

Remediation of vinyl chloride-contaminated groundwater by granular ZVI-biochar

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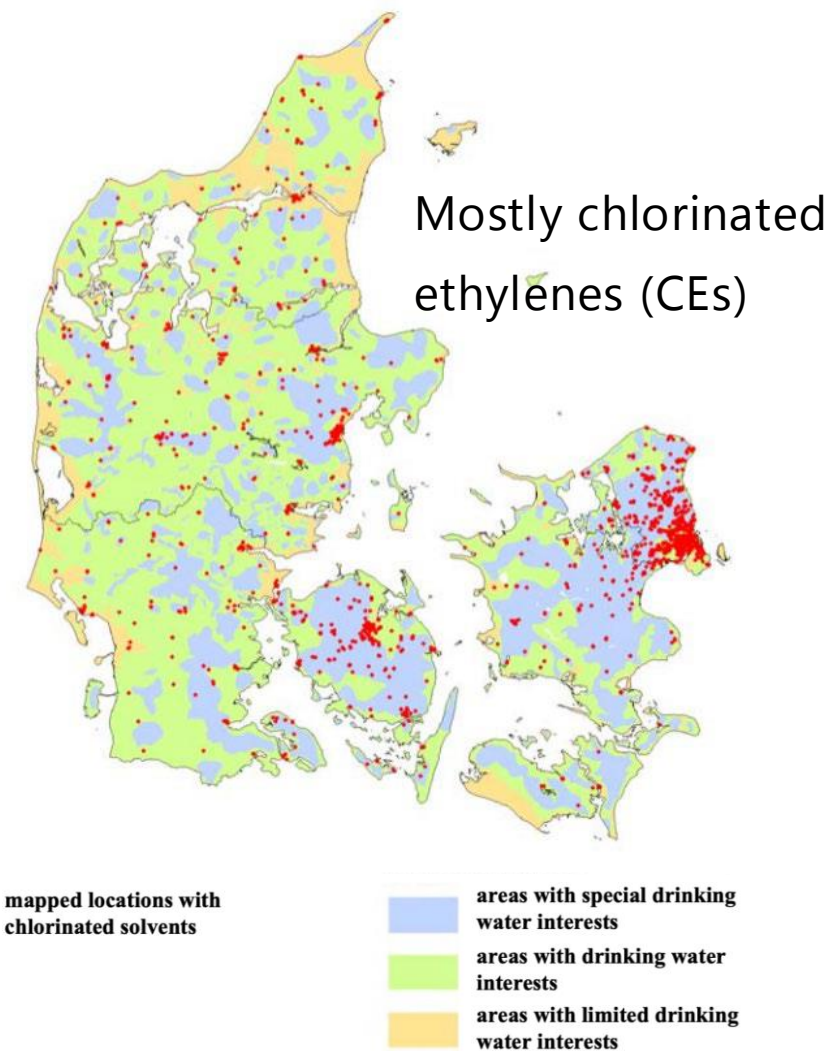
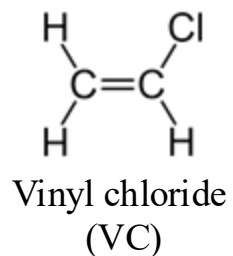
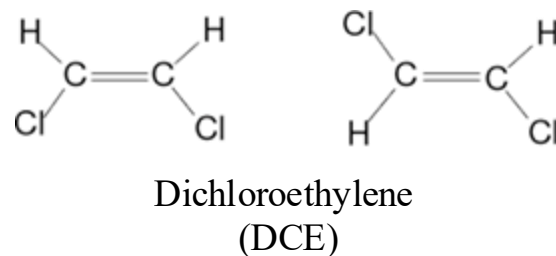
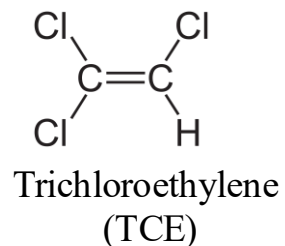
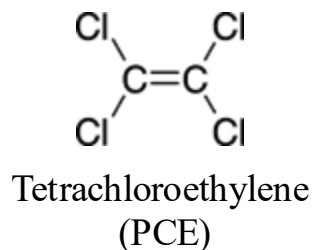
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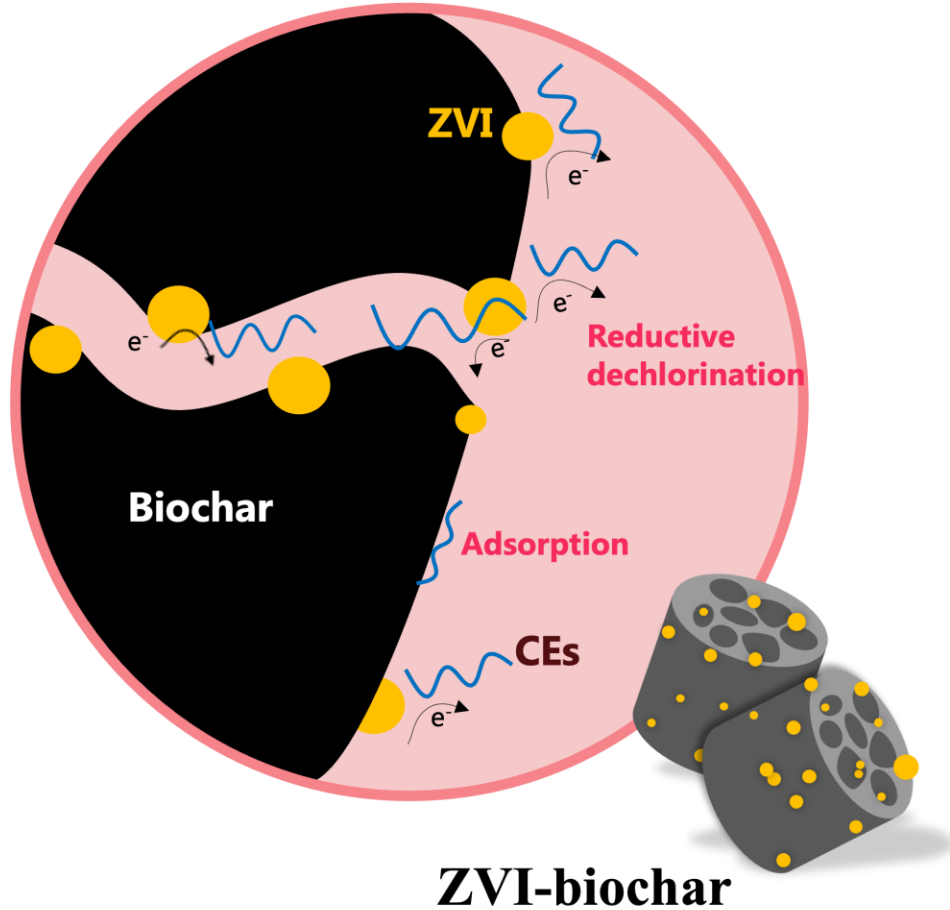
Chlorinated solvents contamination

- **Chlorinated solvents** are widespread groundwater contaminants **globally**.
- CE is posing a direct threats to the country's **drinking water security**.



Chlorinated solvent contamination in Denmark.
(Miljøstyrelsen, 2009)

Why ZVI-biochar?



Zero-valent iron (ZVI)

- Provides reducing power

Biochar support

- Gives high porosity and surface area, i.e., sorption capacity
- Acts as catalyst

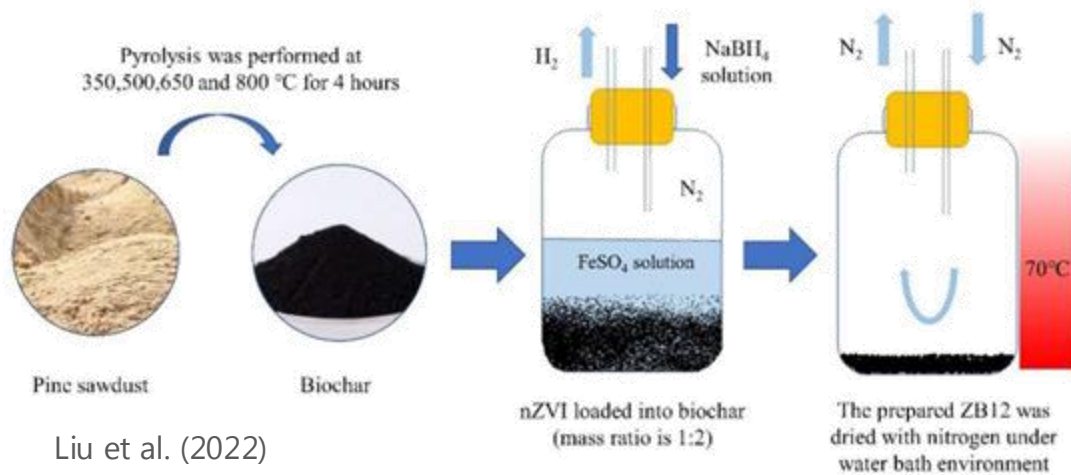


ZVI-biochar

- Combines **adsorption** and **reductive dechlorination**
- Granular material, **stable with high hydraulic conductivity** for permeable reactive barriers

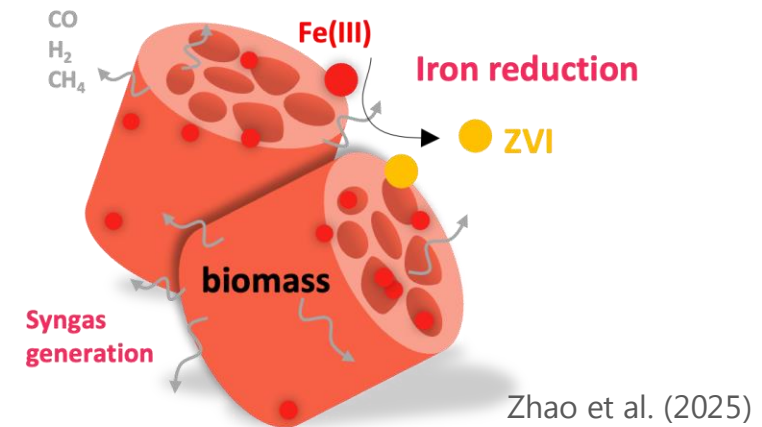
How to make reactive ZVI-biochar?

Borohydride reduction



- Requires strong, expensive reductant
- Creates wastewater
- Environmentally unfriendly

Carbothermal reduction



- ZVI formed during pyrolysis
- Simple and economic
- Raw materials abundant

CO₂-assisted pyrolysis promotes ZVI formation

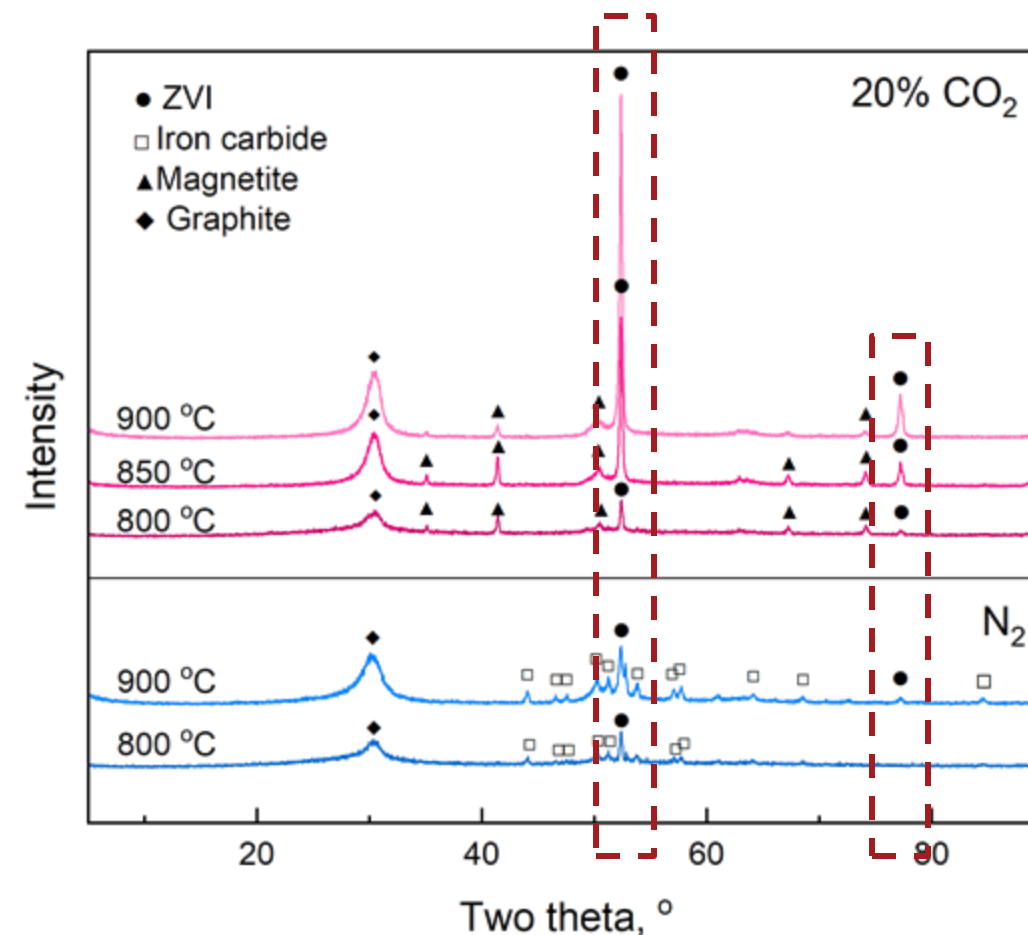
ZVI-biochar production

Beechwood → Pyrolysis → ZVI-biochar
+ FeCl₃ ▪ 800-900 °C
+ urea ▪ N₂ only or with CO₂

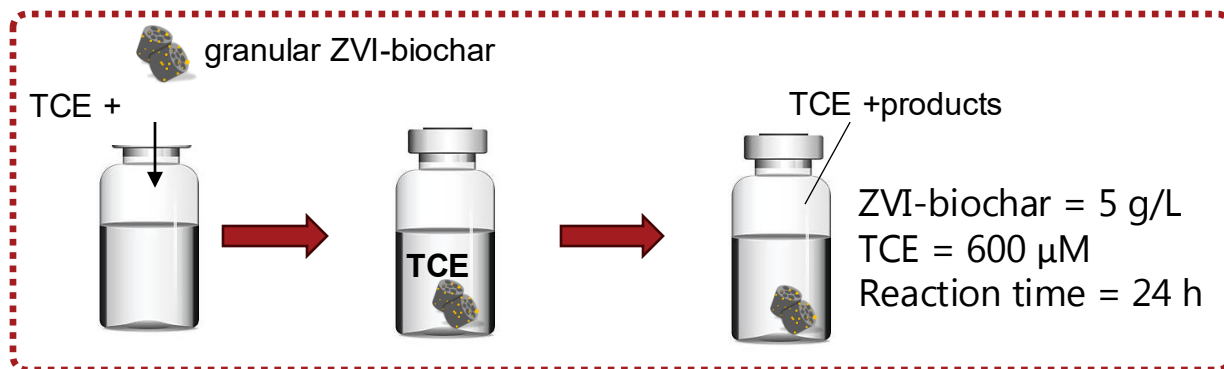


- Introducing CO₂ during pyrolysis **promoted ZVI formation**, potentially **lowering production temperature**.

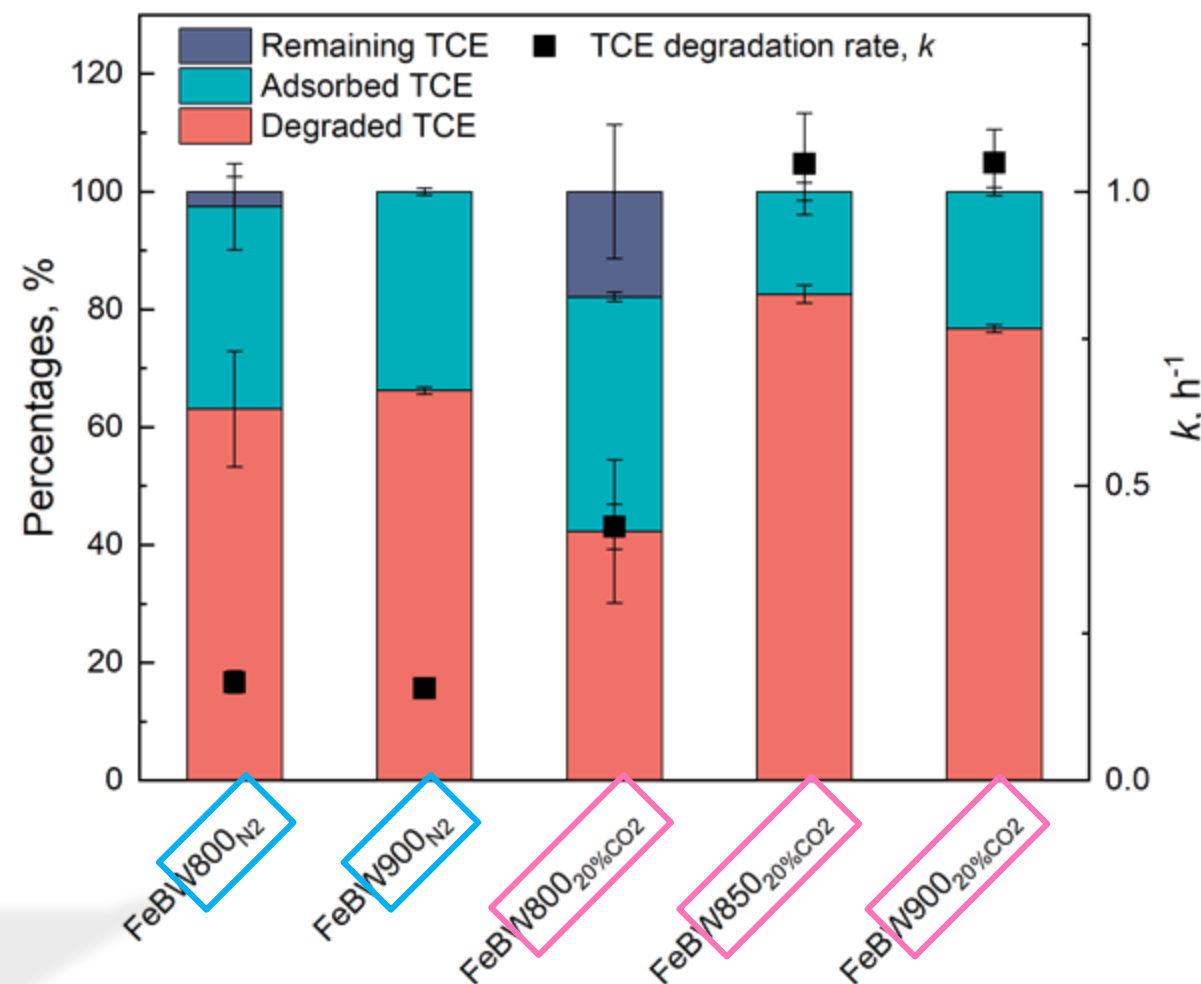
X-ray diffraction



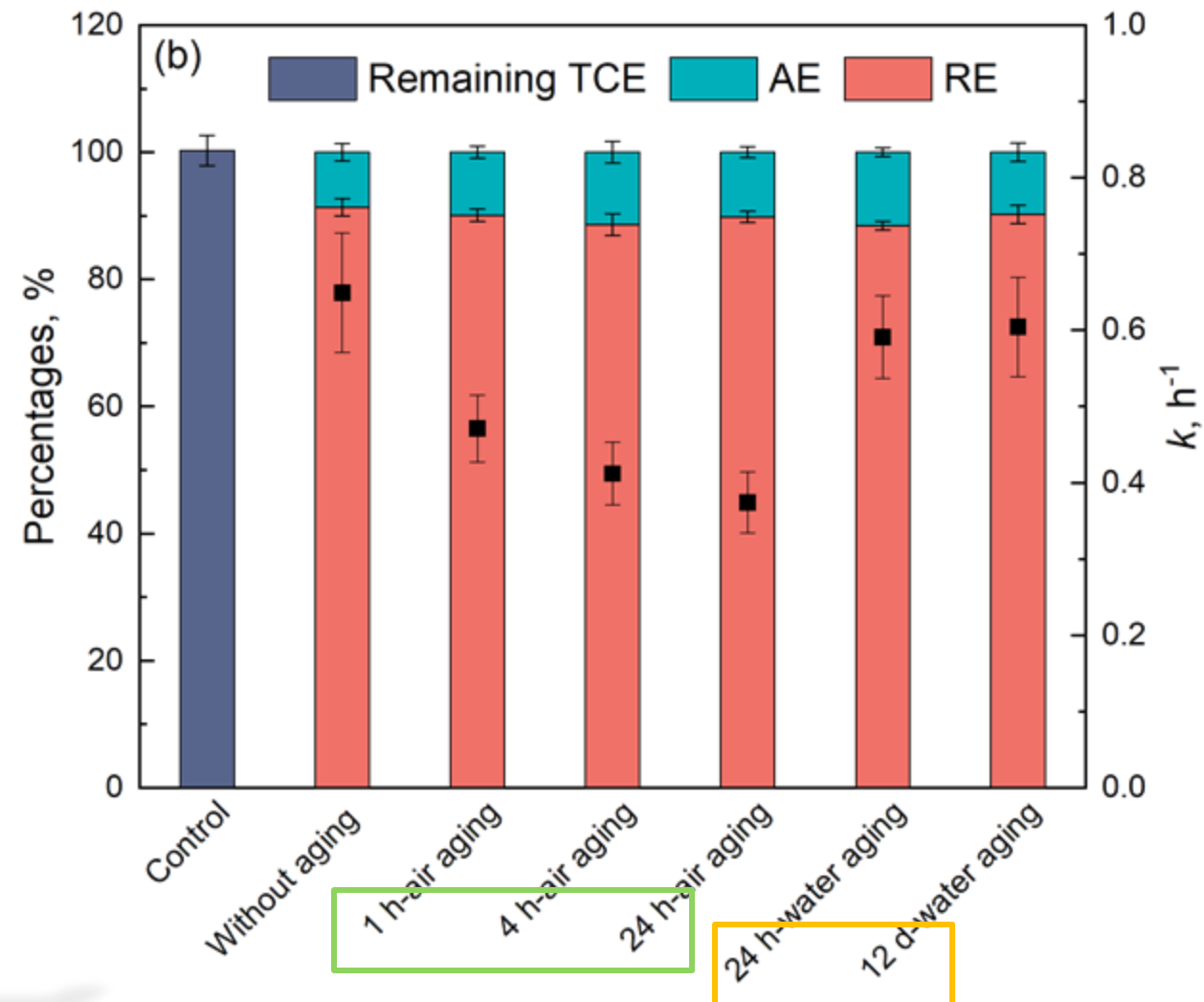
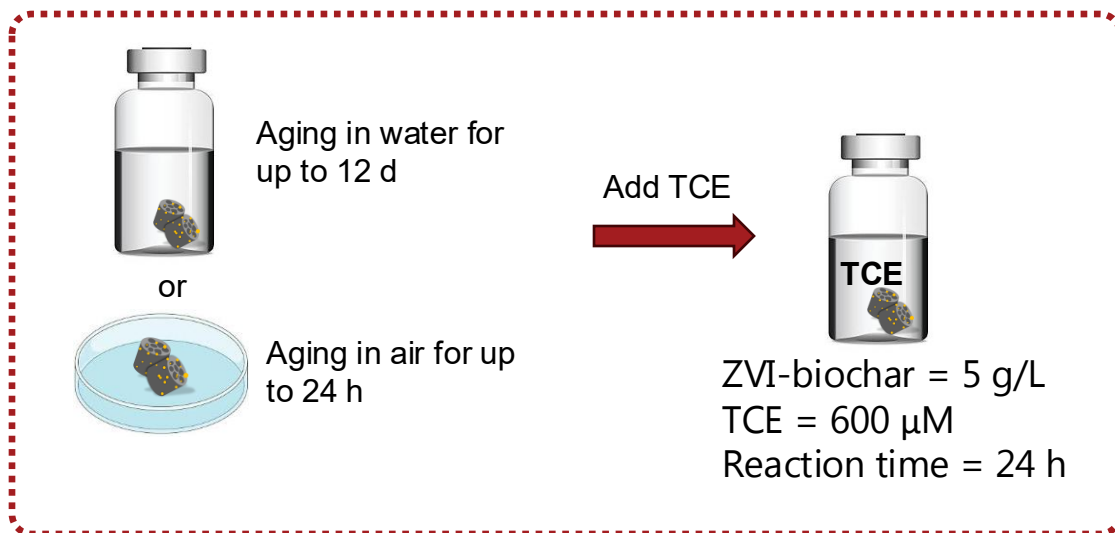
ZVI-biochar reactivity with trichloroethylene (TCE)



- ZVI-biochar produced at $\geq 850^\circ\text{C}$ **completely removed TCE**, mainly through **degradation**.
- CO_2 activation **accelerated TCE dechlorination** rate by up to 6.7-fold and enabled reactive ZVI-biochar production at **lower temperatures**.



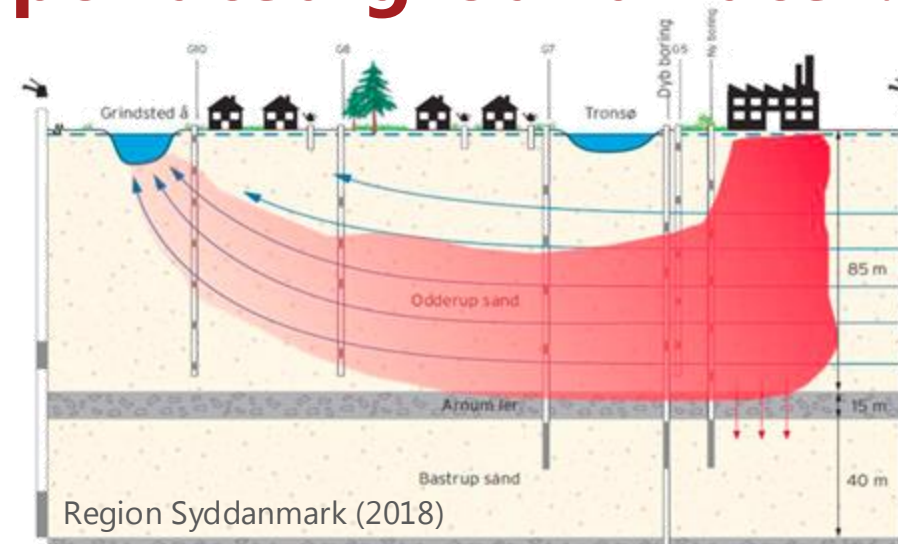
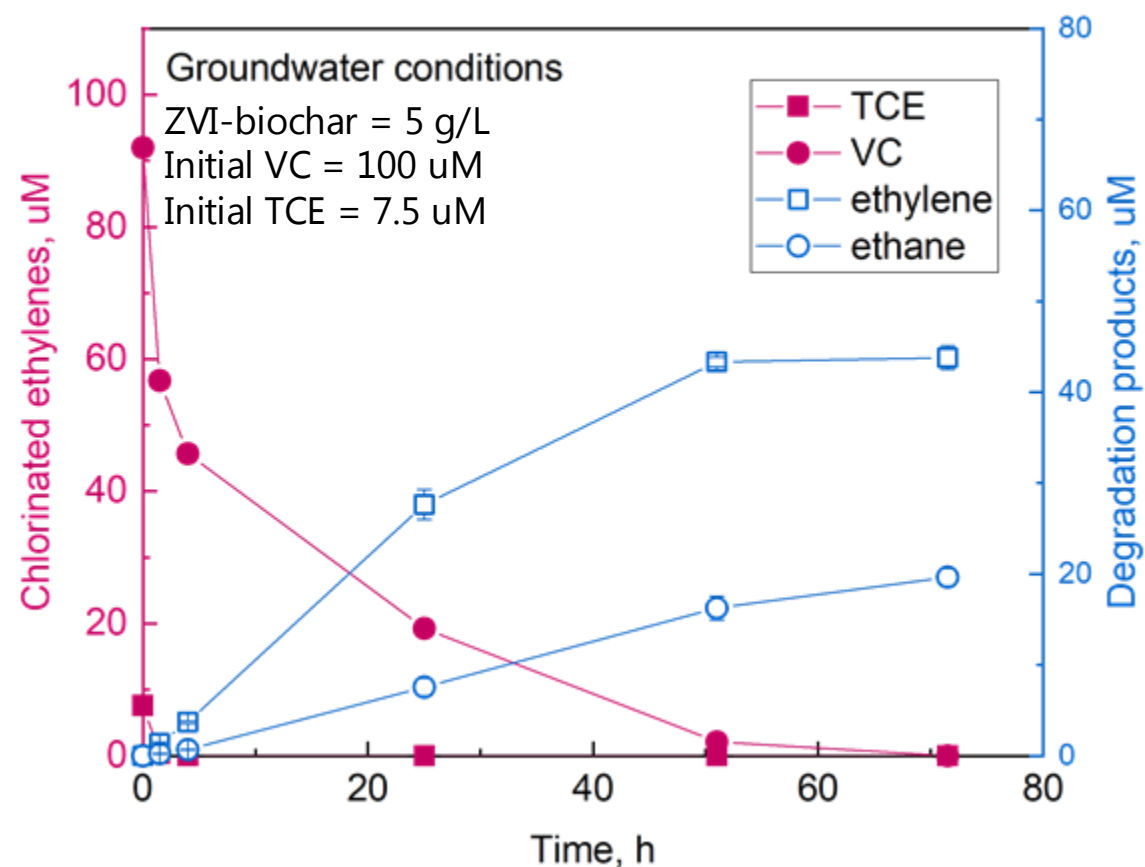
How stable are they?



- Air aging reduced TCE degradation rates, whereas water aging had little effect.
- ZVI-biochar **retained a high TCE degradation extent** after both water and air aging.

How reactive is this ZVI-biochar in polluted groundwater?

- Chlorinated ethylenes (e.g., VC, TCE)
- Co-contaminants: sulphonamides, benzene and barbiturates

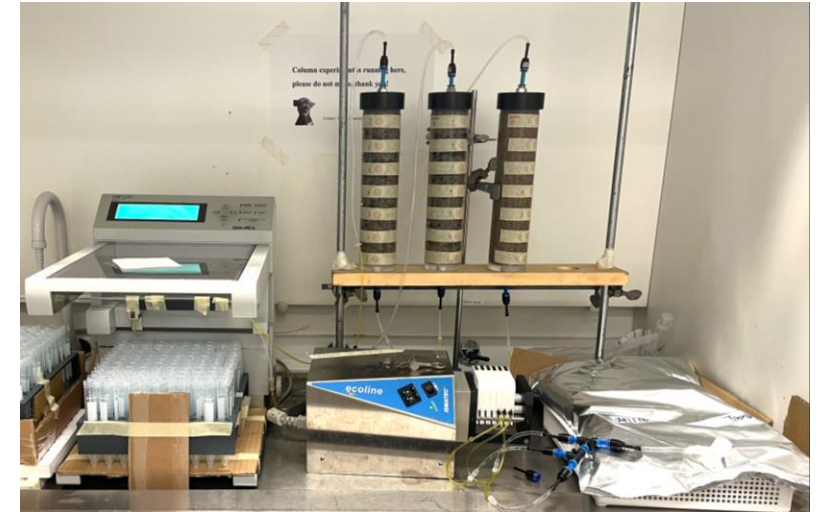


Grindsted (Denmark)

- TCE and **VC** are **rapidly converted to ethylene and ethane** under groundwater conditions.

ZVI-biochar reactivity under continuous flow conditions

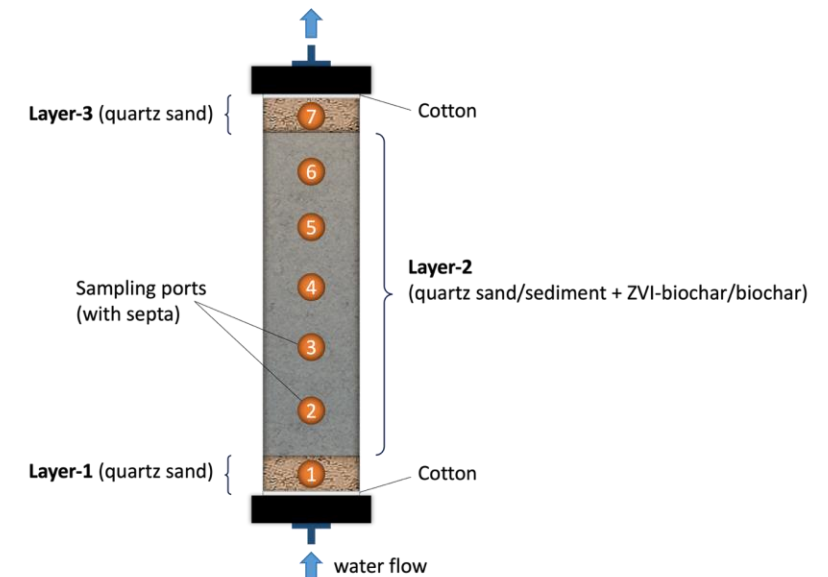
No.	Media	Water type	Purpose
1	Sand only	GW	Background control
2	Sand + biochar	GW	ZVI-biochar reactivity
3	Sand + ZVI-biochar	GW	ZVI-BC reactivity
4	Sand + ZVI-biochar	DDW	Iron corrosion test
5	Sediment only	GW	Sediment control
6	Sediment + ZVI-biochar	GW	Sediment effects



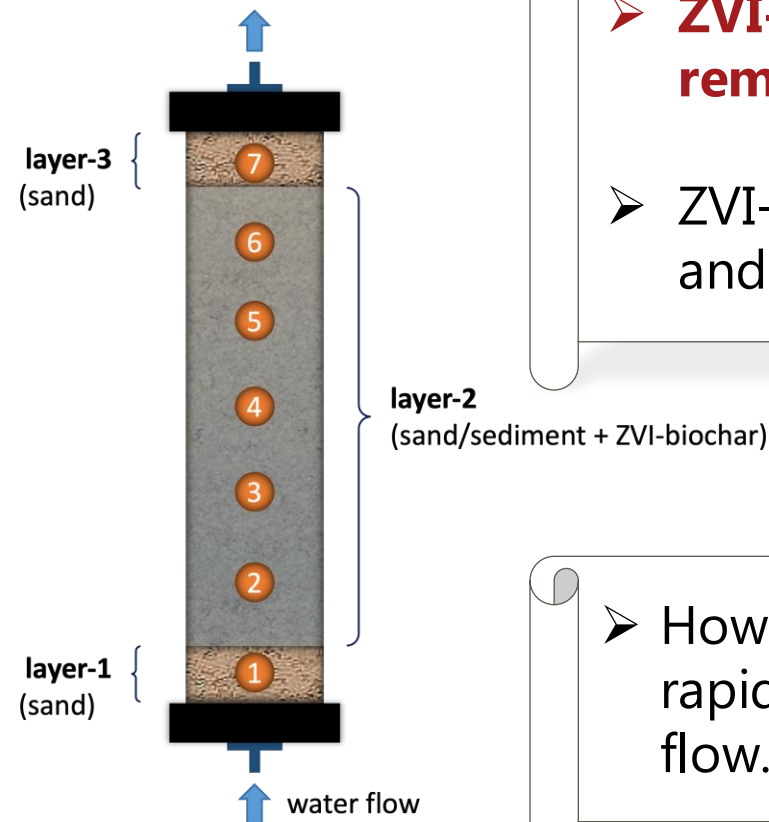
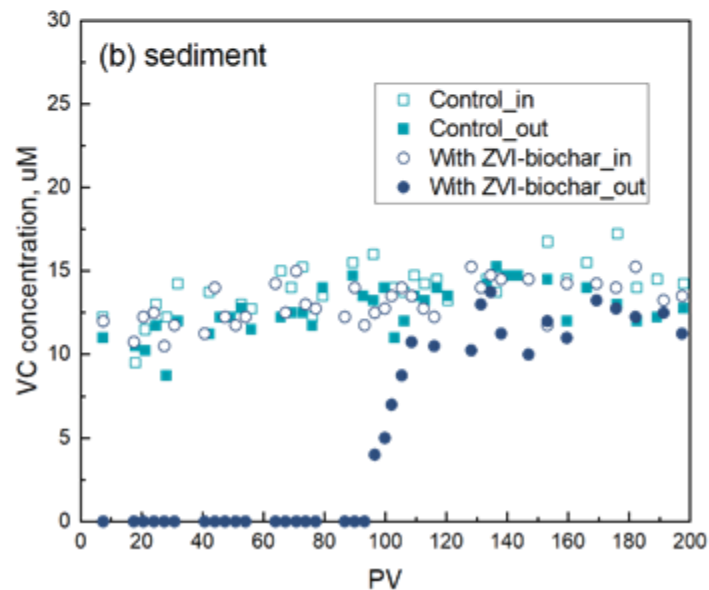
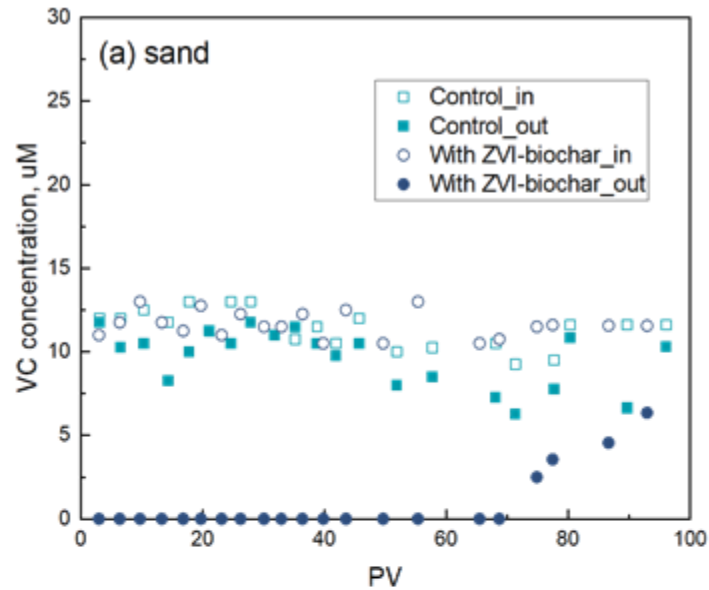
Grindsted site



Sediment and groundwater (GW)



ZVI-biochar reactivity under continuous flow conditions



- Controls showed no VC removal.
- **ZVI-biochar** achieved **complete VC removal** before breakthrough.
- ZVI-biochar also removed sulphonamides and barbiturates through adsorption.

- However, **acidic groundwater** (pH 5.5) rapidly corroded ZVI under continuous flow.

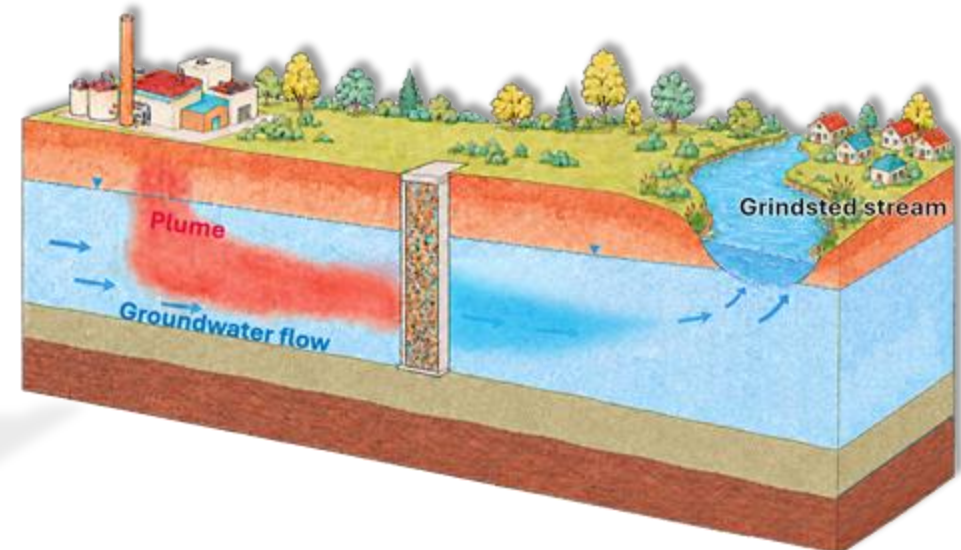
Design of a reactive permeable barrier

VC removal, %	v_p , m y ⁻¹	ZVI-biochar, %	k , h ⁻¹	L , m
99	150	1.4	0.18	4.3
99	150	10	1.3	0.6
99	150	30	3.9	0.2

$$L = \frac{v_p}{k} \ln \frac{c_{in}}{c_{out}}$$

- L (m): thickness of the wall
- v_p (m y⁻¹): pore water velocity in the wall
- k (h⁻¹): degradation rate of VC
- c_{in} : VC concentration before passing through the wall
- c_{out} : VC concentration after passing through the wall

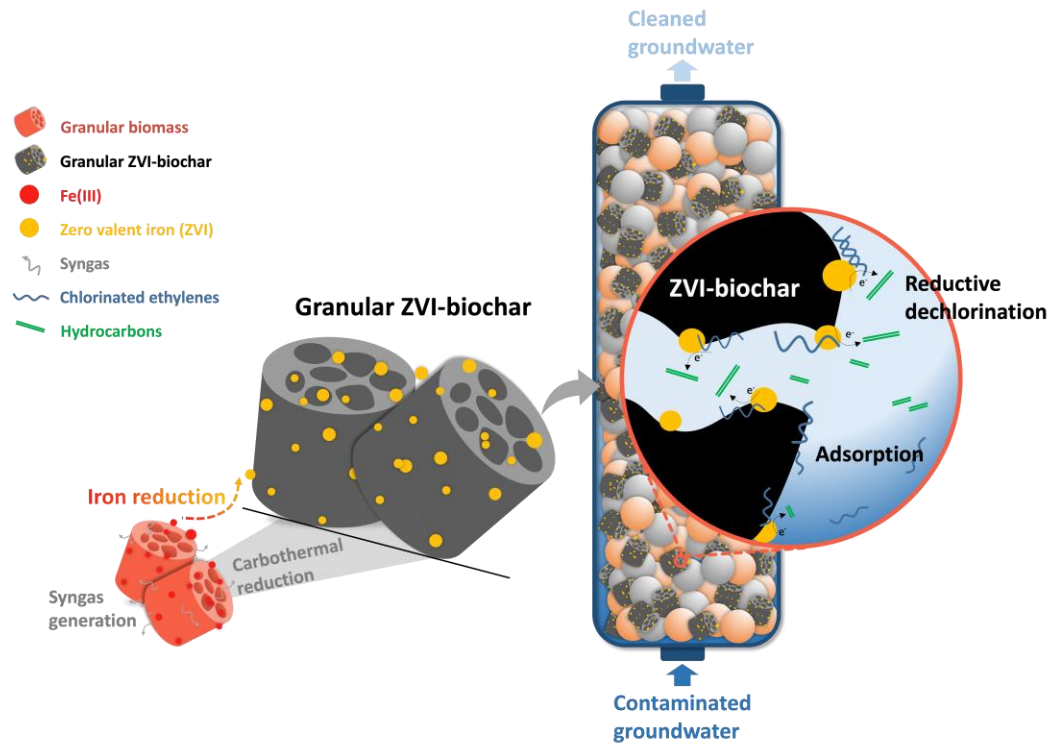
- 99% VC removal at 150 m yr⁻¹: **~0.5 m wall** with 10-30 wt% ZVI-biochar.
- At 30 wt%: **~4-5 years** estimated lifetime.
- **Lifetime could be extended** by controlling acidity and reducing ZVI corrosion.



Take home messages

- ❑ **CO₂-assisted one-step pyrolysis promoted ZVI formation** and enabled the production of granular, highly reactive ZVI-biochar.
- ❑ ZVI-biochar could rapidly degrade TCE and VC in contaminated groundwater and **retained high reactivity** after water/air aging.
- ❑ Under continuous flow, **VC removal was effective**, but **acidic groundwater accelerated ZVI corrosion** and shortened its reactive lifetime.

Future work



- ❑ Extend reactive lifetime by controlling groundwater acidity and reducing ZVI corrosion.
- ❑ Validate long-term performance at field-relevant scale.
- ❑ Assess scalability, environmental impacts and costs through production optimization, LCA and economic evaluation.

THANK YOU!