Porous hydrochars from hydrothermal carbonization of biomasses for soil improvement

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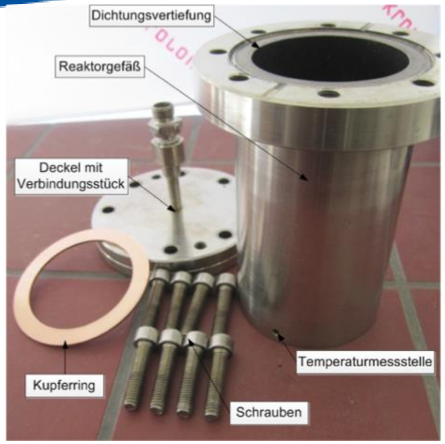
Process of hydrothermal carbonizarion



Biomass + Water → HTC process → Hydro-char + Gas + Liquid phase + Heat

→

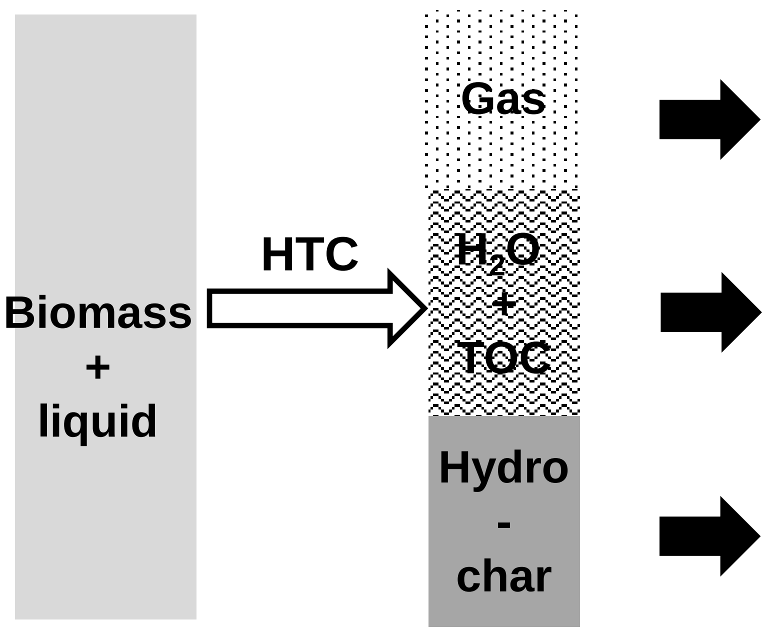
T about 200 ° C
p ca. 20 bar

1 h 3 h 6 h

Fotos: J. Pfingstmann

HTC products

- transformation of biomasses and **wet substrates** into biochar
- heating of biomass in aqueous suspensions to **180 – 250 °C** under elevated pressure
- chars with **high amount of functional groups** and small surface area (< 10 m^2/g)



mainly CO_2; some CH_4 and CO; traces of H_2 and C_nH_m

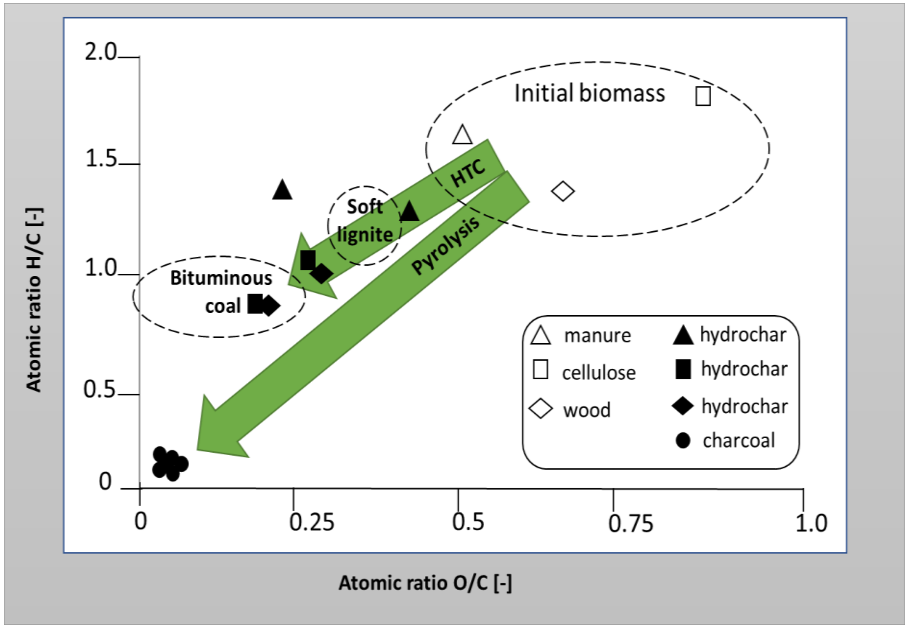
sugar and derivates; organic acids; furanoid and phenolic compounds

lignite-like chars

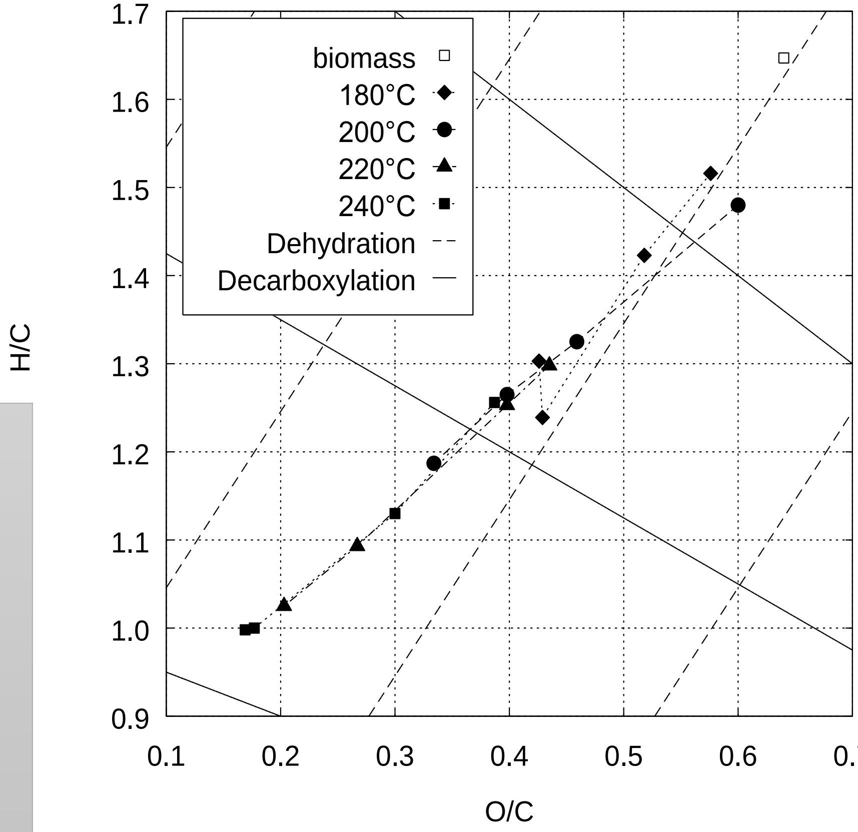
HTC vs. Pyrolysis

- Pyrolysis takes place at temperatures > 300 °C
  - lower H/C ratio
  - high aromatic content

- HTC takes place under pressure (~ 20 bar) and moderate temperature (~ 200 °C)
  - higher O/C ratio
  - high functionality



HTC of landscape management biomass



M. Röhrdanz, T. Rebling, J. Ohlert, J. Jasper, T. Greve, R. Buchwald, P. von Frieling, M. Wark,
Journal of Environmental Management 173 (2016), 72-78,
"Hydrothermal carbonization of biomass from landscape management - Influence of process parameters on soil properties of hydrochars"

HTC – Possibilities and challenges

Biomass + Water → HTC process → Hydro-char + Gas + Liquid phase + Heat

Grass, leafs, maize silage, etc.

Digestate

Manure

Electrode material, Catalyst support

Additive for Bio-Polymers

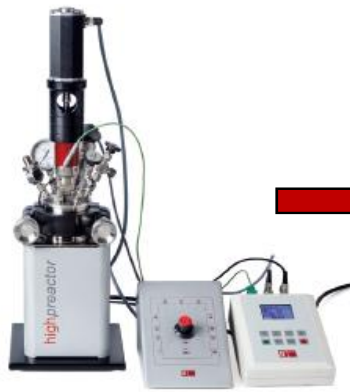
Porous materiai/ adsorbens, filter

Peat substitute/ Soil improvement

<u>Process water treatment</u>

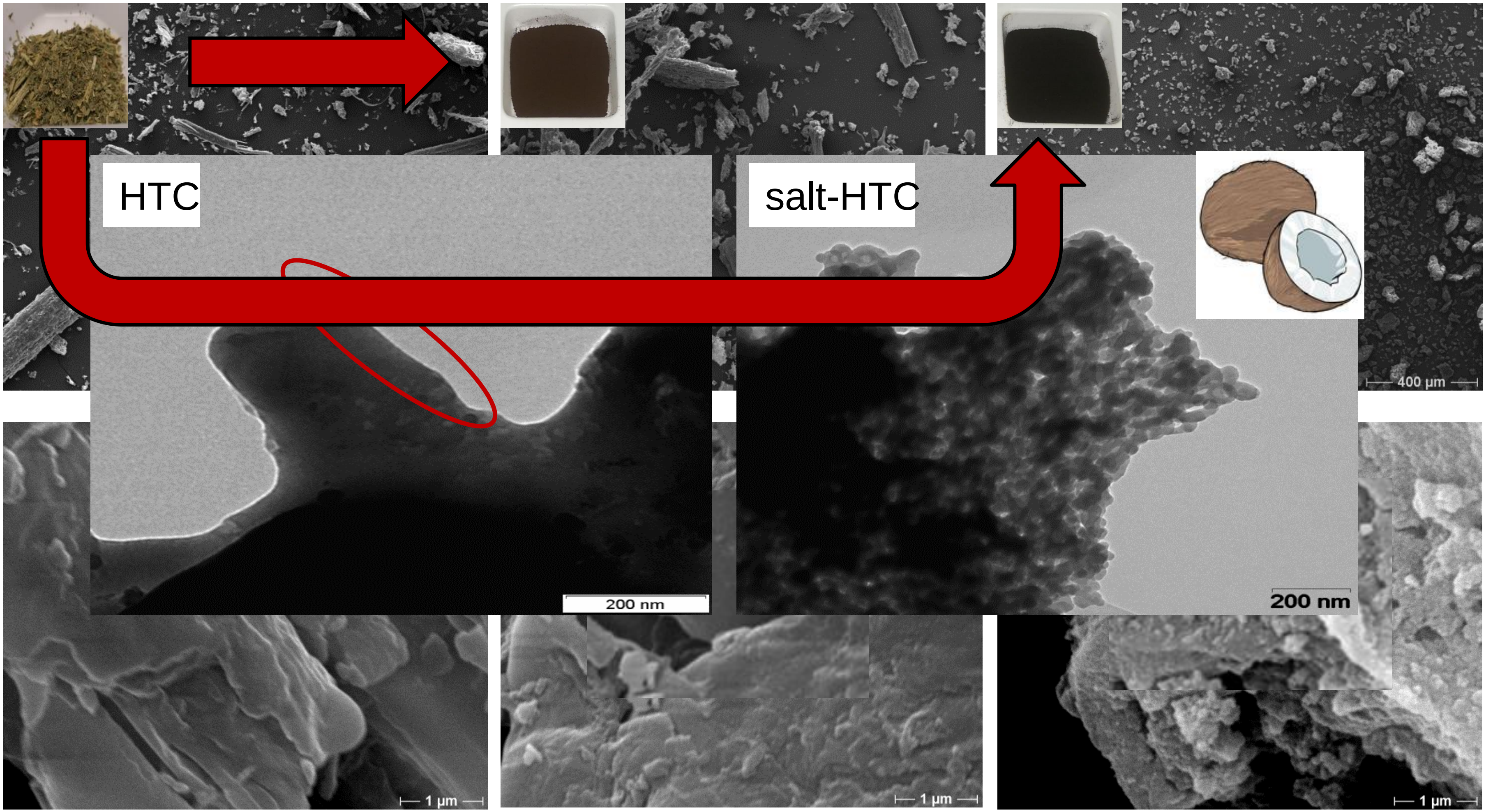
- Analysis,
- Recirculation,
- Use in Biogas plants
- Use as fertilizer
- Feeding of algae
- Photocatalytic degradation

HTC with salt additives

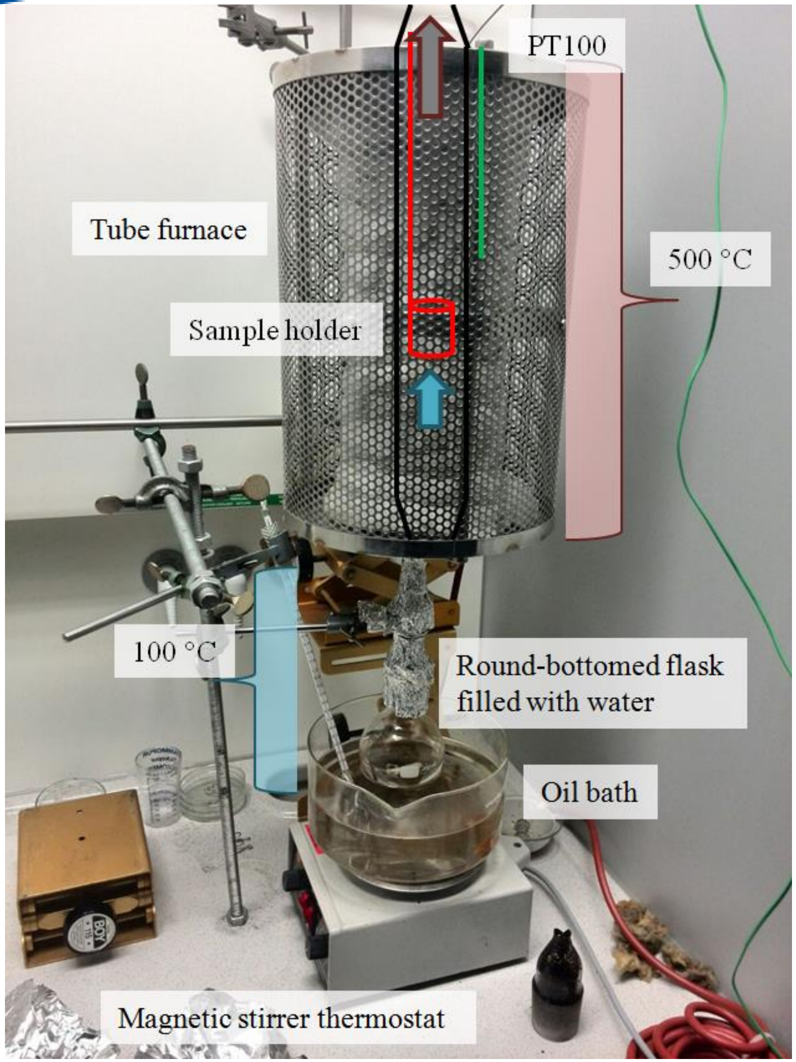
Biomass, water, additive	HTC	Processing	Hydrochars
			
Glucose, HMF, Cellulose, Lignin, Grasses, Coconut shell, Rice husks, Dandelion leaves, Algae, Sawdust LiCl, NaCl, KCl, $ZnCl_2$, $MgCl_2$, Na_2SO_4, Na_2CO_3, ...	180-220 °C 4-36 h 200-2000 mL	Washing, drying, milling	EA, SEM/TEM, XRD, SS-MAS-NMR, FTIR, XPS, gas sorption, TGA, ...

Influence of additives on the morphology

Biomass (grass mixture) | Hydrochar | Salt-Hydrochar

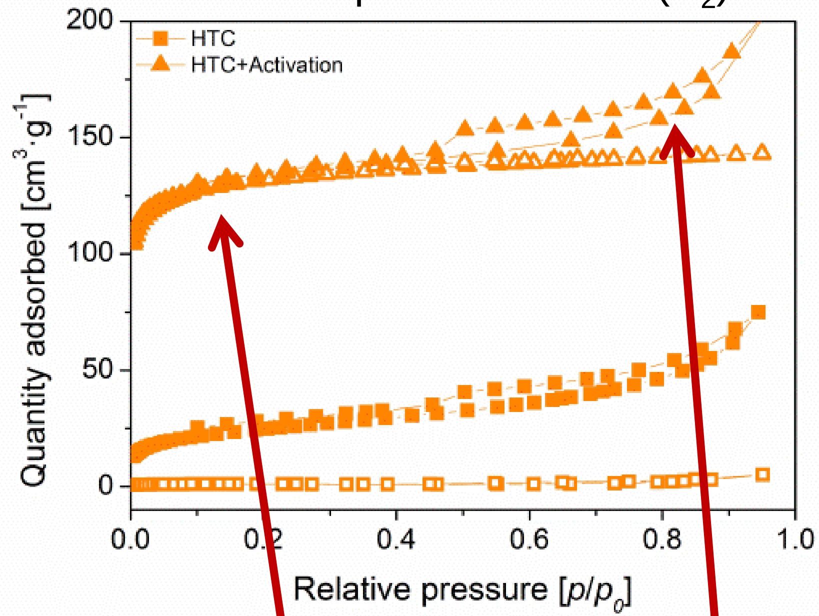


Increased porosity by steam activation



- Sample in crucible
- Tube furnace (e.g. 500 ° C)
- Water vapor flows through the oven
- Yield: 20-30%

Sorption isotherms (N_2)



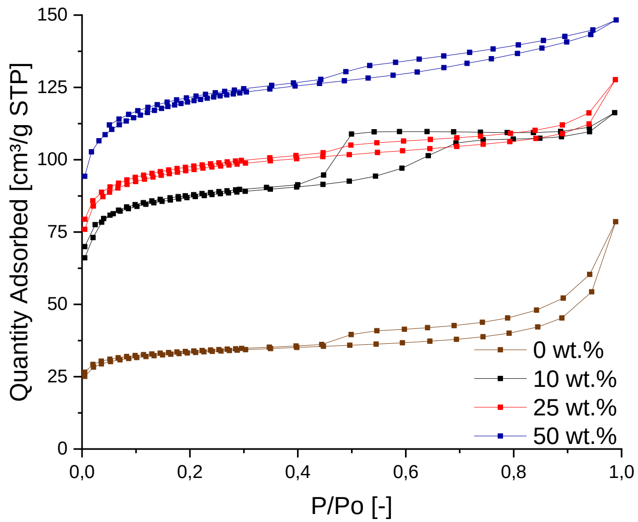
HTC, steam activated: microporous
Salt-HTC, steam act.: micro- and mesoporous

Mixtures of pig manure and coconut shell

Biomass [-]	Reaction time [h]	Amount of Coconut shell [wt.%]	Surface area [m²/g]
Manure	1	0	143
		10	294
		25	401
		50	364
Manure	4	0	125
		10	335
		25	365
		50	454

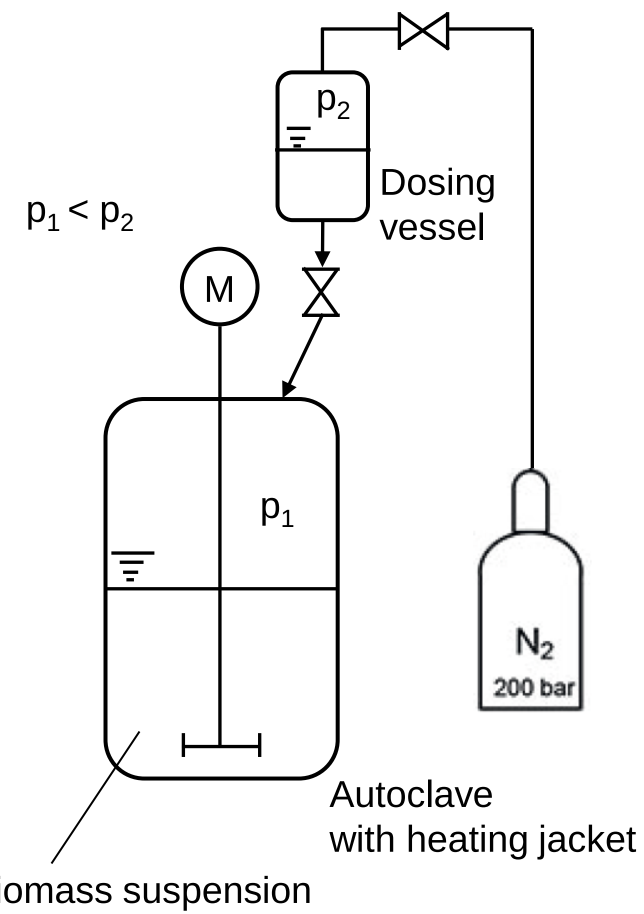
- Hydrochars from mixtures of soft and hard biomass:
  - Higher surface areas (N_2 sorption) than hydrochars from HTC of pure pig manure
  - Comparable properties to hydrochars obtained with salts as additives

4 h ; 220 °C



HTC in presence of bases and/or acids

Addition of solutions during HTC



- Making use of sand (SiO_2 source) – being present in the biomass – for creating porosity (as hard template)
- HTC under alkaline and acidic conditions via addition of NaOH and H_2SO_4

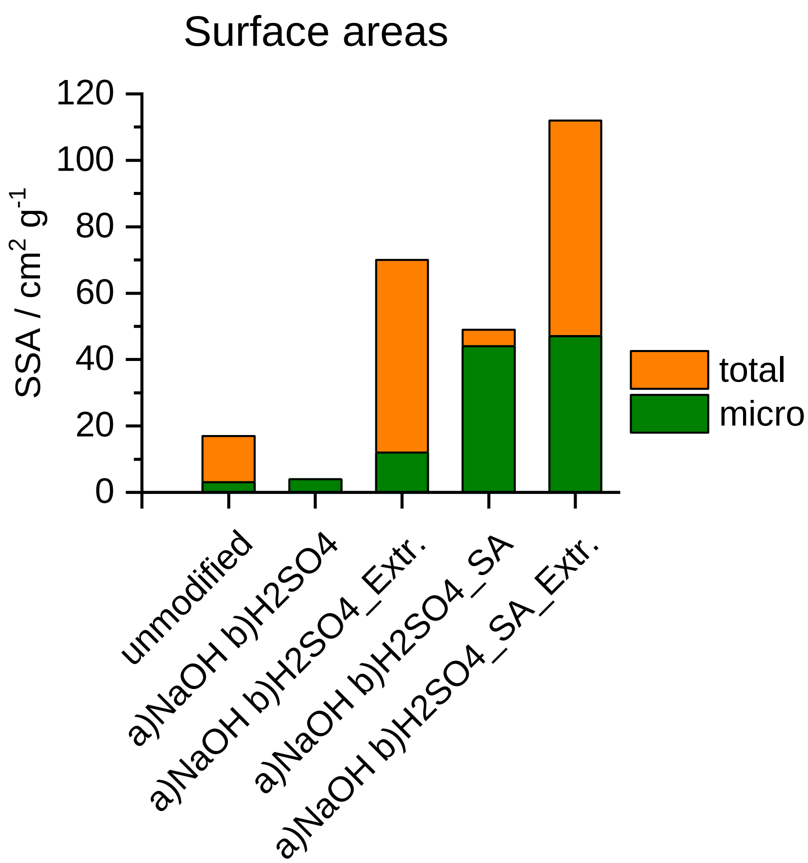
→ Alkaline and acidic one-pot HTC

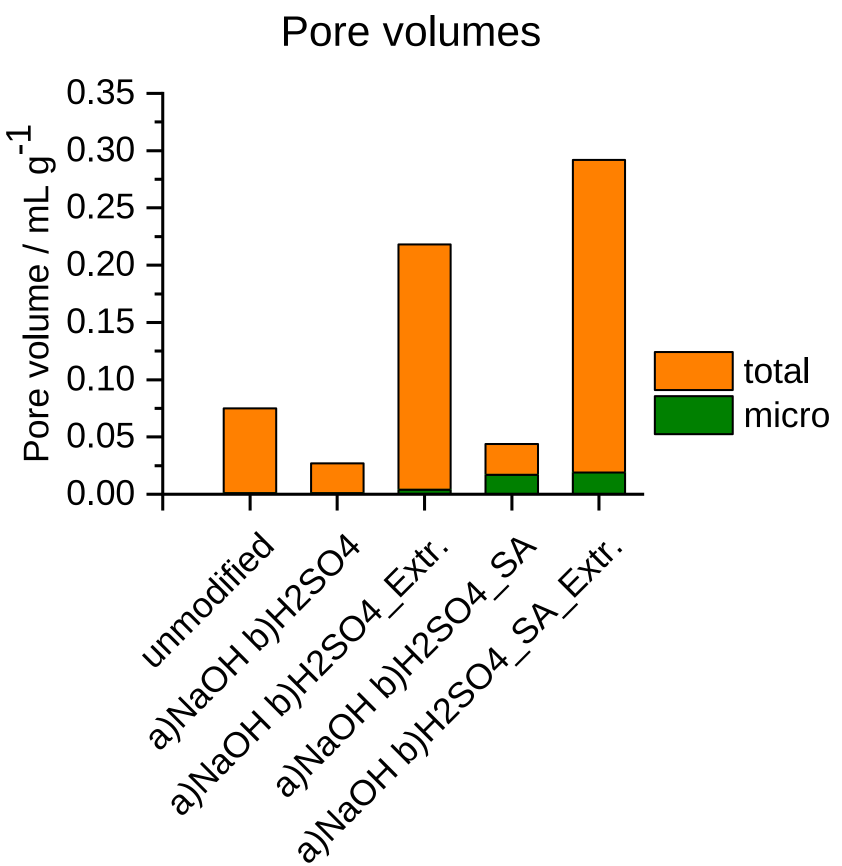
Experiments

Abbreviation	Discription
SA	Subsequent Steam activation, 650 °C, 1h
Extr.	Subsequent Suspension in 0.5 M NaOH solution overnight
NaOH	HTC in 1 M NaOH
H_2SO_4	HTC in 0.5 M H_2SO_4
a) NaOH b)H_2SO_4	HTC in 1 M NaOH, addition of 1 equiv. H_2SO_4 after 9.5 h, cooling down after 12 h

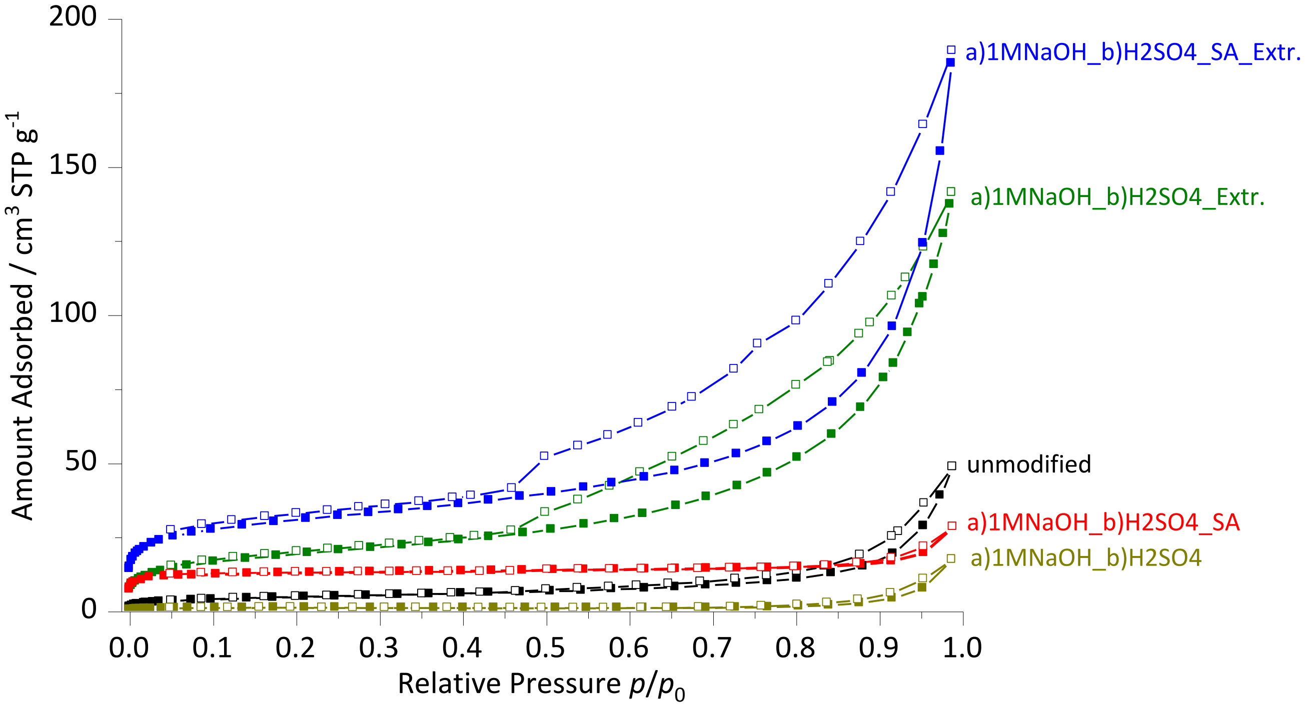
HTC of digestates with base/acid

Use of fermentation residues from a biogas plant (provided by Heidekreis)





HTC of digestates with base/acid



Sample	*SSA*$_{total}$ / m^2 g^{-1}	*SSA*$_{micro}$ / m^2 g^{-1}
Unmodified	17	3
a) NaOH, b) H_2SO_4	4	4
a) NaOH, b) H_2SO_4_Extr.	70	12
a) NaOH, b) H_2SO_4_SA	49	44
a) NaOH, b) H_2SO_4_SA_Extr.	112	47

HTC hydrochar for soil improvement and plant growth

- Commercial hydrochar from Grenol
- Three hydrochar grain sizes: coarse (2 – 6.3 mm), medium (630 µm – 2 mm), fine (< 630 µm)

- Three soil types - Chernozem (silty), Podzol (sandy) and Gleysol (clayey)
- 5% hydrochar addition (based on extensive literature review)
- Pot experiments

Seed Germination:

- **No seed germination inhibition** by pure soil
- No need for mixing with e.g. compost, as typically required

Chernozem

58%

Podzol

76%

Gleysol

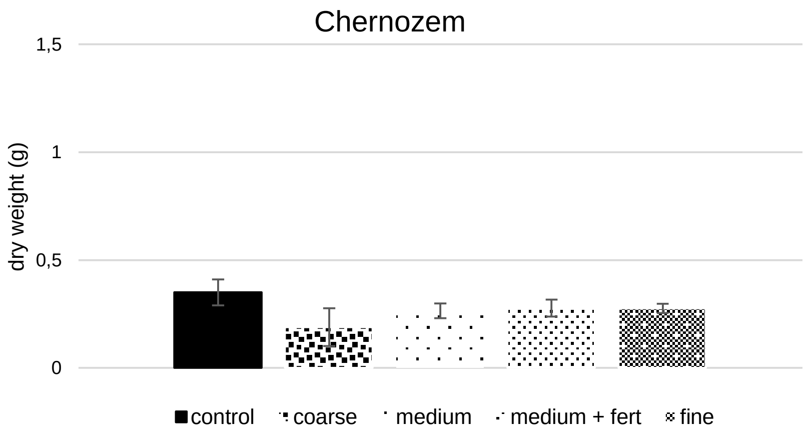
56%

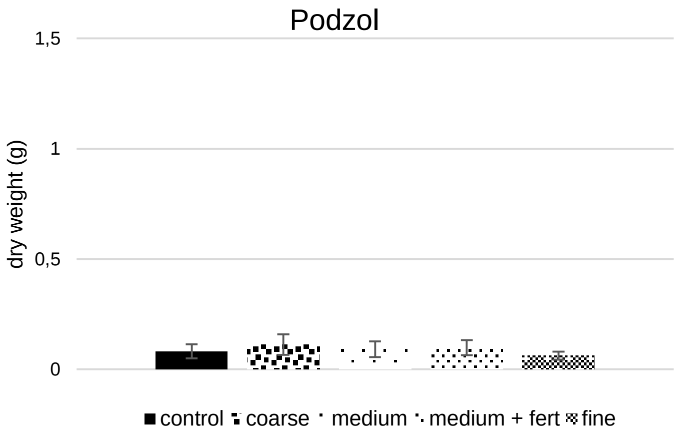
given are the percentages of seeds, which germinated

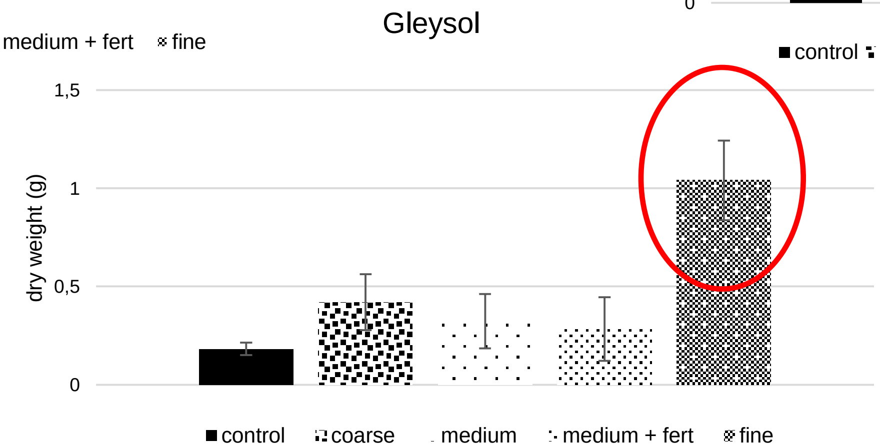
HTC hydrochar for soil improvement and plant growth

Biomass Production:

- Only significant soil with difference in dry weight of the grown plants in the fine grained Gleysol.
- No evident influence of additional fertiliser for all soils, potentially due to:
  - Leaching of fertiliser from soils with watering,
  - Already adequate condition of the agricultural soils by farmers.





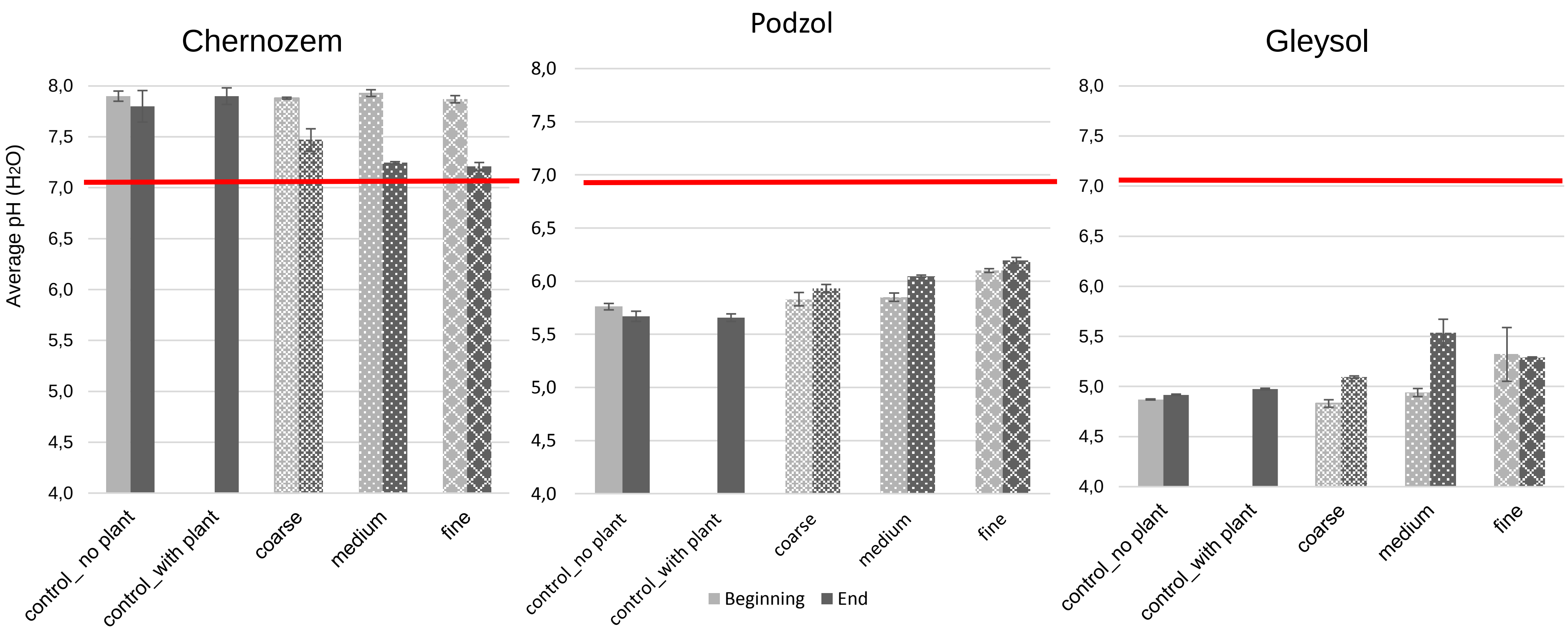


HTC hydrochar – Influence on pH of soil

Result is dependent on pH of hydrochar and soils.

- pH of the soils changed shortly after application of the hydrochar.
    - i.e. decreased in Chernozem and increased for Podzol and Gleysol.
- Most pronounced in finer grain size.
- pH of the soils compensated for the pH of the hydrochar (red line).

pH of digestate hydrochar: 7.2



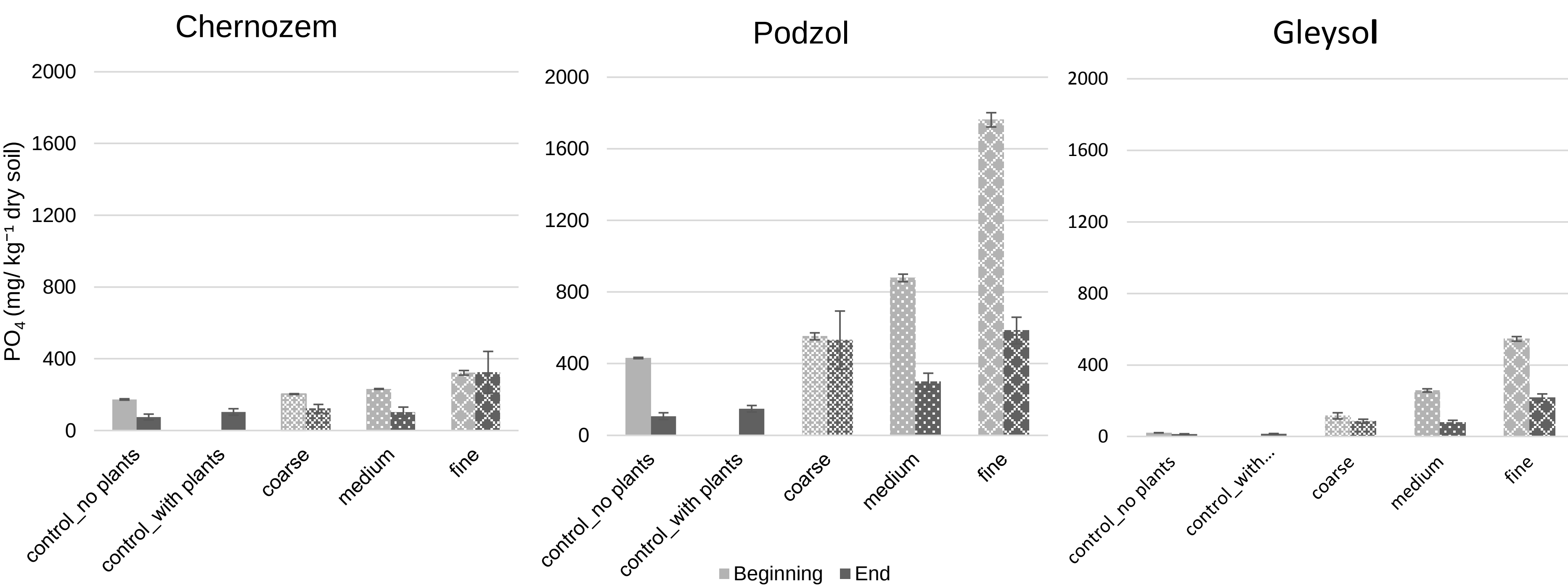
- *Beginning*: ~ a few weeks after application of hydrochar
- *End*: ~ after 3 months of plant growth

HTC hydrochar – Influence of PO_4^{3-} in soil

Phosphate (PO_4^{3-})

PO_4^{3-} of digestate hydrochar: 2034.60 (mg/kg)

- Initial increase with hydrochar addition, particularly in finer grained treatments.
- Hydrochar – high PO_4^{3-} content – direct contribution to soils.
- Increased mineralisation of finer hydrochar.
- Decrease in PO_4^{3-} content at end of experiment – uptake by plants and incorporation into microbial biomass.
- **Similar trend** occurred for other nutrients, **potassium (K^+) and N_{min}**

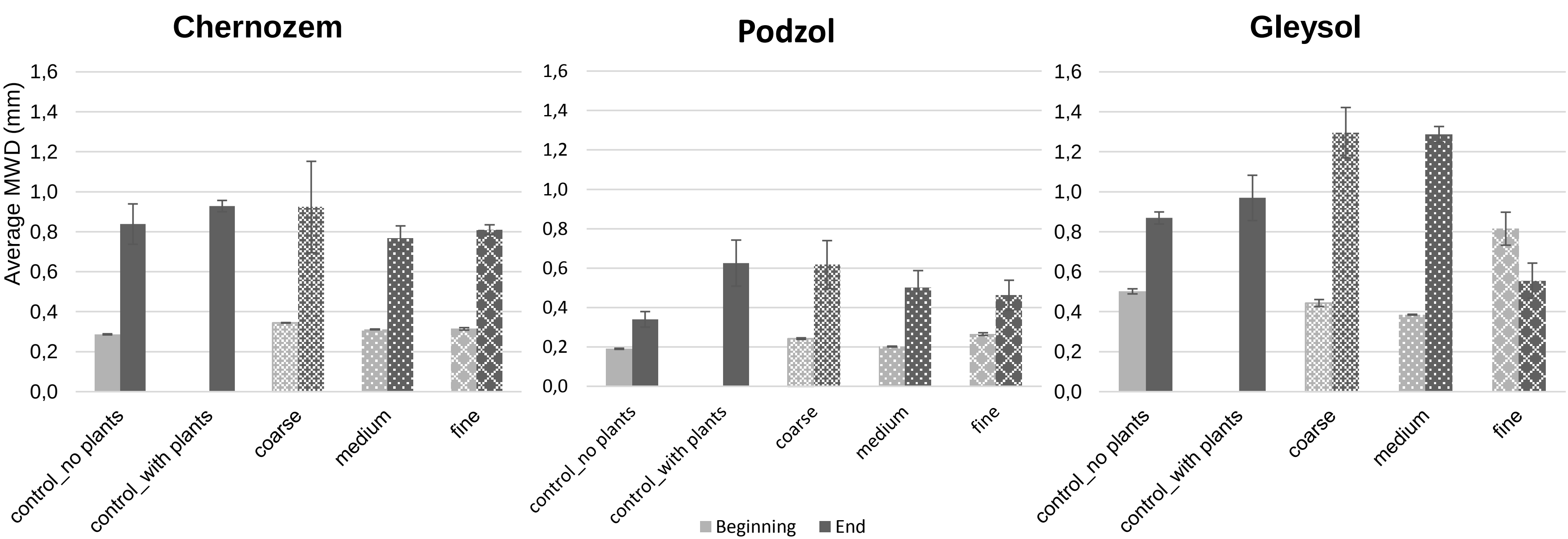


- *Beginning*: ~ a few weeks after application of hydrochar
- *End*: ~ after 3 months of plant growth

Hydrochar – Influence on water aggregates

Water Aggregate Stability

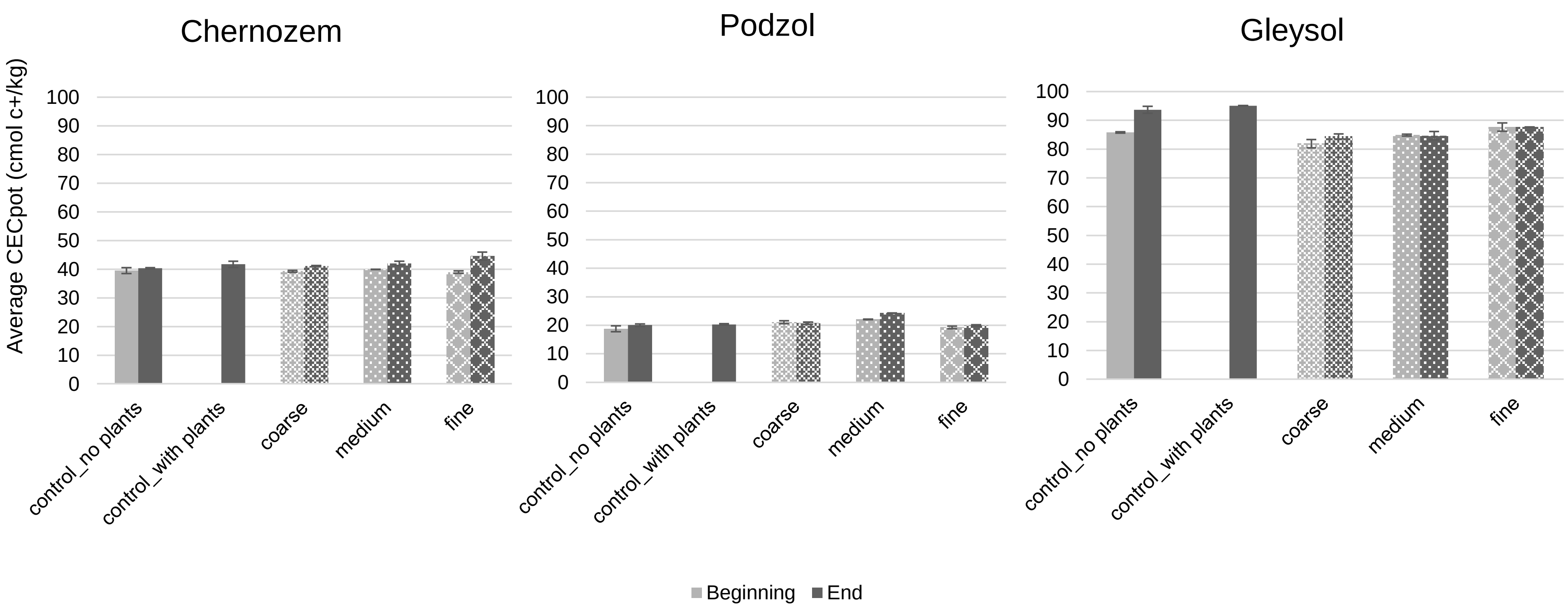
- At the beginning, hydrochar addition had little impact on stability (similar to controls).
- With time, aggregate stability increased substantially for all soils for all treatments, as well as controls.
- Exception of Gleysol fine grained treatment – decreased stability at end of experiment.



- *Beginning*: ~ a few weeks after application of hydrochar
- *End*: ~ after 3 months of plant growth

Cation Exchange Capacity

- Relatively little impact by hydrochar addition.
- Slight increase over time for all soils and treatments, incl. controls.
- Most improved - fine grained Chernozem (14 % increase).



- *Beginning*: ~ a few weeks after application of hydrochar
- *End*: ~ after 3 months of plant growth

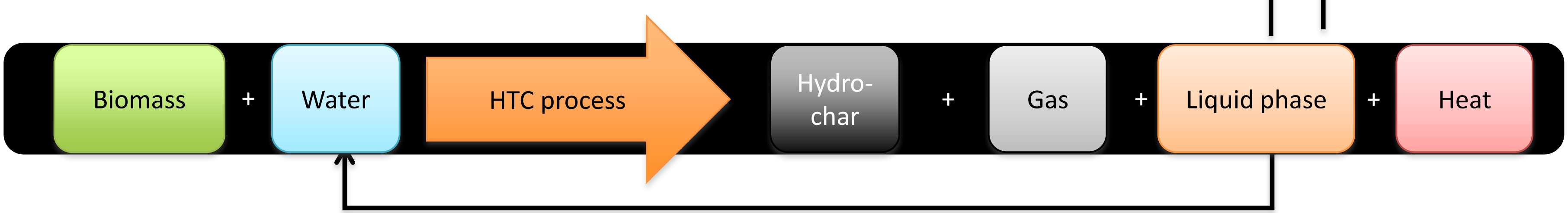
Cleaning of the HTC water phase

- Direct from HTC process:
  Chemical oxygen demand (COD): 10 – 70 g/l
- Required: COD < 1 g/l
- Solution: extraction of valued products,
  degradation of organics?

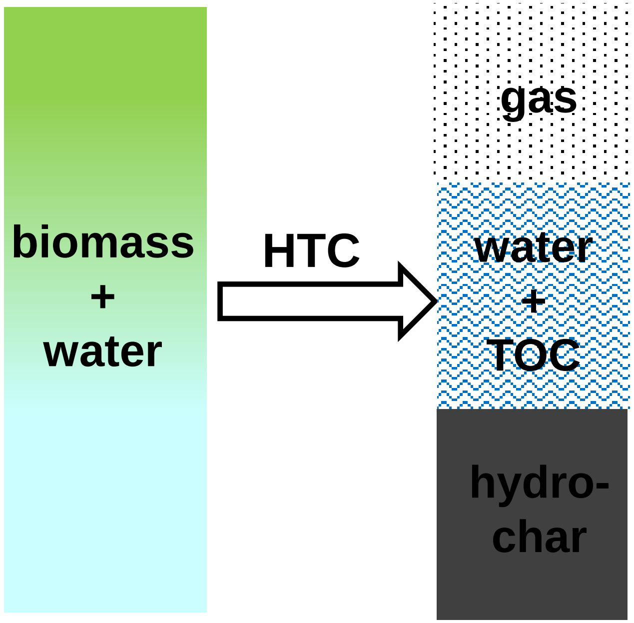
Extraction of chemicals, , e.g. 5-HMF, phenols

Water	200°C 15 min	200°C 60 min

Make-up:
By chemistry? physics? biology?



Phases in HTC



mainly CO_2;
some CH_4 und CO;
traces of H_2

Total organic content (TOC):
sugars- and derivatives;
organic acids;
phenols….

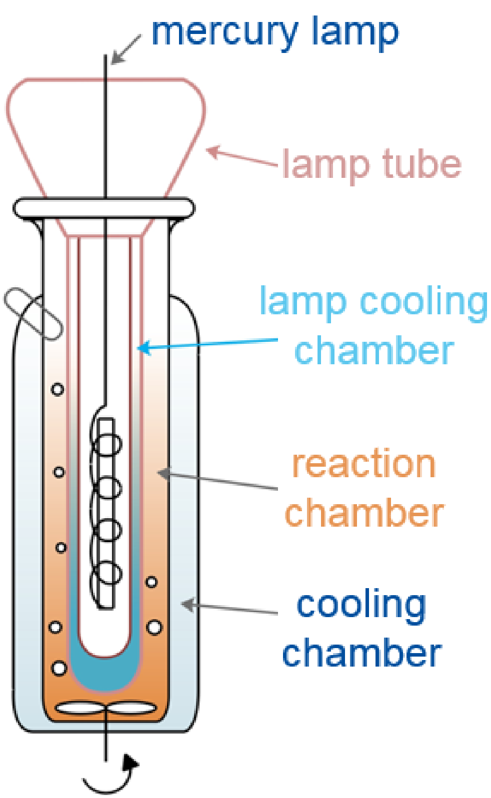
polymerized
hydrocarbons

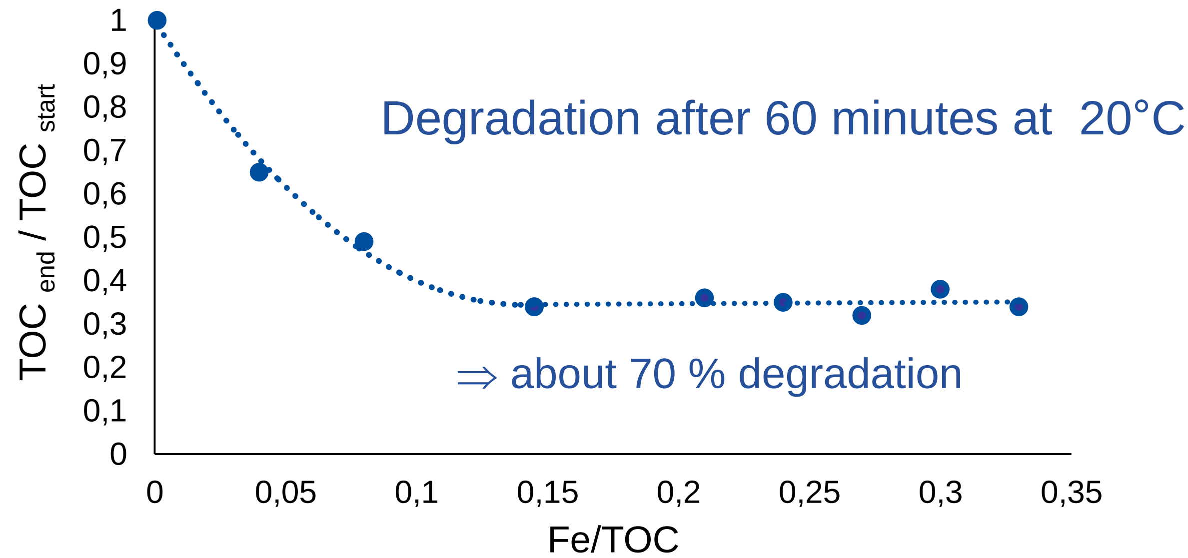
Main research
→ Qualitative and quantitative analysis of the aqueous HTC process water

Main aims
→ Reduction of TOC
→ Getting information about it‘s composition

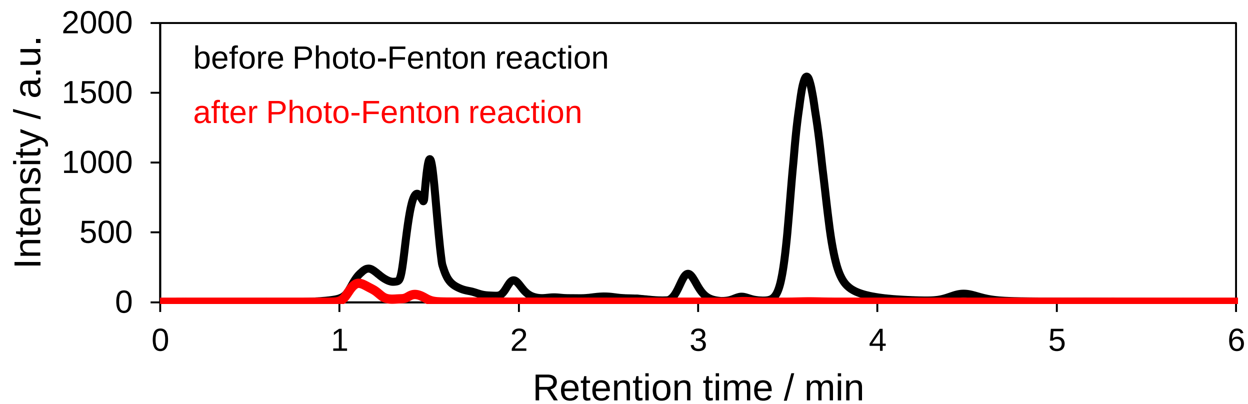
Degradation of the organic compounds: Photo-Fenton reaction

700 mL Volumen





Gas chromatography analysis

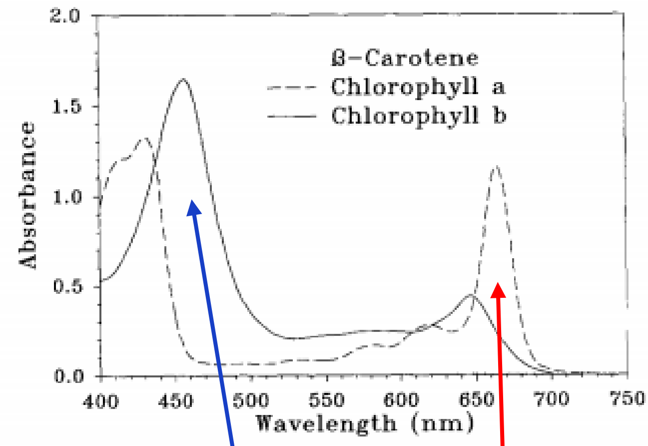


Reagents:

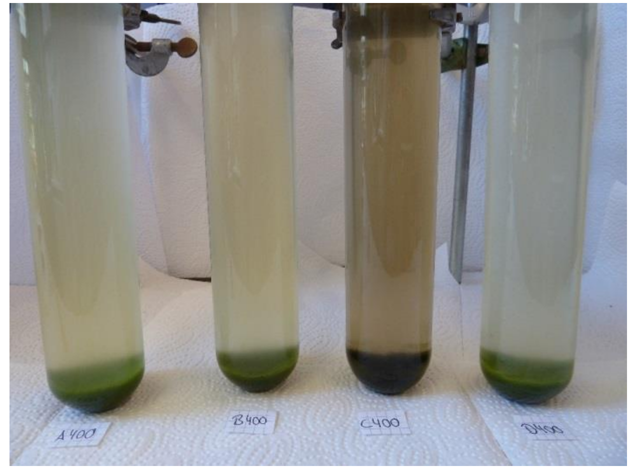
- HTC water phase
- Fe(II) salt
- H_2O_2

- peak areas decrease by about 95%,
- some compounds are not UV active ⇒ not detectable

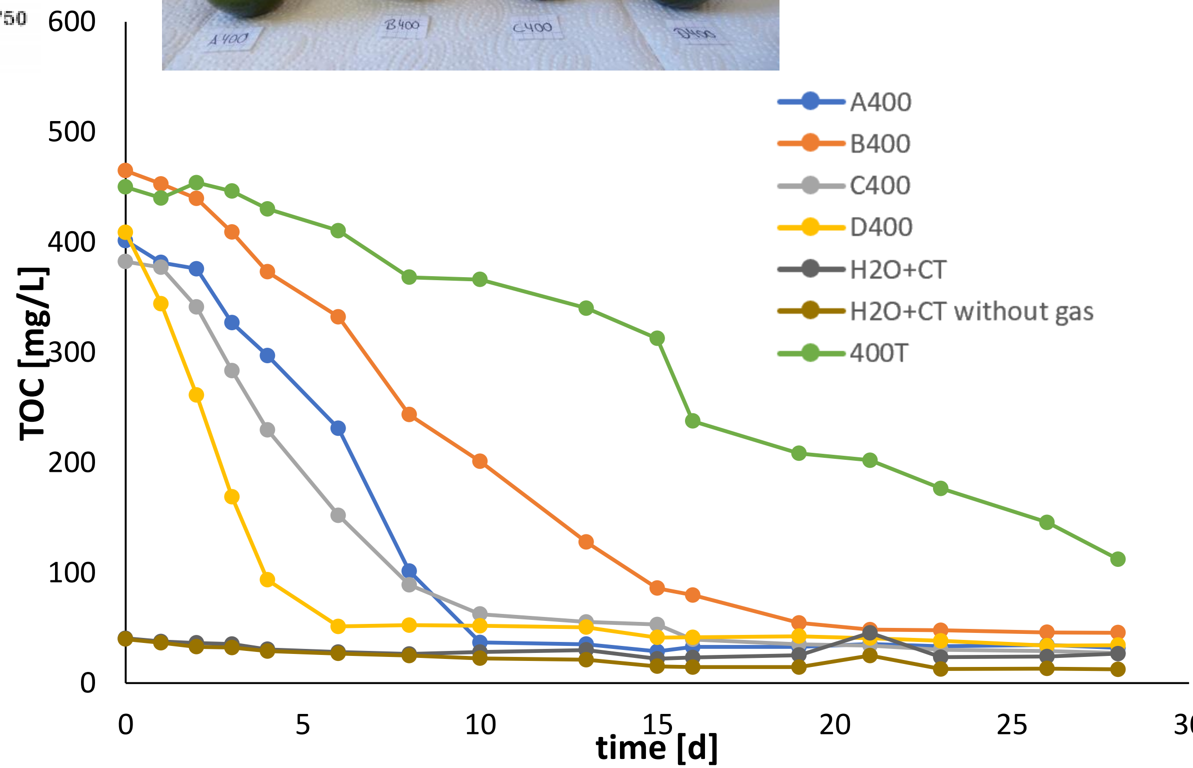
Degradation of the organic phase by algae



LED	blue	green	red
λ [nm]	467-470	570-575	620-625
Status	max	off	max



A	insoluble in hexane
B	non-polar
C	aromatics
D	NSO compounds

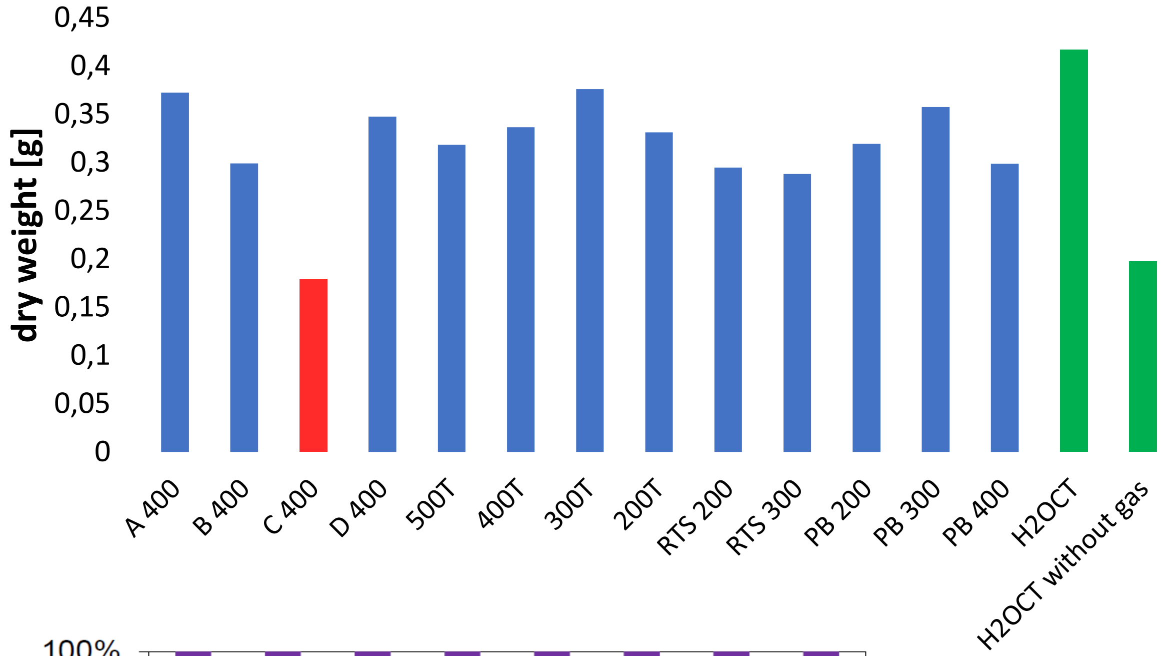


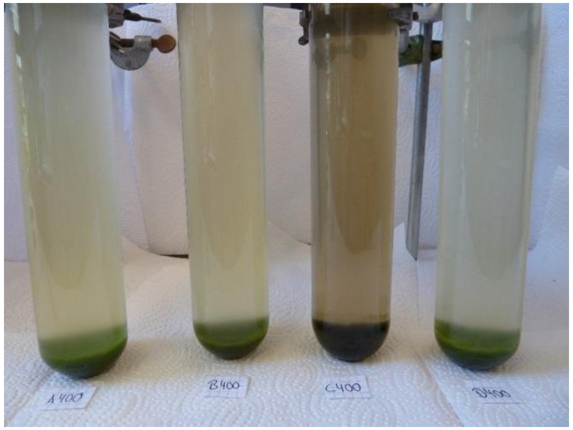
Degradation of the organic phase by algae

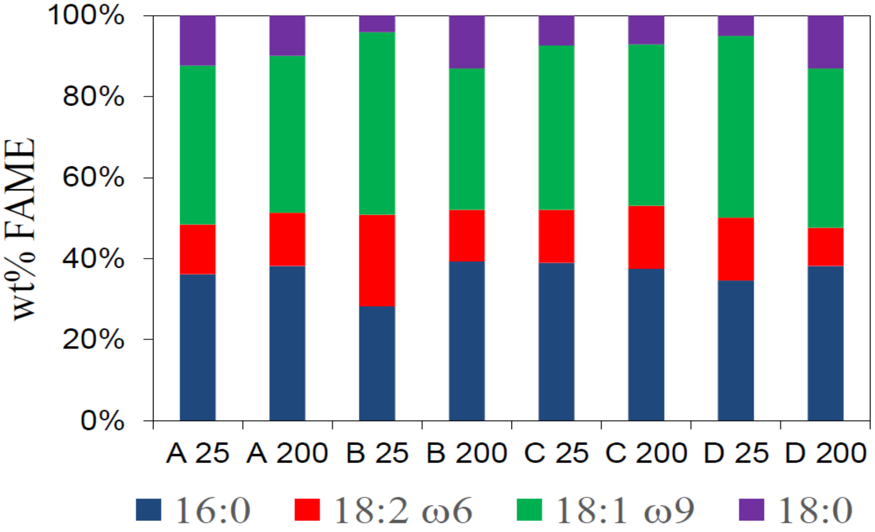
Dry mass of the grown algae

Organic phases for feeding the algae:

A	insoluble in hexane
B	non-polar
C	aromatics
D	NSO compounds
T	terephthalic acid
RTS	pig manure
PB	cattle manure







Composition of the formed fatty acids

Summary

- Hydrothermal Carbonization leads to hydrochars with more chemical functionality (functional groups for interaction with other species) than biochar from pyrolysis.
- HTC hydrochars are peat or brown coal (lignite) like.
- HTC hydrochars show a potential for applications as „green activated carbons“ (adsorption of gases, dyes, herbicides, pesticides, etc.), filter materials, catalyst supports, …
- Tailored mixtures of soft and hard biomasses can create porosity / inner surface without use of additives after activation with steam. Lignin structures act possibly as internal templating agent. However, the chemical functionality is partly lost due to the treatment with steam.
- Addition of hydrochar (digestate feedstock) to soil was shown to release nutrients (P (PO_4^{3-}), K^+ and N_{min}) resulting in a trend to increase the CEC (only slightly), and influence soil pH.
- The water aggregate stability increased with hydrochar addition for all the soils.
- Most pronounced influence with the addition of **fine grained hydrochar**.
- The total organic content (TOC) of the HTC water phase can be lowered significantly by Photo-Fenton reaction (requiring hydrogen peroxide) or the use of algae. The (somewhat stressed) algae produce more fatty acids than under ideal growth conditions.

Many thanks for your kind attention