Bioactive GW + limestone **+ FeS** (+donor)

Bioaugmented (+donor) GW +limestone + **FeS**

Bioaugmented (+donor) GW + limestone

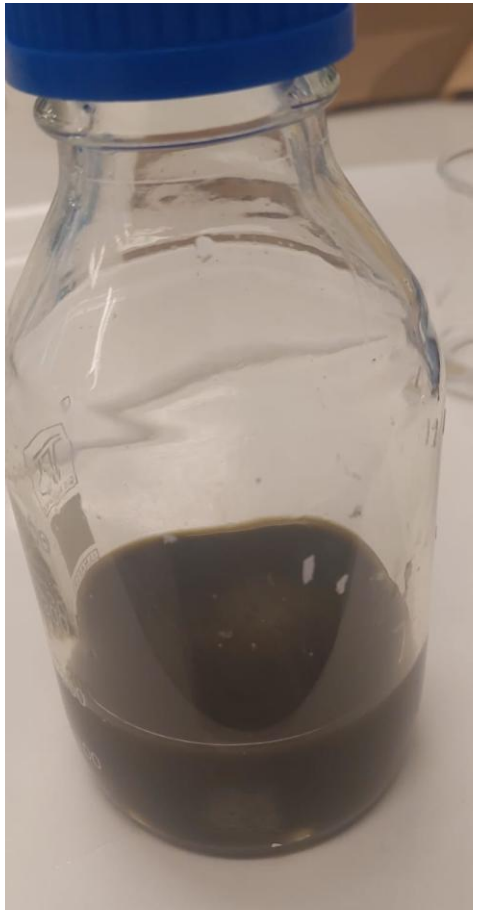
EVONIK
Leading Beyond Chemistry



BiRD conditions

Products	Composition	Treatment Mechanisms		
			Abiotic Reduction	
		Biotic Reduction	Reductive Minerals	ZVI
GEOFORM® Soluble	Soluble sulfate and ferrous iron mix added to an emulsified organic carbon substrate	x	x	
GEOFORM® Extended Release	Extended release organic carbon, sulfate ferrous iron, micro-scale, ZVI	x	x	x

Commercial BiRD products available



GeoForm

1000 mg/L Iron and sulfate

ELS Microemulsion (15g/L)

0.113 g of H_2 produced

Dehalococcoides containing batches set up

Bioactive GW + Limestone

Bioactive GW + limestone **+ FeS** (+donor)

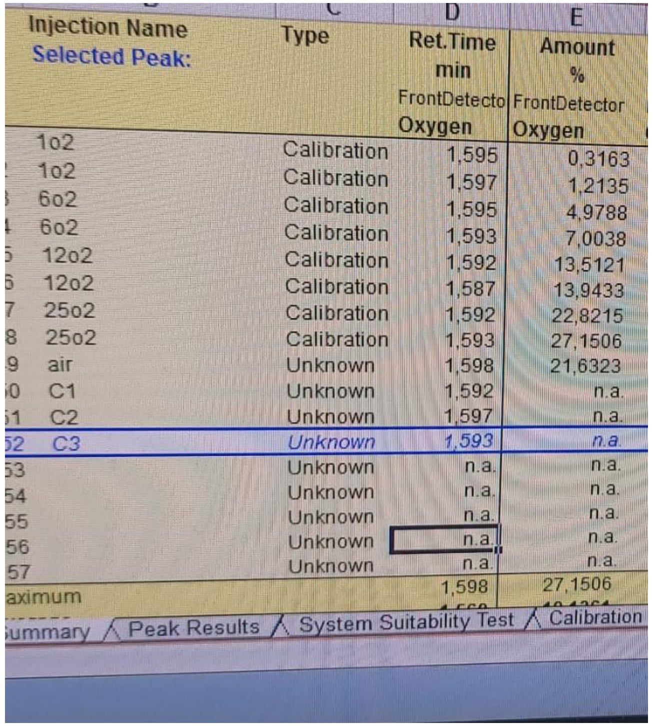
Bioaugmented (+donor) GW +limestone + **FeS**

Bioaugmented (+donor) GW + limestone

Microemulsion (15 g/L) with GeoForm
0.113 g of H_2 produced

Addition of ELS Microemulsion

O2 checked



	Injection Name	Type	Ret.Time min FrontDetecto Oxygen	Amount % FrontDetector Oxygen
	1o2	Calibration	1,595	0,3163
	1o2	Calibration	1,597	1,2135
3	6o2	Calibration	1,595	4,9788
4	6o2	Calibration	1,593	7,0038
5	12o2	Calibration	1,592	13,5121
6	12o2	Calibration	1,587	13,9433
7	25o2	Calibration	1,592	22,8215
8	25o2	Calibration	1,593	27,1506
9	air	Unknown	1,598	21,6323
0	C1	Unknown	1,592	n.a.
1	C2	Unknown	1,597	n.a.
52	C3	Unknown	1,593	n.a.
53		Unknown	n.a.	n.a.
54		Unknown	n.a.	n.a.
55		Unknown	n.a.	n.a.
56		Unknown	n.a.	n.a.
57		Unknown	n.a.	n.a.
aximum			1,598	27,1506

ummary / Peak Results / System Suitability Test / Calibration

1.08mg/L O2, >0.2mg/L
4.5 mL of KB-1 added

Checking Oxygen levels after Microemulsion

SiREM KB-1®

10^8 - 10^9 cells/mL -> 9.0 ml

KB-1

Results from batch experiment

$$C_w = M_t / (V_w + k_d \cdot M_s + K_h \cdot V_a)$$

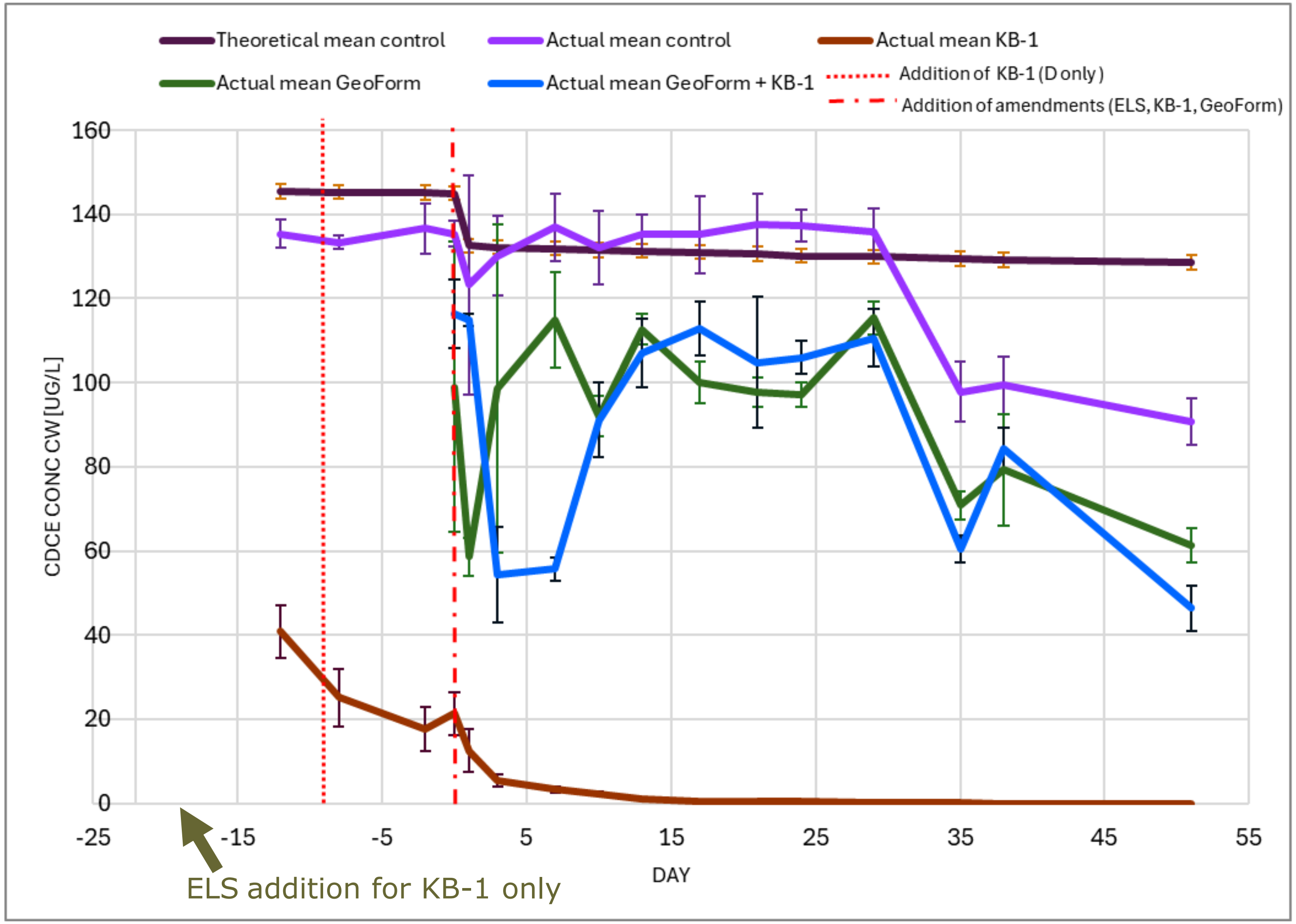
Bioactive GW + Limestone

Bioactive GW + limestone **+ FeS** (+donor)

Bioaugmented (+donor) GW +limestone + **FeS**

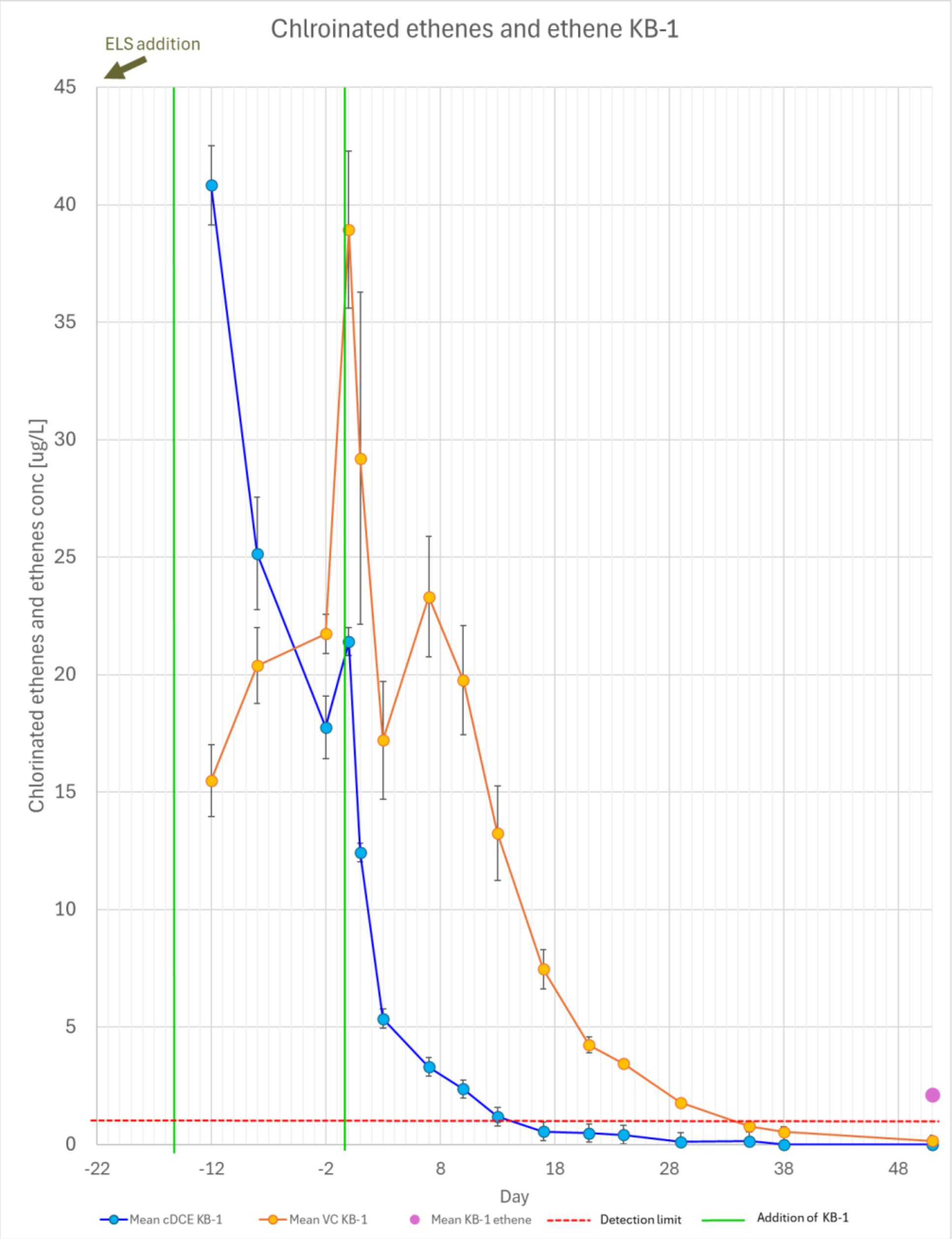
Bioaugmented (+donor) GW + limestone

- Biotic control is relatively stable except for the decrease in cDCE concentration from day 35 but no VC/ethene and the last day was from a different lab
- Theoretical curve used 150 ug/L as initial concentration (day -22)
- Little difference start and end of the experiment and large variation for GeoForm-containing batches
- GeoForm-only did not produce VC/ethene



Average cDCE concentration of all the batches over time

DTU



CE and ethene concentration over time

Bioactive GW + Limestone

Bioactive GW + limestone **+ FeS** (+donor)

Bioaugmented (+donor) GW +limestone + **FeS**

Bioaugmented (+donor) GW + limestone

Microcosms

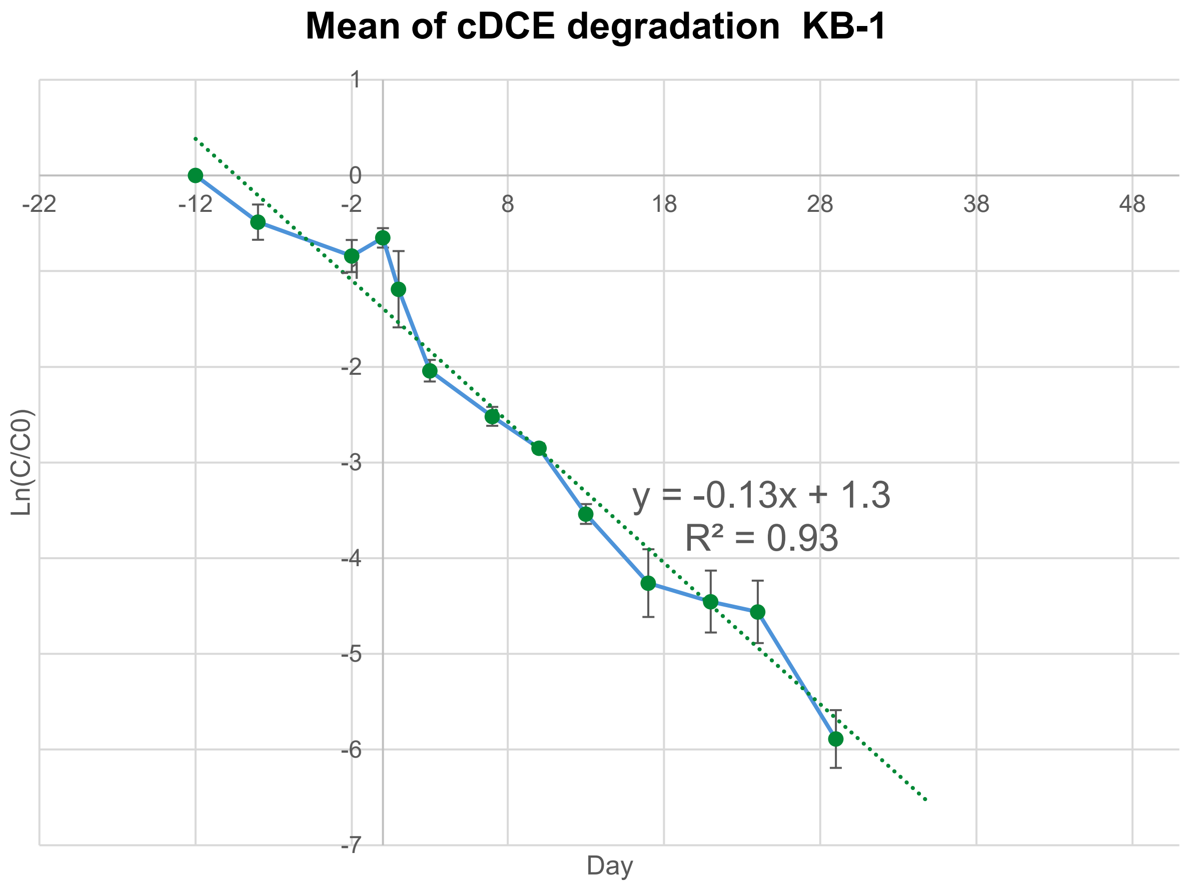
First-order rate constant

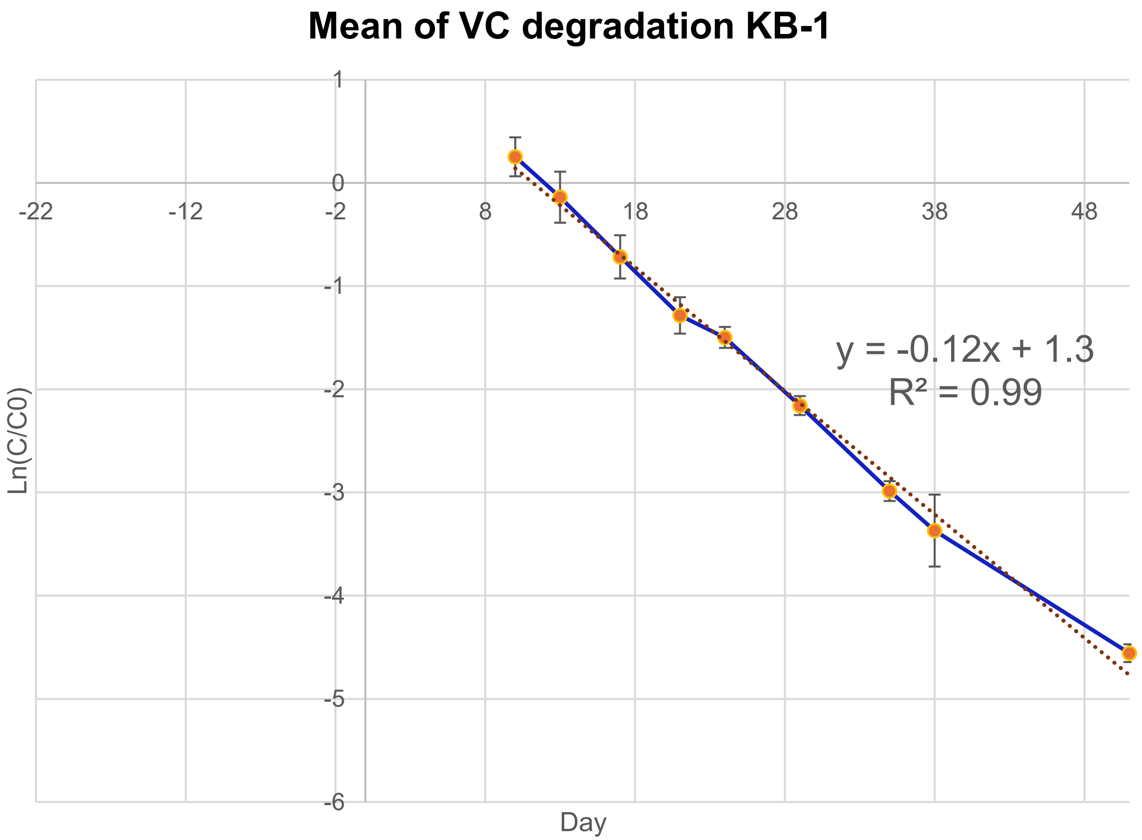
Bioactive GW + Limestone

Bioactive GW + limestone **+ FeS** (+donor)

Bioaugmented (+donor) GW +limestone + **FeS**

Bioaugmented (+donor) GW + limestone





Lower degradation rate than Yaru Li et al., 2021

Bioactive GW + Limestone

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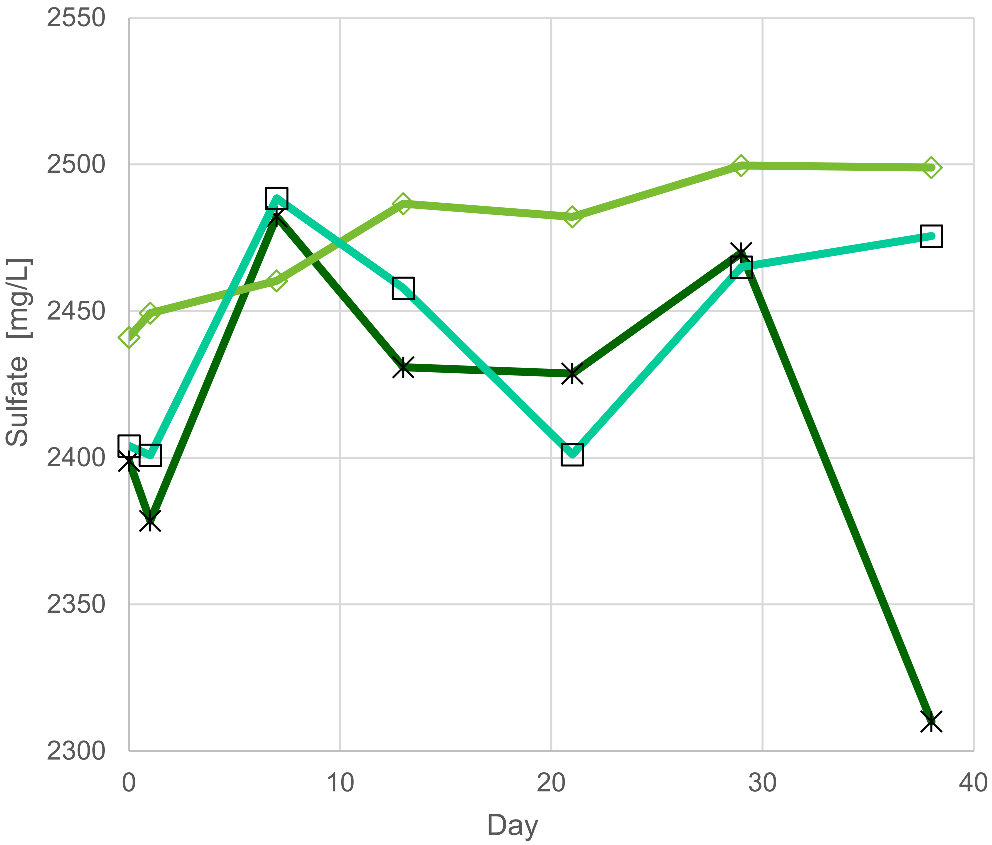
Bioaugmented (+donor) GW +limestone + **FeS**

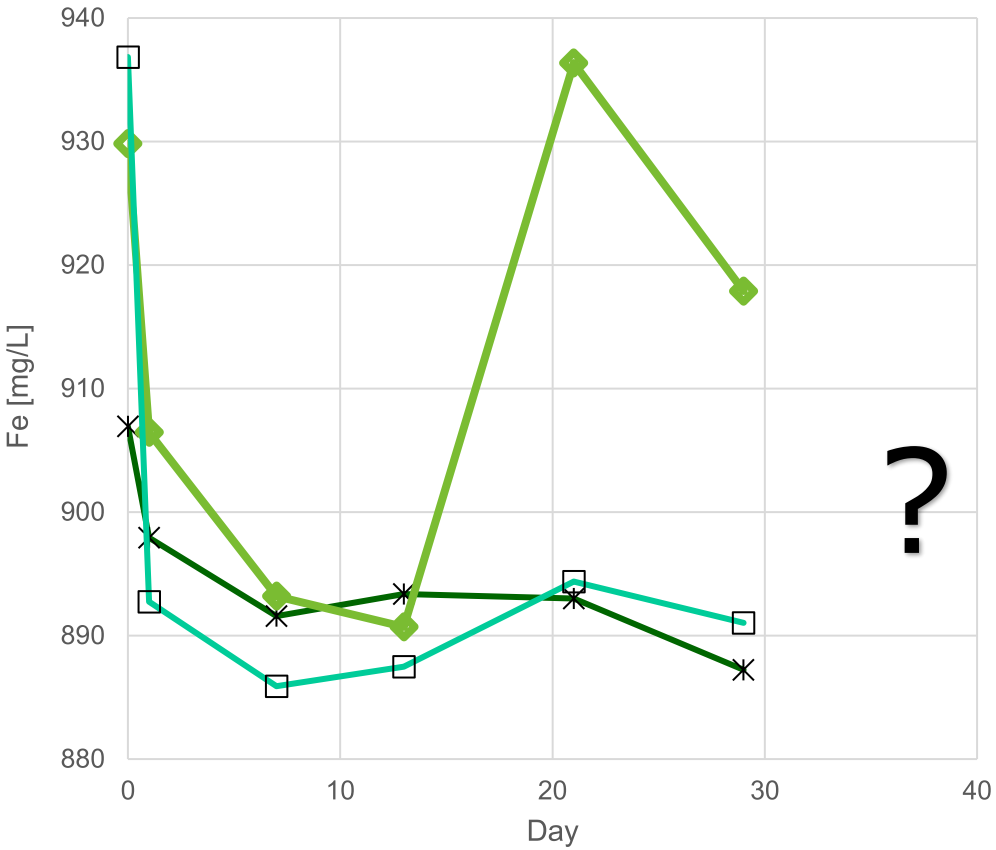
Bioaugmented (+donor) GW + limestone

Sulphate concentration over time



Sulphate reduction only seen on the 38th day of B1 coinciding with the darkening of the batch

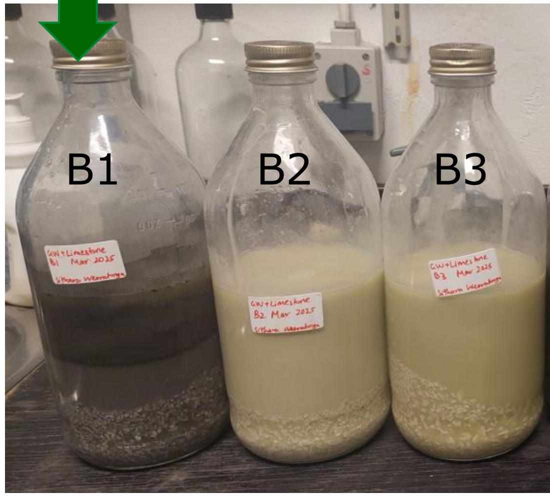
Dissolved iron concentration over time



All 3 showed iron-reduction

Microcosms day 0

?



Microcosms day 43

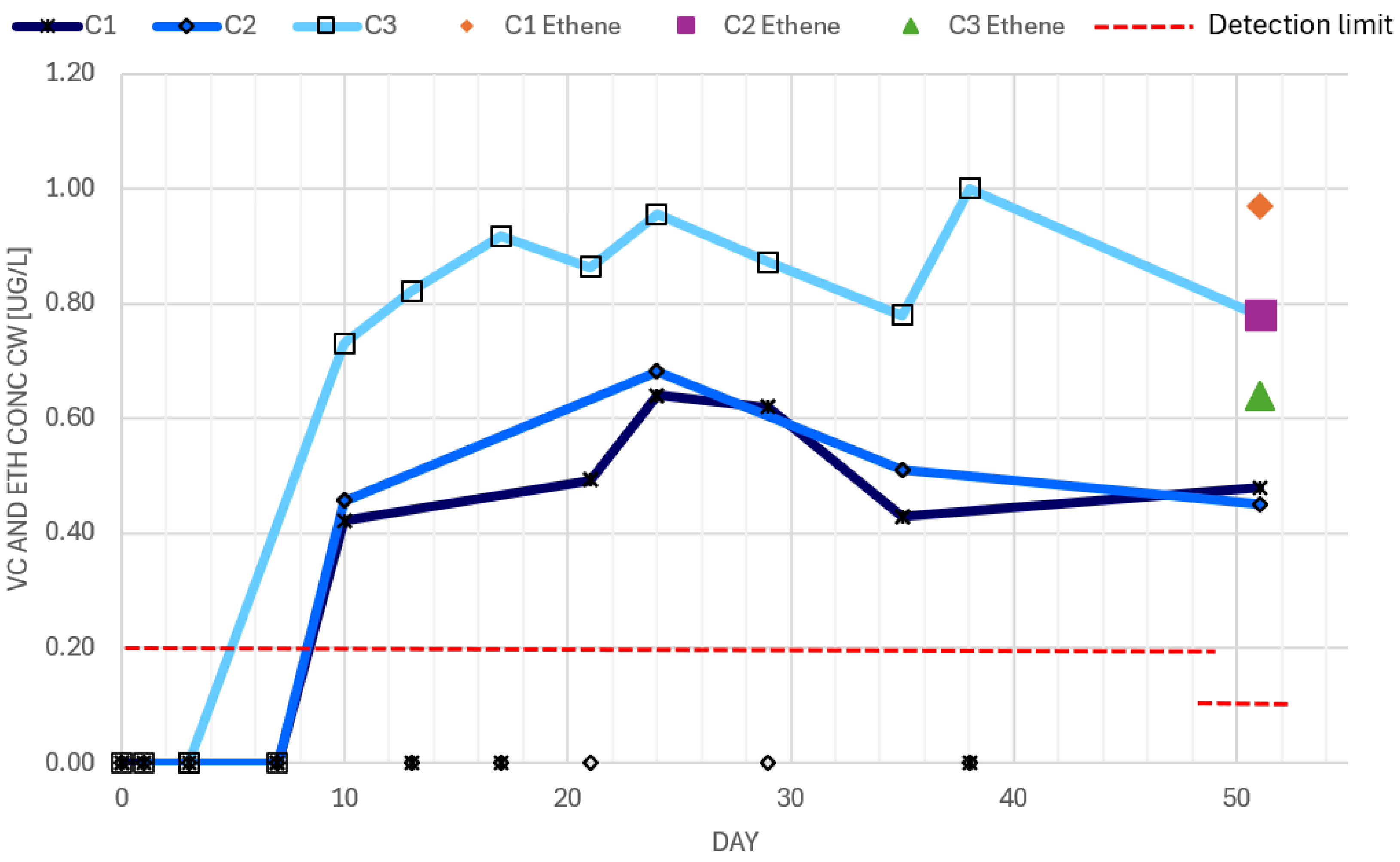
Bioactive GW + Limestone

Bioactive GW + limestone **+ FeS** (+donor)

Bioaugmented (+donor) GW +limestone + FeS

Bioaugmented (+donor) GW + limestone

VC and Ethene concentration over time



Bioactive GW + Limestone

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Bioaugmented (+donor) GW +limestone + FeS

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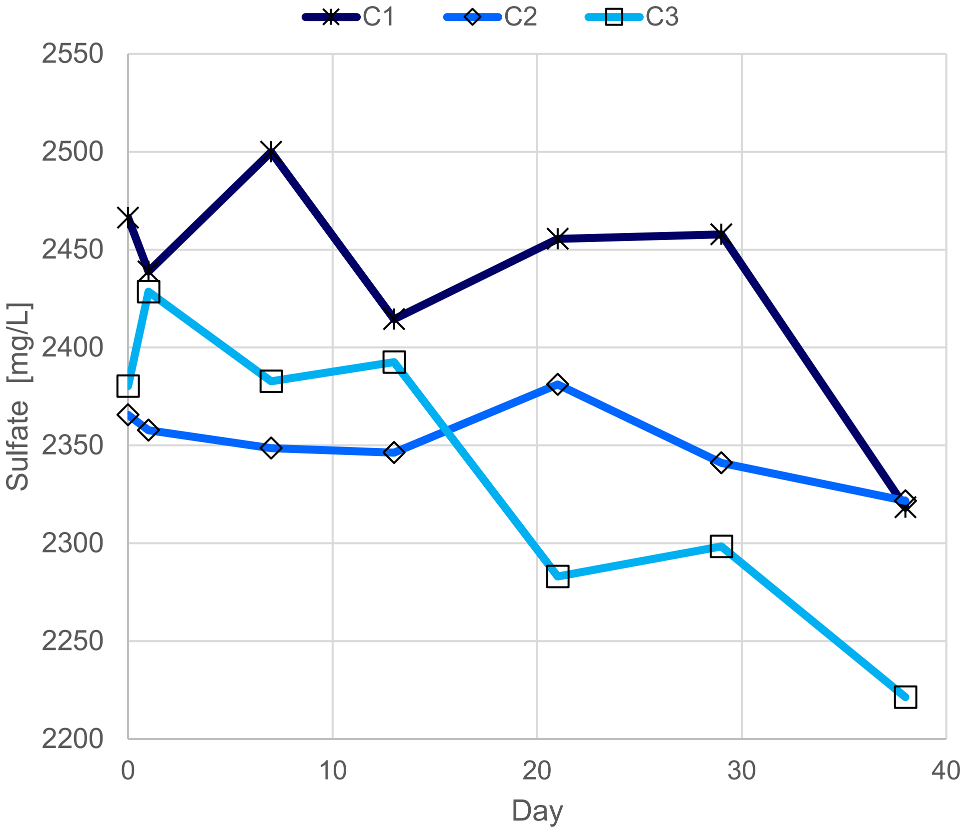
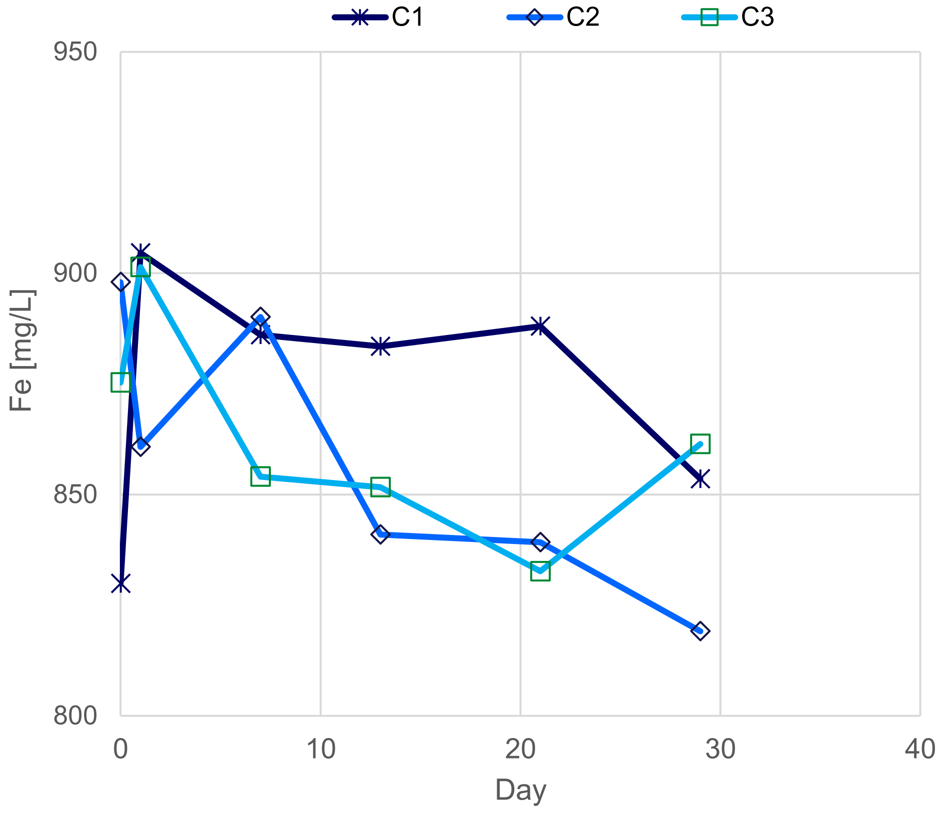
Sulphate concentration over time

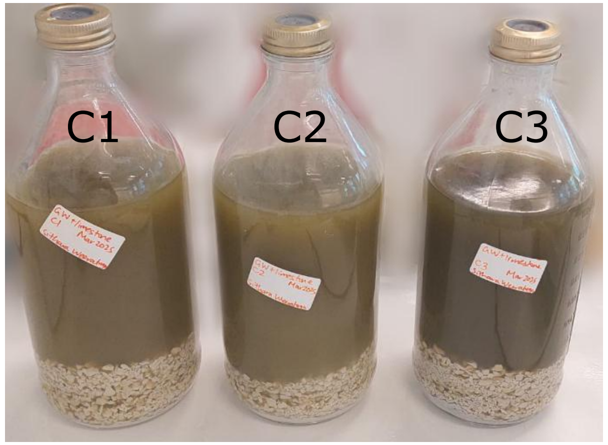


Sulphate reduction seen from day 13

Dissolved iron concentration over time



Iron reduction is seen from the start



Microcosms day 3

Microcosms day 43

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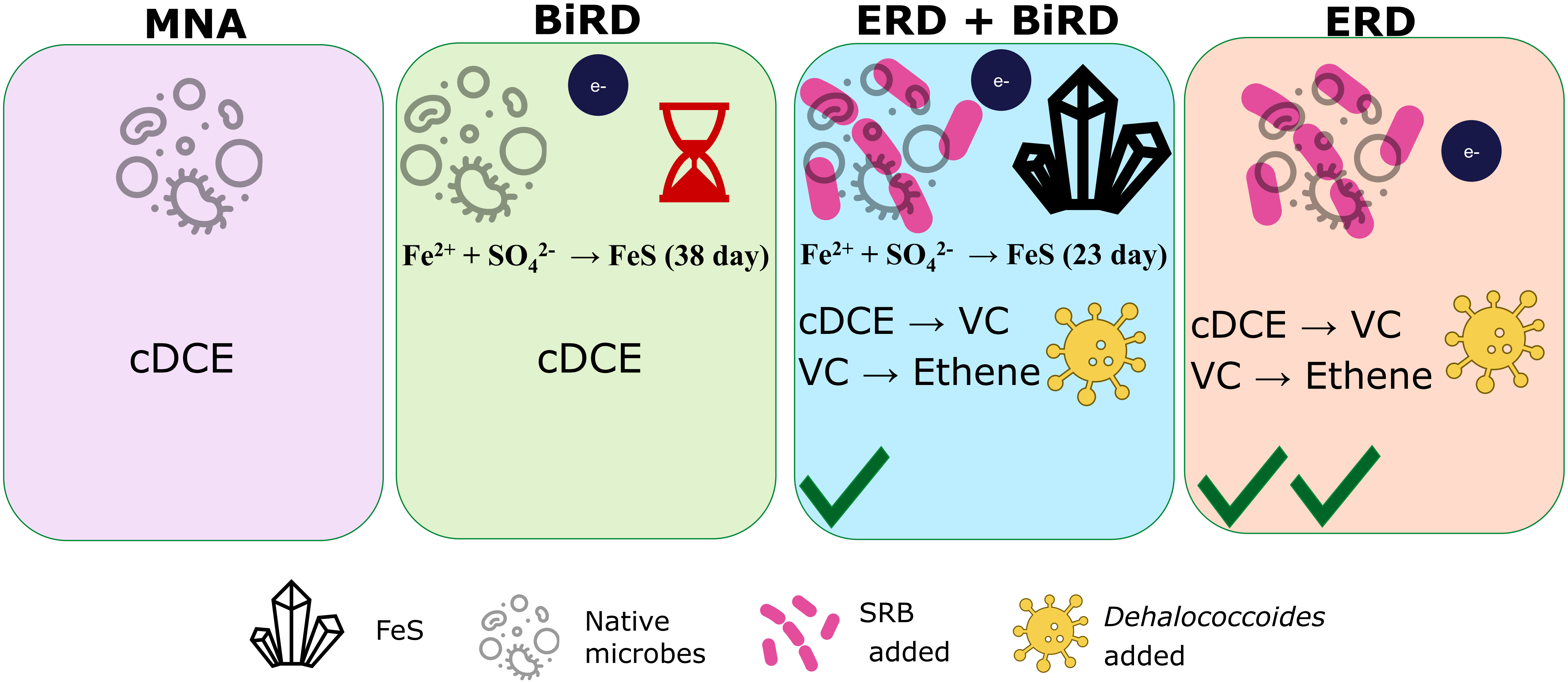
Conceptual understanding



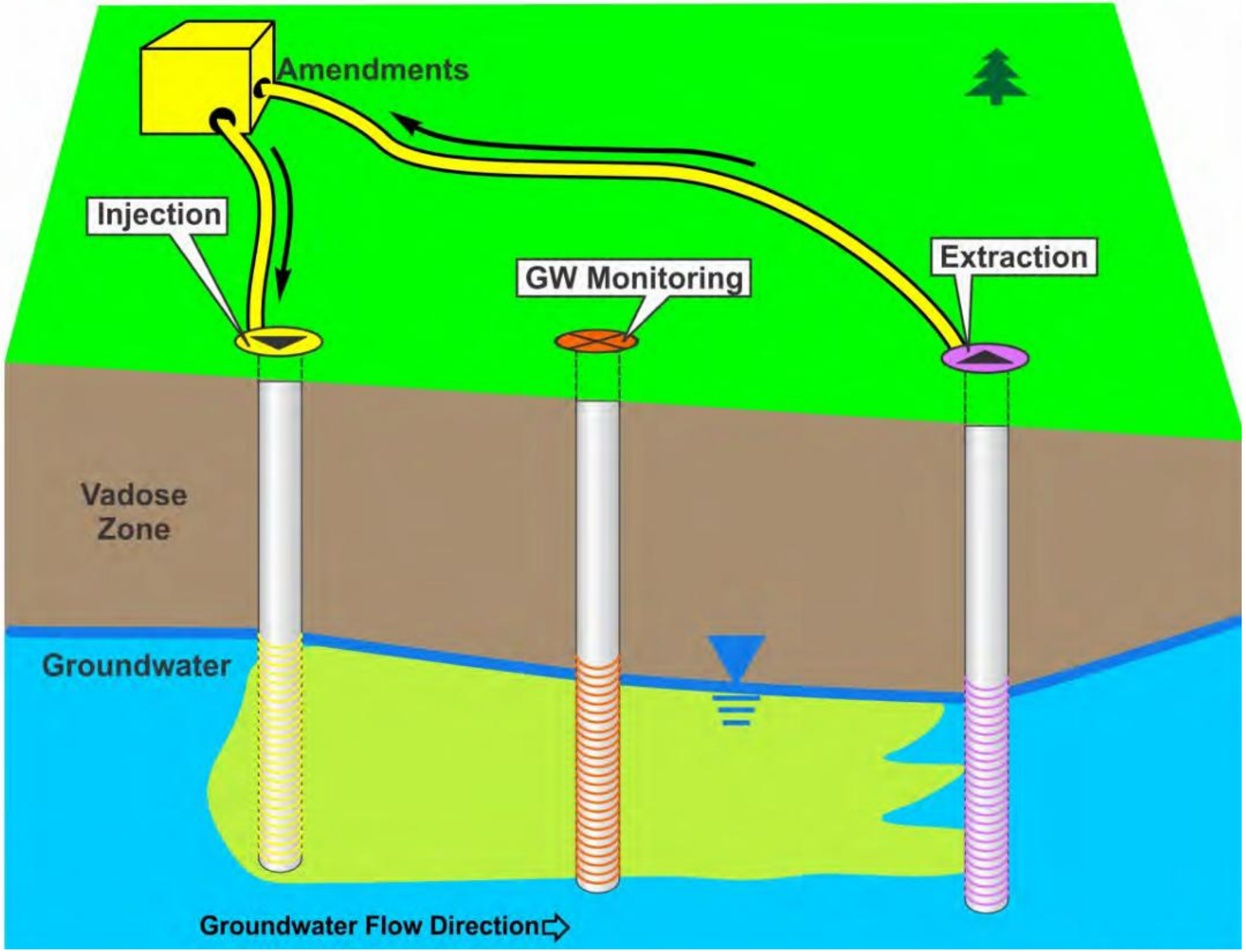
Perspectives and Field application

Perspectives for batch experiments

- Naverland sediments
- No air bubble
- It was intended to run for longer
  – Or run at room temperature

Field application

- ERD
- Recirculation to ensure distribution
- The site is not reduced enough for GeoForm® Soluble alone but could be combined with KB-1® for increased abiotic degradation (lower concentration than in this experiment)



Recirculation system configuration for engineering ISBGT [Darlington and Rectanus, 2015]

Conclusion

- Batch tests compared MNA, GeoForm® Soluble, KB-1®, and a combination

- ERD using KB-1® was the most effective → recommended recirculation to enhance amendment delivery in the fracture for field-scale applications

- However, compared to literature, much slower
  ($5\ \mu mol L^{-1}\ day^{-1}$ compared to $25\ \mu mol L^{-1}\ day^{-1}$)

- BiRD, which showed limited effectiveness under the given time frame and redox conditions as there was a delay in the formation of FeS

- SRB in KB-1® accelerated the production of FeS but still insufficient precipitation occurred to enable abiotic degradation within the duration of the experiment

- High iron sulphide concentration slowed down biotic reductive dechlorination but still led to the formation of VC and ethene biotic degradation

Thank you for listening and
Thank you to the Capital Region of Denmark for funding