Degradation of chlorinated solvents using biochar as catalyst

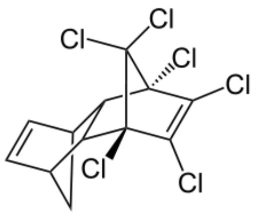
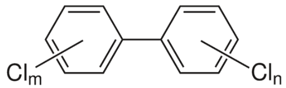
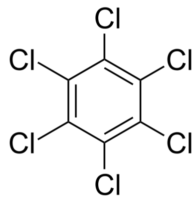
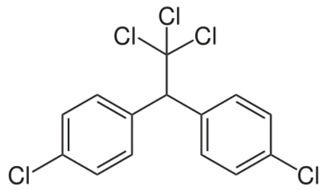
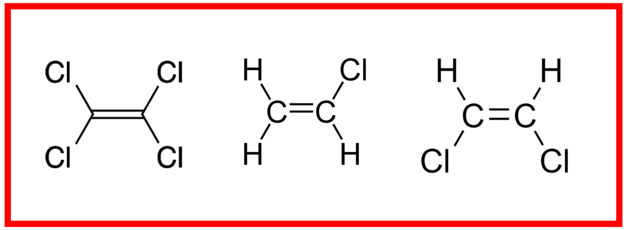
Hans Christian Bruun Hansen
Environmental Chemistry
Department of Plant and Environmental Sciences
University of Copenhagen



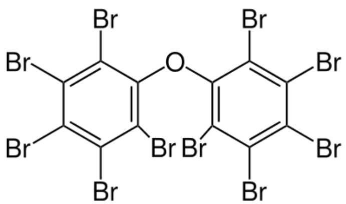
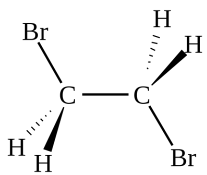
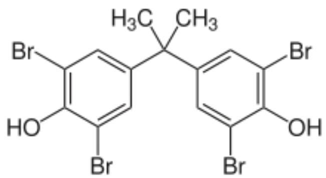
Halogenated compounds – environmental POP nightmares!

Halogen substitutions in organic compounds make them more durable, less soluble, more lipophilic, thermal stable, and not easily ignited. This is also what make them nasty pollutants → Stockholm Convention.

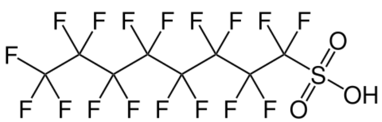
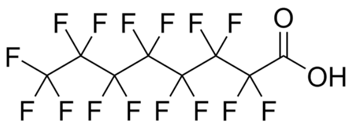
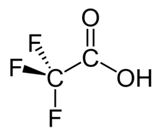
Chlorinated compounds (solvents, insecticides, lubricants, coolants···) the first to show up (Rachel Carson)

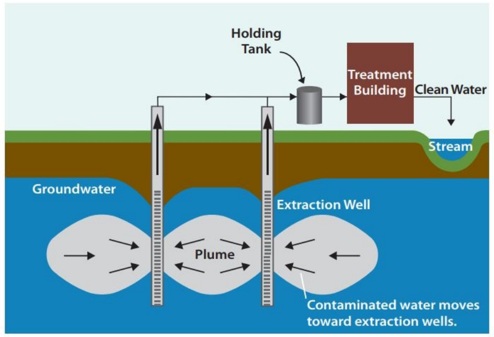
Brominated compounds (solvents, fuel additives, flame retardants)

Fluorinated compounds (surfactants in a huge number of applications, flame retardants)

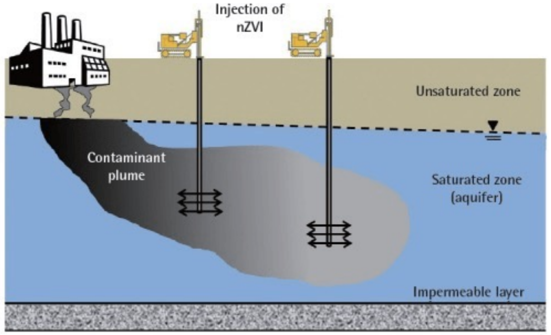
Chlorinated solvents cleanup – multiple solutions



https://enviraj.com/envipedia/pump-and-treat.html

Pump and treat

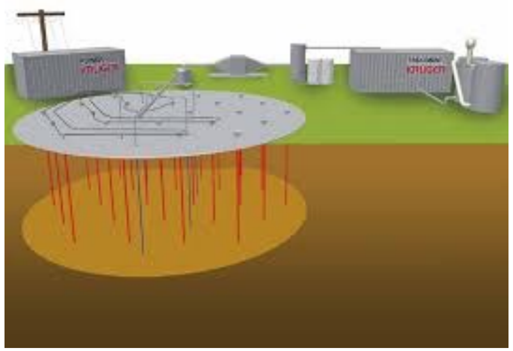
- Time consuming (> 30 y)
- Energy demanding



https://www.bioenergyconsult.com/zero-valent-iron/

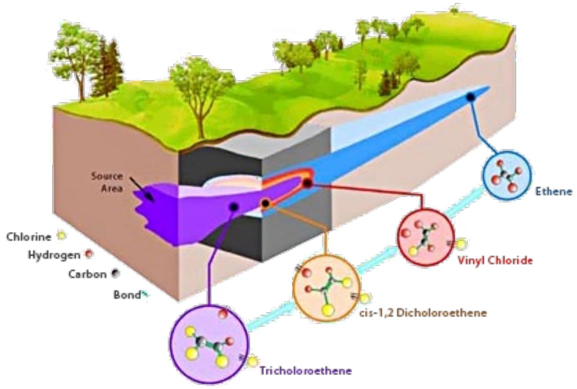
Zero-valent iron (ZVI)

- Not all ZVI capacity available
- Reacts with water (H_2)
- ZVI passivation; repeated treatment



Thermal desorption

- Energy intensive
- Soil destructive

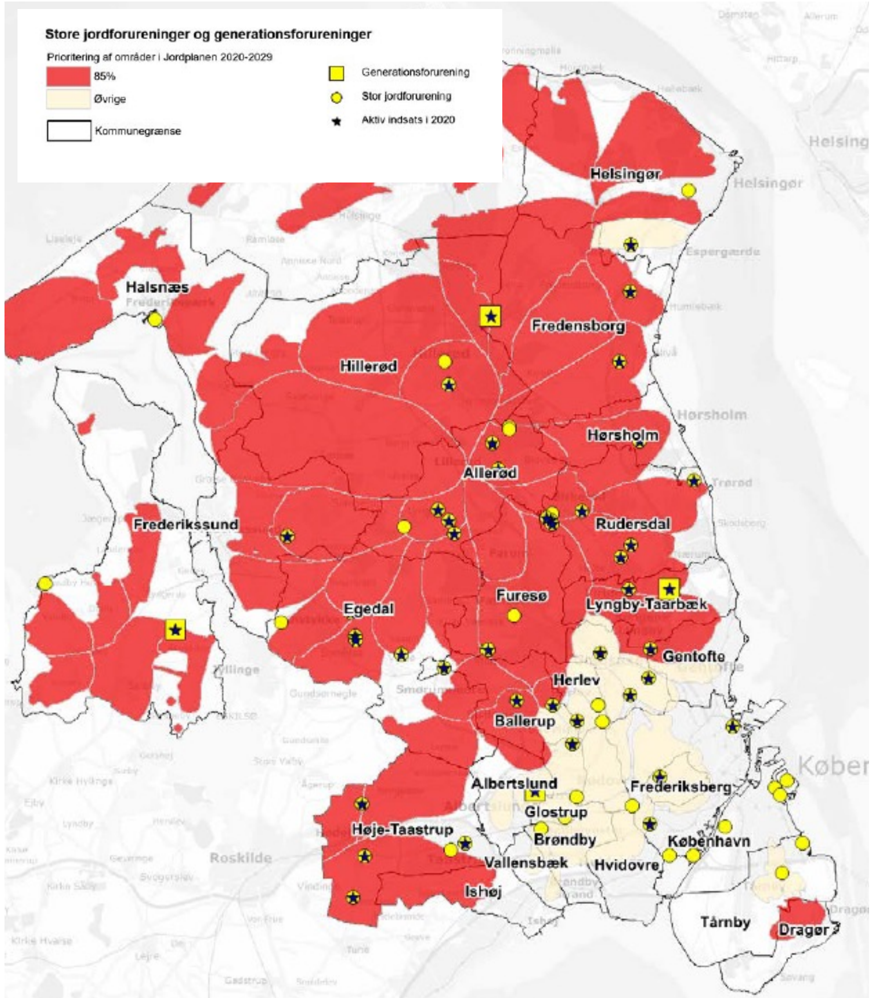


USEPA

Microbial dehalogenation

- Biostimulation
- cDCE and VC may accumulate
- Bioaugmentation (e.g. Dehalococcoides)

Chlorinated solvents dominating



RegH: Indberetning om Jordforurening 2020

145 **large contaminated sites** in Denmark; 65 located in Region Hovedstaden

BTEX, PAHs, heavy metals, chlorinated solvents, etc.

10 **XXL contaminated sites** ("generations-forureninger") in Denmark; 4 located in Region Hovedstaden

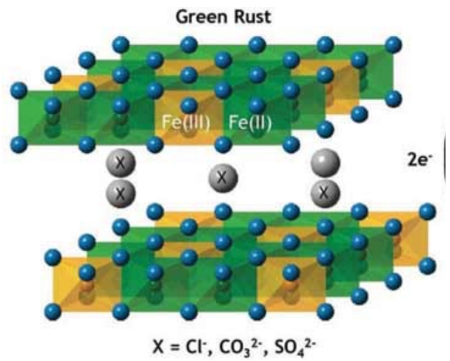
- Collstrop site – arsenic (copper, chromium)
- Lundtoftevej, Lyngy – chlorinated solvents
- Naverland, Albertslund – chlorinated solvents
- Vestergade, Skuldelev – chlorinated solvents

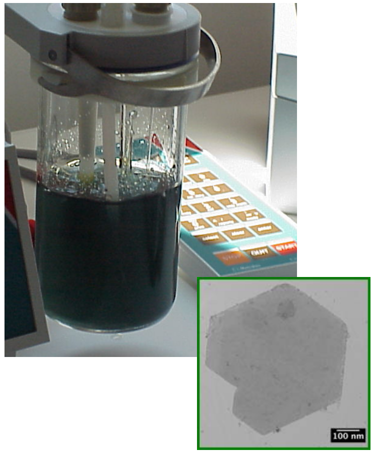
Green Rust and Biochar

Green Rust. A layered blue-green iron(II)-iron(III) hydroxide.

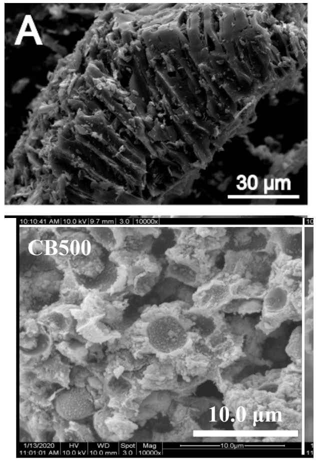
- Highly reactive reducing agent.
- Easy to synthesize.
- Sensitive to oxidation.
- Single particles about 1 μm wide

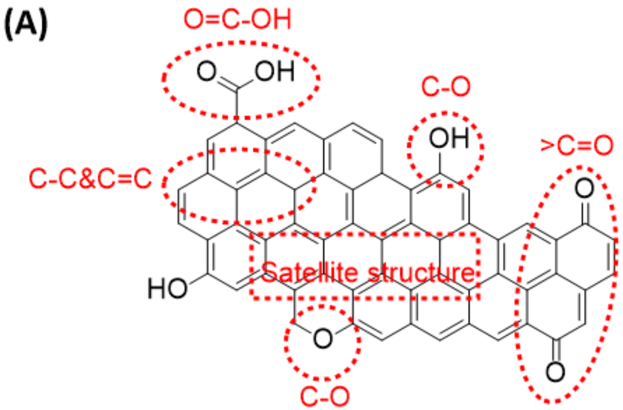
$$[Fe^{II}_{6-x}Fe^{III}_{x}(OH)_{12}]^{x+}[A_{x/n}\cdot yH_2O]^{x-}$$



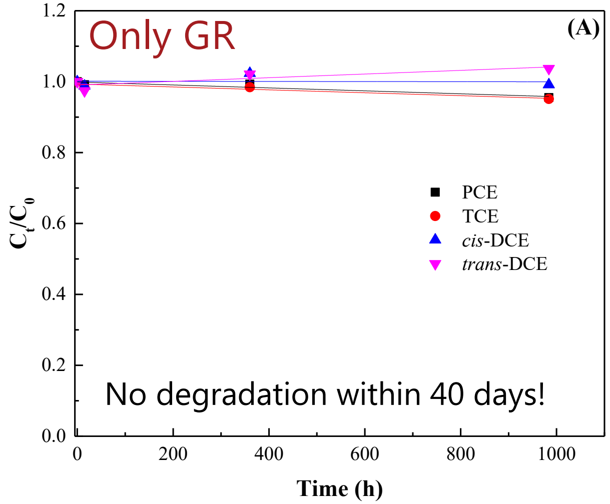


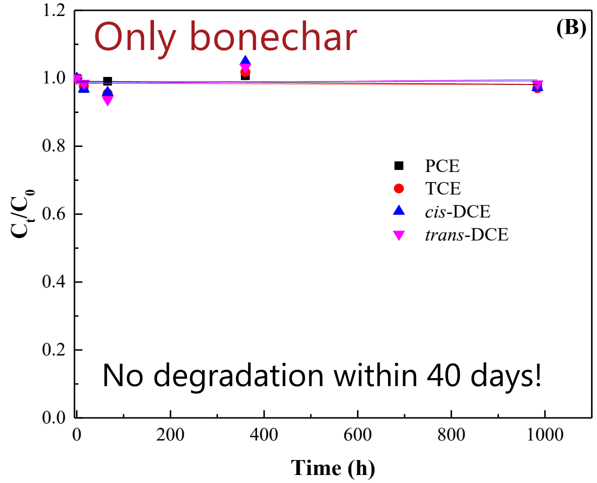
Biochar: Produced by pyrolysis of biomass (300 – 1000 °C) in absence of oxygen. Properties extremely dependent on which biomass is used.

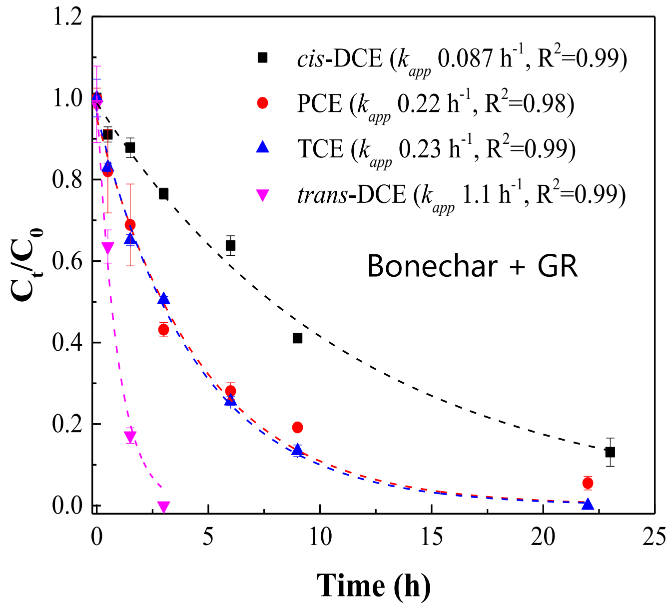


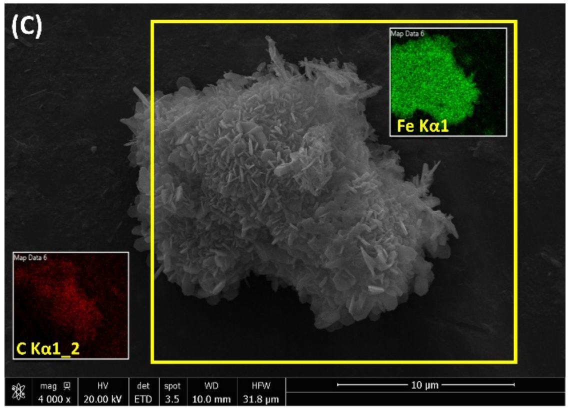


New discovery: Bone char + Green Rust









Bonechar coated with GR particles

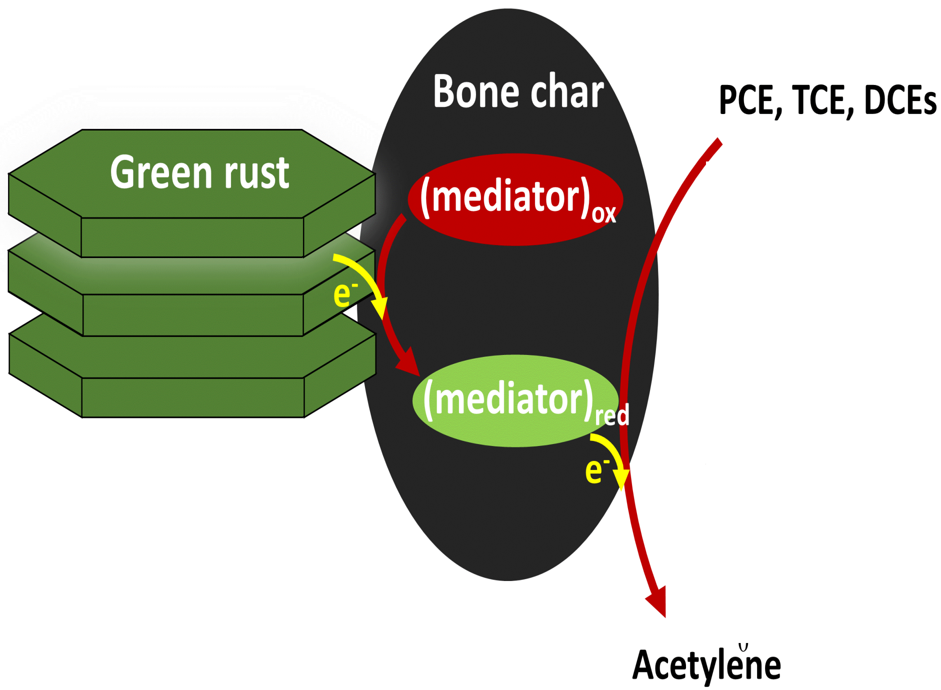
Reactivity rate sequence:

***trans*-DCE > TCE ≈ PCE > *cis*-DCE**

- Acetylene is the main product.
- Chlorinated ethylenes fully dechlorinated and detoxified
- Rate constants same order of magnitude as with nZVI and S-nZVI

Jing Ai (2020)

Reaction platform



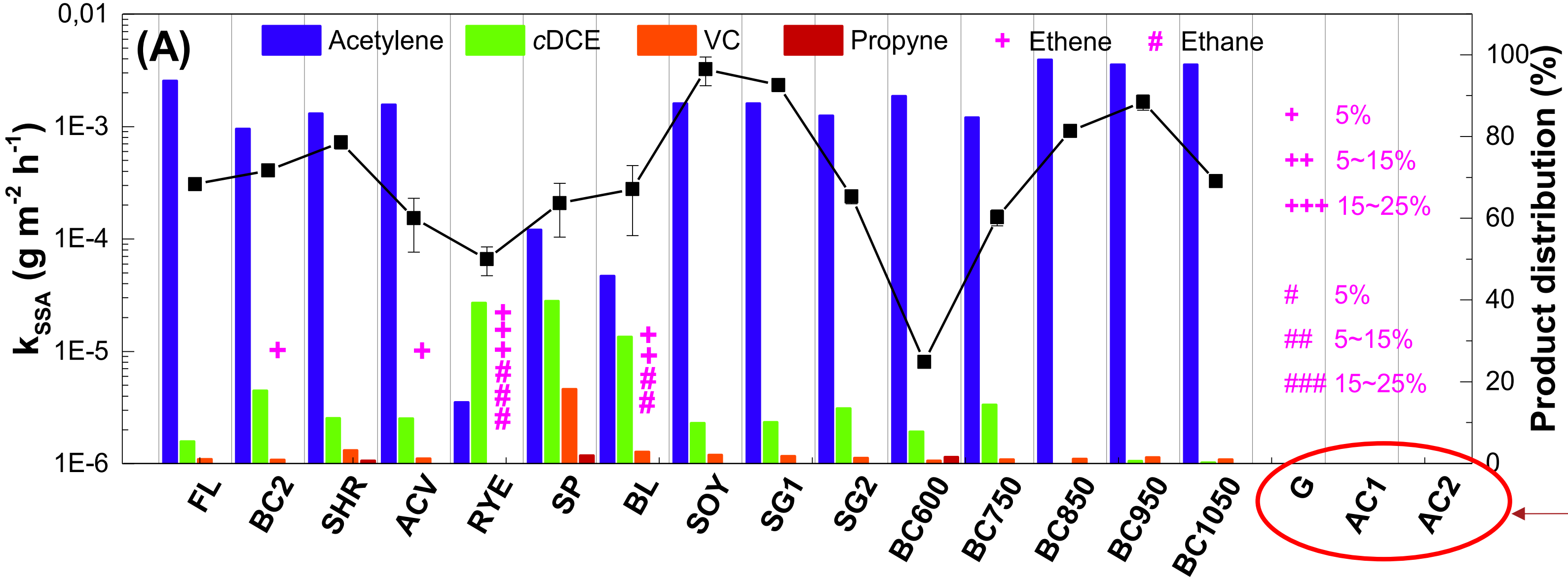
Biochar triple role: Sorption + electron mediation + reactive site

Green Rust provides the electrons

Optimization of reactivity

- Biochar electrical conductivity
- Biochar reactive groups – capacity ("battery")
- Green rust – biochar connectivity
- Sorption properties
- Particle size
- Steric factors?

Biochar is not just biochar

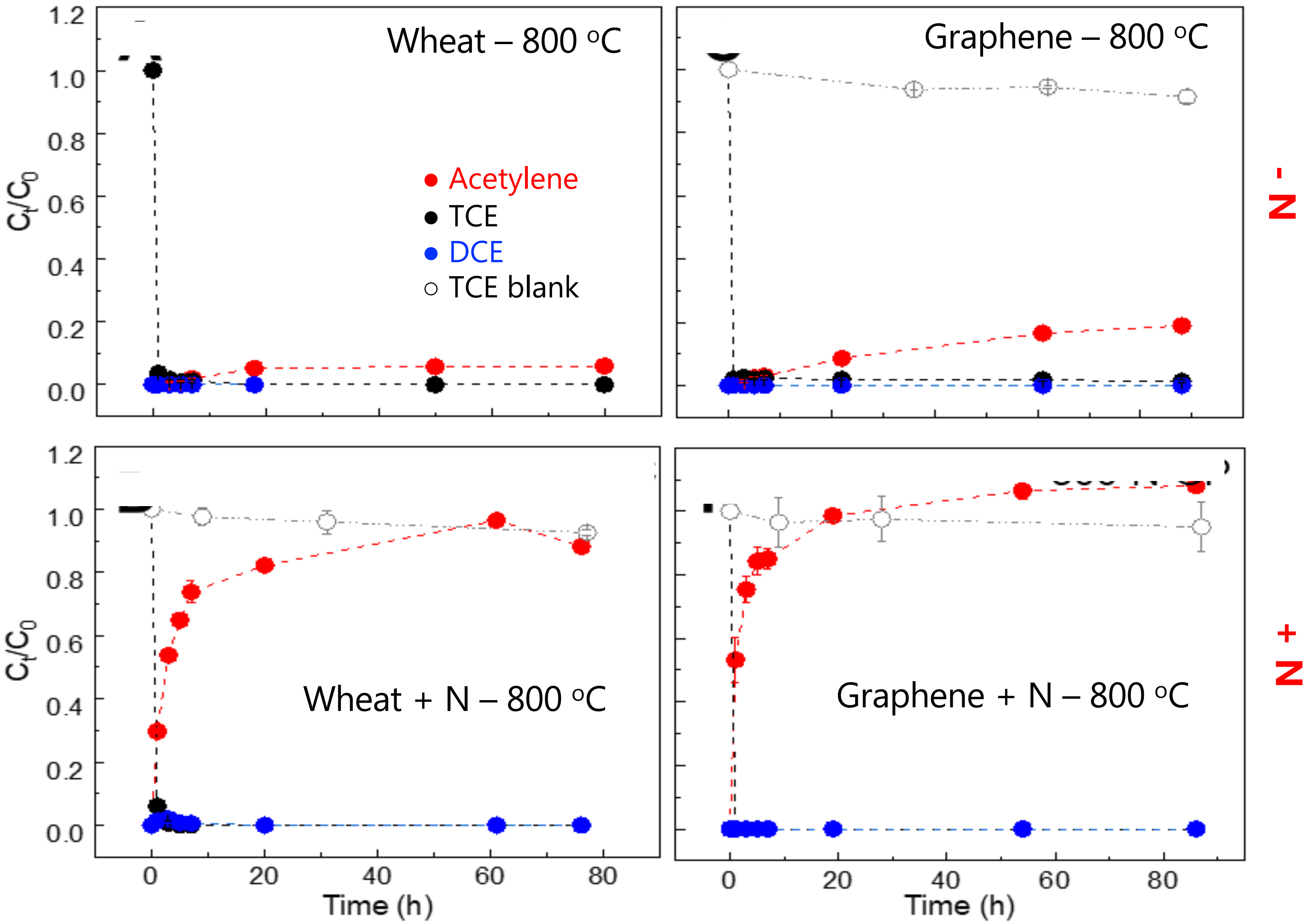


Reduction of TCE in GR-biochar/carbon systems (**FL, BC**: bone meal, **SHR**: shrimp, **ACV**: anchovy, **RYE**: rye, **SP**: algae, **BL**: blood, **SOY**: soybean, **SG1/2**: waste water sludges, **G**: graphite, **AC1, AC2**: activated carbon (PT 950 °C)

- The substrate is critical for the catalytic ativity. Nitrogen-rich substrates usually show highest reactivity.
- Reactivity increases with pyrolysis temperature up to 950 °C.
- Some biochars may lead to by-products such as DCE and VC.
- Activated carbon is inreactive

Jing Ai (2020)

Nitrogen boosts reactivity

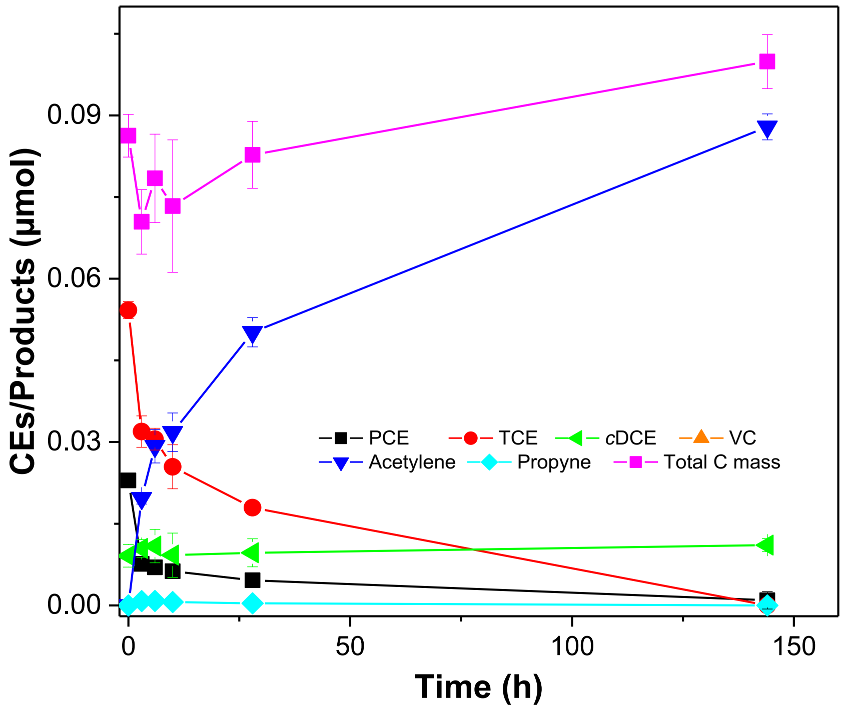


Reactivity of **wheat straw** (BC) and **graphene** (GP) pyrolysed at 800 °C without/with extra nitrogen (urea).

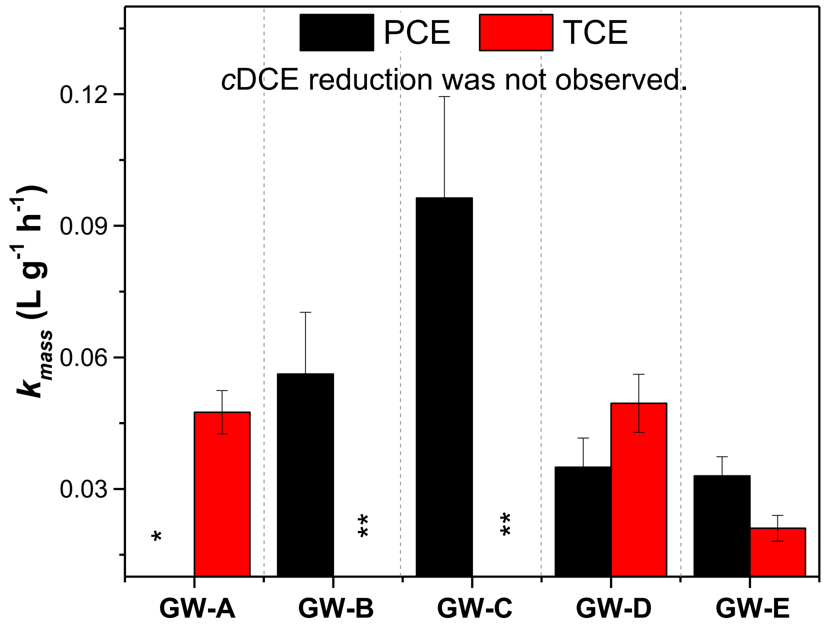
- Reactivity increases dramatically by N amendment
- TCE is rapidly adsorbed and subsequently reduced to acetylene
- Mystery: The N effect has nothing to do with N content!

Hui et al. (2022); unpublished

It works with contaminated groundwater



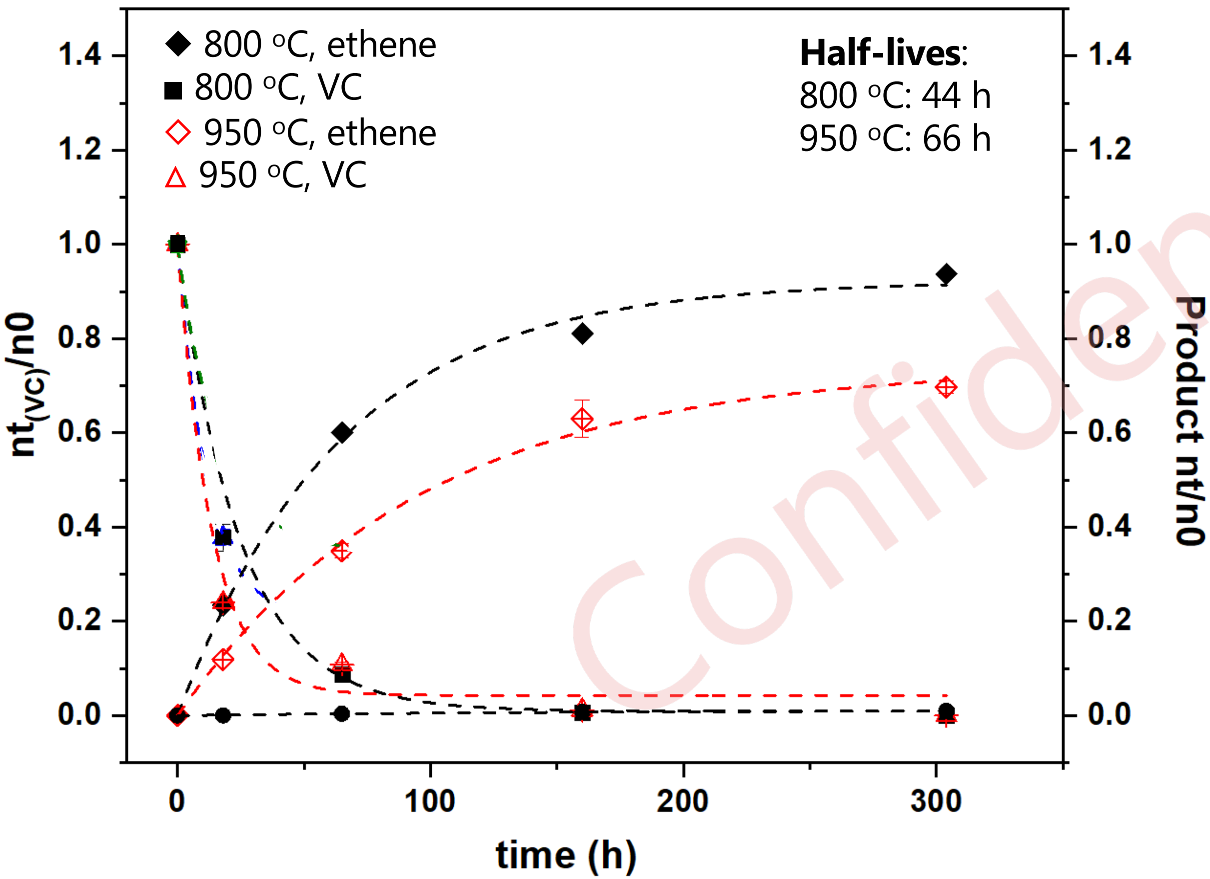
Reduction of PCE and TCE i groundwater from contaminated site, Naverland, Glostrup, Copenhagen



Ai *et al.* (2021)

- Rate constant for PCE and TCE reduction in 5 different contaminated groundwaters
- The rate constant is 10 – 20x slower in ground water compared with lab water experiments
- Bicarbonate (water hardness) the main inhibitor; tested waters have high water hardness

...it also degrades vinyl chloride



Reaction sequence:
PCE > TCE > DCE > VC

VC is the slowest to degrade, but biochar can also boost that reaction

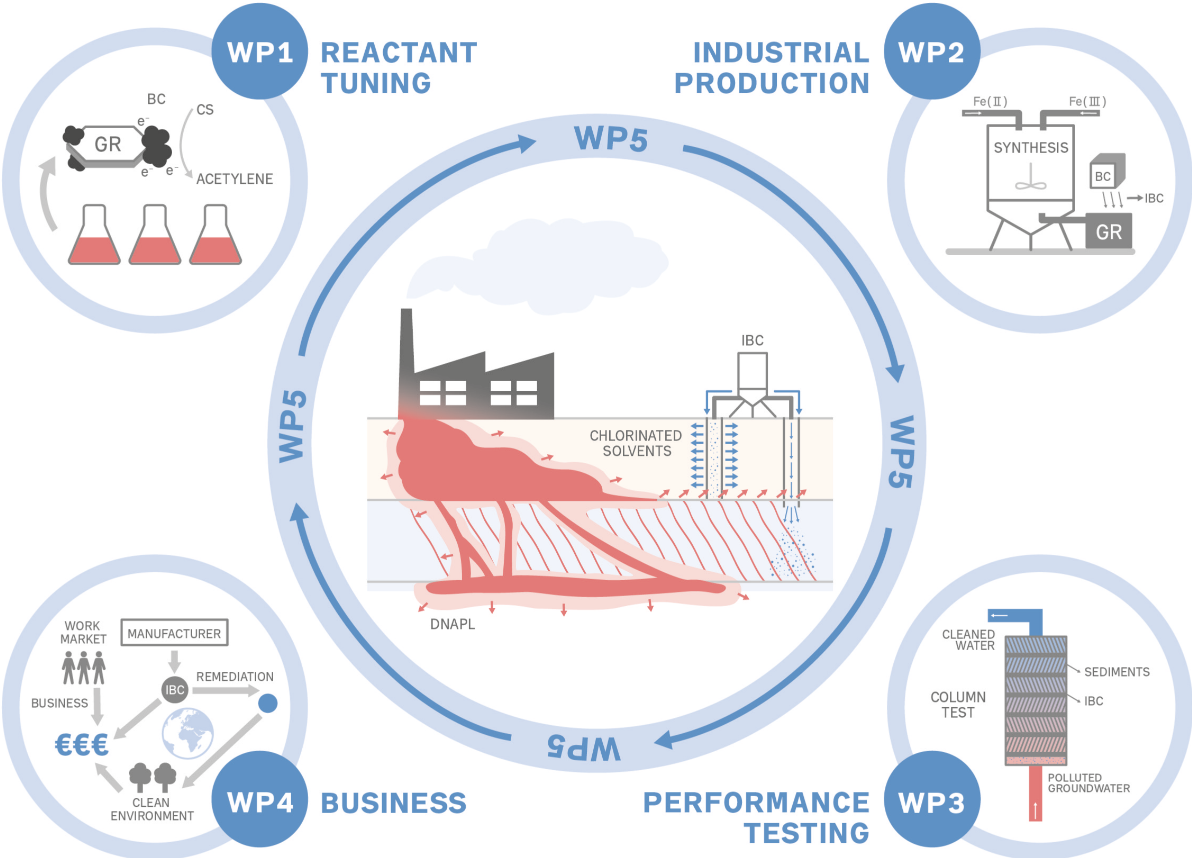
Nitrogen enriched sugar beet residue biochar

Product of VC reduction is ethene.

Hao, Y. (2022)

GreenCat – an Innovation Fund project

Greenrust-biochar for *in-situ*
remediation of chlorinated solvents - 2020 to 2024.



REGION H

GEUS

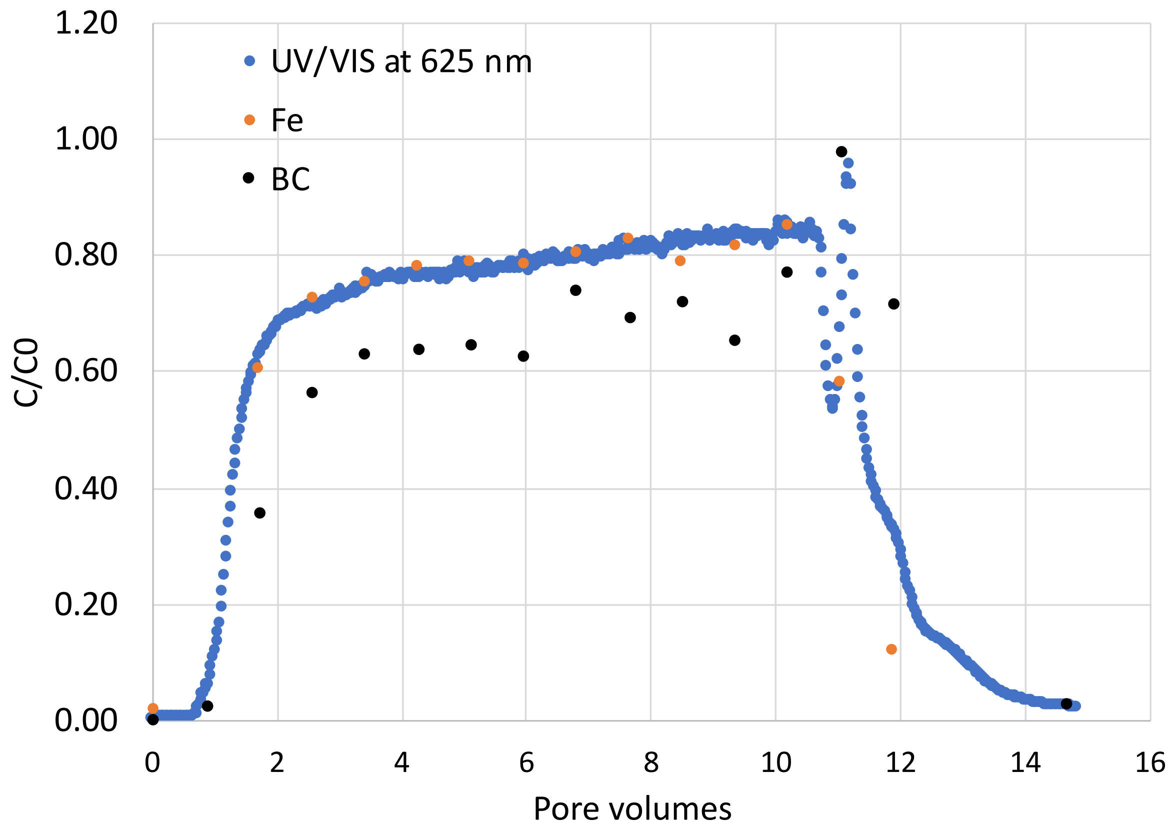
Geo SUBSURFACE EXPERTISE

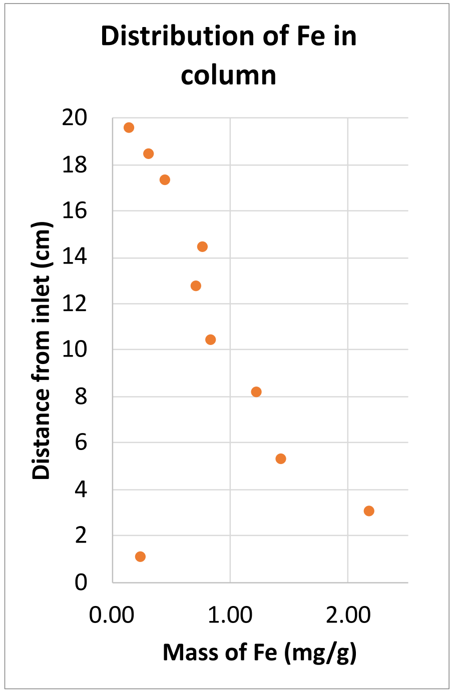
AMPHOS 21 SCIENTIFIC AND STRATEGIC ENVIRONMENTAL CONSULTING

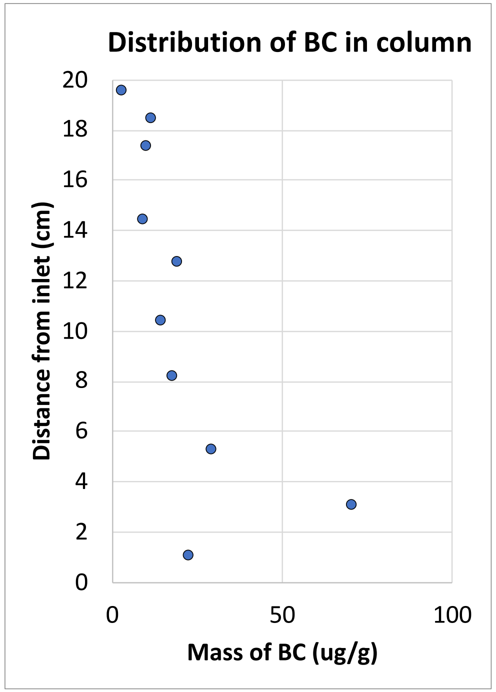
ALUMICHEM

UNIVERSITY OF COPENHAGEN

Greenrust + biochar transport in sand







2 g/L green rust, 0.15 g/L bonechar, passed 63 um screen
Average particle size 10 um
5 g/L Carboxymethylcellulose (CMC)
Dansand (0.5 mm), 2 mL/min

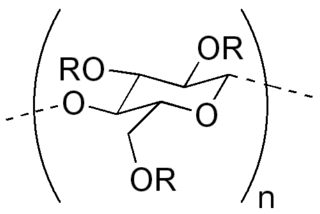
Conclusions

- Fast breakthrough
- Green rust + biochar moves together
- Deposition of the material in the column, but filtering as well

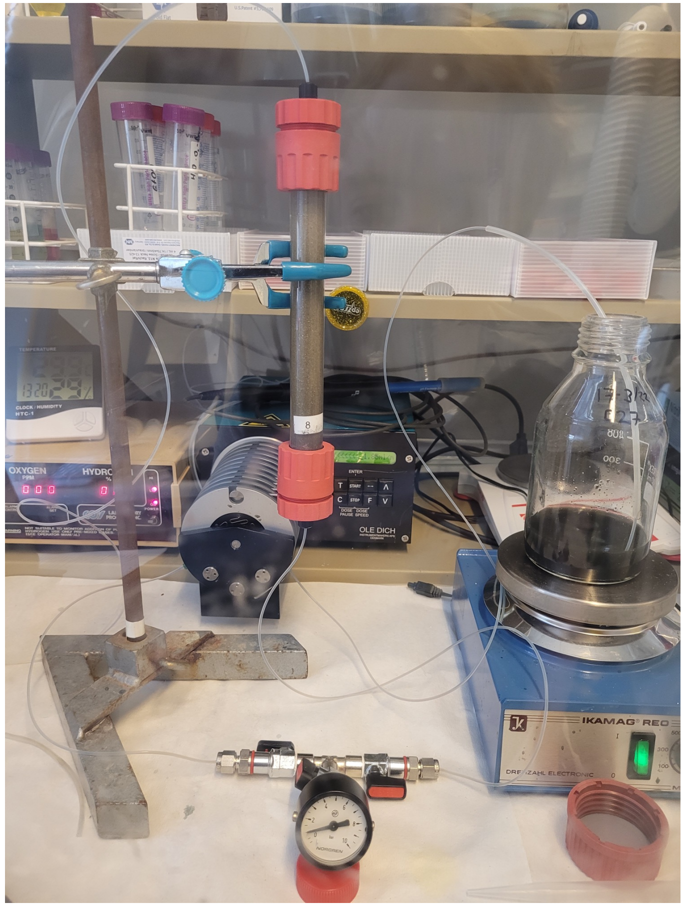
GEUS

A word on carboxymethylcellulose (CMC)

- Needed to make green rust + biochar particles mobile (keep particle aggregation low)
- CMC binds strongly to green rust
- CMC protects green rust from oxidation – easier handling and storage
- CMC also blocks for dehalogenation!
- CMC can be flushed away and dehalogenation reactivity restored



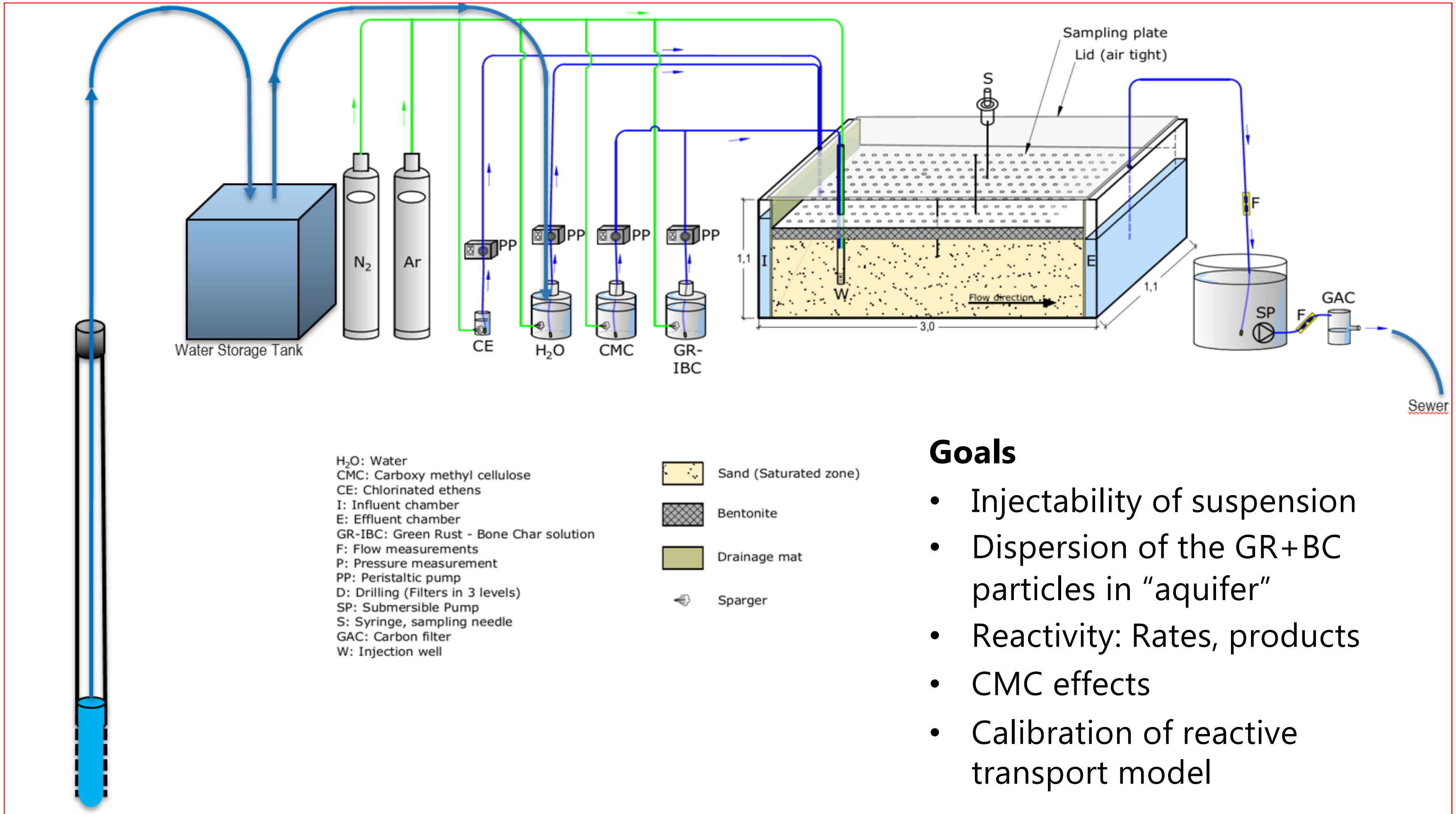
R = H or CH_2CO_2H



GEUS

Experimental aquifer experiment

- Simulate direct push injection -



Goals

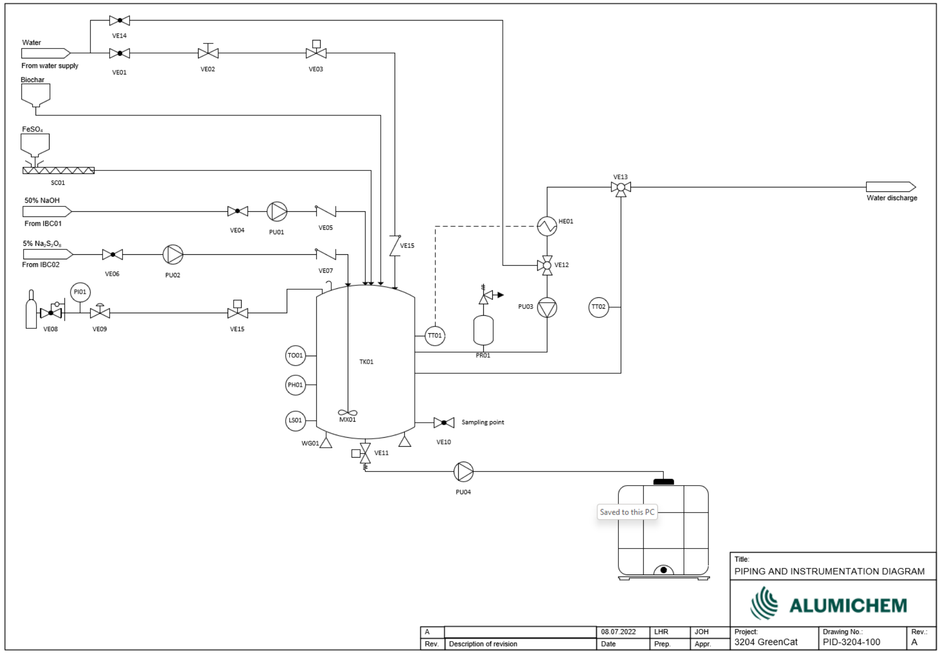
- Injectability of suspension
- Dispersion of the GR+BC particles in "aquifer"
- Reactivity: Rates, products
- CMC effects
- Calibration of reactive transport model

AlumiChem: New synthesis method + upscaling

- New method (Haldor-Topsoe) to enable upscaling
  Iron(II) sulphate precipitated with NaOH to produce $Fe(OH)_2$
  Oxidation by potassium persulfate → green rust
- Reactivity independent of when biochar is added!
- Final product has 15 g/L green rust and 0.7. g/L biochar
- Pilot plant ultimo 2022

Safety: Eye irritant.
Spills and disposal: Non-toxic

ALUMICHEM



GR + Biochar profile

- **Green**, sustainable remediation product; waste to value carbon-based catalyst
- **High reactivity** with all known chlorinated ethylenes incl. cDCE and VC; non-toxic products
- Biochar reactivity is **independent of sorption**
- **Not sensitive to temperature** (5 – 25 ^{o}C)
- **Specific reaction** - GreenCat product reacts specifically with the chlorinated ethylenes with no H_2 production. All redox capacity used for targetted compounds.
- **Long shelf-life** (at least 6 mths)
- **Longevity** - No corrosion shells or passive layers are forming on particle surfaces
- **Flexible design** - the composite can be tailored to target specific contaminant profiles
- **CMC triple function**: On/off switch, facilitates transport, microbial stimulant
- The GR component can be used for **remediation of other pollutants**: immobilisation/fixation/(reduction) of arsenate/arsenite, chromate, selenate/selenite, uranyl/neptunyl, reduction of nitrate and nitro-aromatic compounds.
- **Competitive price**

Publications

- Ai, J.; Yin, W.; Hansen, H.C.B. (2019) Fast dechlorination of chlorinated ethylenes by green rust in the presence of bone char. *Environ. Sci. Technol. Lett.* **6**, 191 - 196.
- Ai, J.; Ma, H.; Tobler, D.J.; Mangayayam, M.C.; Lu, C.; van den Berg, F., Yin, W.; Hansen, H.C.B. (2020) Bone char mediated dechlorination of trichloroethylene by green rust. *Environ. Sci. Technol.* 54, 3643 – 3652.
- Ai, J.; Lu, C.; van den Berg, F.W.J.; Yin, W.; Strobel, B.W.; Hansen, H.C.B. (2021) Biochar catalyzed dechlorination – Which biochar properties matter? *J. Hazard. Mater.* 406: 124724.
- Ai, J.; Tobler, D.J.; Duncan-Jones, C.G.; Manniche, M.E.; Andersson, K.E.; Hansen, H.C.B. (2021) Chlorinated solvent degradation in groundwater by green rust-bone char composite: solute interactions and chlorinated ethylene competition. *Environ. Sci: Water Res. Technol.*: d1ew00484k.
- Ma, H.; Ai, Jing; Lu, C.; Hansen, H.C.B. (2022) Enhancement of biochar catalysis by chemical amendments for trichloroethylene dechlorination. *Chem. Engin. J.* 438:132496
- Ai, J.; Hansen, H.C.B.; Dideriksen, K.; Tobler, D.J. (2022) Fine-tuning green rust-bone char composite synthesis for efficient chlorinated ethylene remediation. *Chem. Engin. J. 446:* 136770