



The potential of hydrochar for soil improvement and carbon sequestration



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Chapter 1: Introduction

Chapter 2: The influence of hydrochar from biogas digestate on soil improvement and plant growth aspects

Chapter 3: An investigation of the effects of hydrochar application rate on soil amelioration and plant growth in three diverse soils

Chapter 4: The stability of carbon from a maize-derived hydrochar as a function of fractionation and hydrothermal carbonization temperature in a Podzol

Chapter 5: Conclusions and future perspectives





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Chapter 1:

Introduction

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Chapter 1



Introducing the problems



Exponential world population growth results in:



Intensive agriculture, excessive fertilizer use



Enhanced energy production



Land use change



Deforestation, poor agricultural practices



Introducing the problems







Introducing the problems



By-products: biomass wastes_{2,3}



Crop residues

Biogas digestate

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Chapter 1







Thermochemical conversion:

Pyrolysis_{4.5}





Biochar - Pyrolysis

- High C sequestration potential_{7,8,9}
 - 50% original C content, recalcitrant_{3.6}
- Soil amendment tool
 - Nutrient content from feedstock_{10,11,33}
 - pH (liming effect)_{6,11}
 - Physico-chemical structure_{6,11,20,22,23}





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Pyrolysis - biochar

Releases GHG's (50% CO₂)₁₂

Restricted to dry biomass₁₃

Energy for intensive predrying₁₃



VS



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Releases GHG's (50% CO₂)₁₂

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Energy for intensive predrying₁₃ Hydrochar - Hydrothermal Carbonisation

- Thermochemical conversion
 - Closed, water-saturated system
 - 180 260°C, ca. 20 bar
 - Variable reaction times (mins days)
 - 60-84% original C content
 - Different physico-chemical structure₁₆



VS



Biochar - Pyrolysis

- High C sequestration potential_{7.8.9}
 - 50% original C content, recalcitrant_{3.6}
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Hydrochar - Hydrothermal Carbonisation

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Pyrolysis - biochar	HTC - hydrochar		
Releases GHG's (50% CO ₂) ₁₂	Carbon neutral (ca. 5% CO_2) ₁₄		
Restricted to dry biomass ₁₃	Converts wet biomass ₁₅		
Energy for intensive pre- drying ₁₃	Minimal additional energy ₁₅		





Hydrochar by HTC

- Most research focused on BC
- HC is also suitable for:
 - ✓ Soil amelioration
 - ✓ C sequestration
 - ✓ Reduced GHG emissions
 - ✓ Enhanced plant growth
 - Promotes biological activity
- Conflicting results_{16,36,47,60}
- Results vary depending on: 17,18,19,32,34

Feedstock, process conditions, HC characteristics, soil properties, environmental conditions, plant species and application rate.







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Research is lacking

Feedstock, process conditions HC characteristics soil properties, environmental conditions, plant species and application rate





 Analyse the influence of the grain size of hydrochar on soil improvement and germination- and biomass success in three diverse soils
Chapter 2





 Analyse the influence of the grain size of hydrochar on soil improvement and germination- and biomass success in three diverse soils
Chapter 2

 Identify the effects of different application rates of hydrochar on nutrient availability and physico-chemical properties of three soils, as well as germination success and biomass production Chapter 3





 Analyse the influence of the grain size of hydrochar on soil improvement and germination- and biomass success in three diverse soils
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3. To investigate the influence of HTC production temperature on the relative **degradability and subsequent fate of HC-C** within the free-, occluded within aggregates- and organo-mineral SOM fractions **Chapter 4**





Chapter 3:

An investigation of the effects of hydrochar application rate on soil amelioration and plant growth in three diverse soils

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Chapter 3



The influence of HC application rate



Biochar https://doi.org/10.1007/s42773-021-00089-z

ORIGINAL RESEARCH



An investigation of the effects of hydrochar application rate on soil amelioration and plant growth in three diverse soils

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Abstract

The hydrothermal carbonization (HTC) of biogas digestate alters the raw materials inherent characteristics to produce a carbon (C)-rich hydrochar (HC), with an improved suitability for soil amelioration. Numerous studies report conflicting impacts of various HC application rates on soil properties and plant growth. In this study, the influence of HC application rate on soil improvement and plant growth aspects was investigated in three diverse soils (Chernozem, Podzol, and Gleysol). Pot trials were conducted in which all soils were amended with 5, 10, 20 and 30% (w/w) HC in quintuplicate, with two controls of pure soil (with and without plants, respectively) also included. Prior to potting, soil samples were collected from all HCamended soils and controls and analyzed for soil pH, plant available nutrients (PO₄-P and K), and microbial activity using standard laboratory and statistical methods. Immediately after potting, a 6-week seed germination experiment using Chinese cabbage was conducted to determine germination success, followed by a plant growth experiment of equal duration and plant species to determine biomass success. At the end of the study (after a total plant growth period of 12 weeks), each pot was sampled and comparatively analyzed for the same soil properties as at the beginning of the study. Soil pH shifted toward the pH of the HC (6.6) in all soils over the course of the study, but was most expressed in the 20% and 30% application rates, confirming the well-documented liming effect of HC. The addition of HC increased the PO₄-P and K contents, particularly with 20% and 30% HC amendments. These results are proposedly due to the large labile C fraction of the HC, which is easily degradable by microorganisms. The rapid decomposition of this C fraction prompted the quick release of the HCs inherently high PO4-P and K content into the soil, and in turn, further stimulated microbial activity, until this fraction was essentially depleted. HC addition did not inhibit seed germination at any rate, presumably due to a lack of phytotoxic compounds in the HC from aging and microbial processes, and furthermore, showed no significant impact (positive or negative) on plant growth in any soil, despite improved soil conditions. In conclusion, although less pronounced, soil improvements were still achievable and maintainable at lower application rates (5% and 10%), whereas higher rates did not ensure greater benefits for plant growth. While the addition of high rates of HC did not detrimentally effect soil quality or plant growth, it could lead to leaching if the nutrient supply exceeds plant requirements and the soil's nutrient retention capacity. Therefore, this study validates the previous study in the effectiveness of the biogas digestate HC for soil amelioration and suggests that smaller regularly repeated HC applications may be recommendable for soil improvement.

Keywords Biogas digestate · Hydrochar application rate · Soil improvement · Nutrient availability · Microbial activity

Chapter 3



Background



Conflicting results on application rate







Higher HC application rates will result in:

- 1) Greater pH changes
- 2) Increased nutrient content (PO₄-P and K) and microbial activity
- 3) Germination inhibition and reduced plant growth



Materials



Hydrochar:

- Digestate feedstock (crop residues and beef and swine manure)
- ~ 200 °C, 18-20 bar,
- ~ 3 hr residence time,
- ~ 1.5 hr heating and cooling rate

<u>Soils:</u>

- Three soil types (dissimilar properties and agricultural value)
- Pot experiments
- · Homogenously mixed with hydrochar
- Controls (no hydrochar)

Soil type	Sand Silt		Clay	Texture	
son type	(%)			(FAO, 2006)	
Chernozem	16	43	41	Silty clay	
Podzol	66	21	13	Sandy loam	
Gleysol	1	6	93	Clay	







Chapter 3



Methodology





Chapter 3



Methodology



Hydrochar application rates:

- 5, 10, 20 and 30 % (w/w)
- C,H,N,S,O and ash content

Methodology:

- Standard pedological methods
- Euro Elemental Analyzer
- Kruskal-Wallis H Test and Mann-Whitney U test (SPSS, ver. 26)

Soil properties:

- pH (H₂O)
- plant available nutrients (phosphate (PO₄-P) and potassium (K))
- microbial respiration rate
- seed germination and biomass success



Table 1 The ash content, elemental composition (CHNS and O), and resultant molar element ratios of the hydrochar derived from biogas digestate

Ash content (wt %)	Elemental	composition (wt %)			Molar ele	ment ratio		
	С	Н	Ν	S	0	H/C	C/N	O/C	
47.2	35.2	3.8	2.7	0.9	10.2	1.3	15.2	0.2	23



Results and discussion:





The addition of the acidic hydrochar (6.6) shifted the soil pH to the pH of the hydrochar

Greatest change at higher application rates

Stabilization of pH over time

Liming effect due to:25

- High ash content₂₄
- Contribution of major cations and exchange processes_{25,26}
- pH response is dependent on initial soil and HC pH₂₇

Repeated application for sustainable effect

Results and discussion: Phosphate (PO₄-P)





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Hydrochar PO_4 -P = 6544,3 mg kg⁻¹

Direct contribution of PO₄-P

Increased with increasing application rate

Increased from $t_1 - t_2$ = contradicts previous findings

- Inherently high P content of feedstock₂₈
- Less resistant to decomposition_{6,30,42}
- Liberation of P from Fe-, Al- and Ca phosphates_{18,29,38}
 - pH-dependent change
- Plant uptake and microbial biomass incorporation₃₂ reached maximum
- Excess may be harmful to plant growth₄₃

Repeated smaller applications recommended

Results and discussion: Phosphate (PO₄-P)





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- Excess may be harmful to plant growth₄₃

Repeated smaller applications recommended

Results and discussion: Potassium (K)





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Hydrochar K = 2384 mg kg⁻¹

Direct contribution of K

Increased with increasing application rate

Greater increase in low K content soils

- Relatively easily degradable HC fraction_{30,31}
- · Plant and microbial uptake/ leaching

Not significant (n.s)

 Risk of enhanced leaching, especially in sandy soils₂₇

Sustainable supply of K at higher application rates

Significant difference



Results and discussion: Microbial Respiration





Initial stimulus

Higher activity at higher application rates

Decreased activity over time

- Initial stimulus due to:
 - Labile C fraction of HC_{44,45}
 - Response to pH change₄₆
- Reduced respiration rate at t₂:
 - Limited C source_{47,48}
 - Competition from plants
- Mediated respiration rate
 - Improved biological soil status

Results and discussion: Seed germination and biomass success



Average percent germinated seeds for the controls and HC-amended soils over two rounds of the germination experiment.

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Soil	Chernozem	Podzol	Gleysol
5011		Avg. %	
Control	87	54	91
5 %	79	80	89
10 %	84	77	87
20 %	76	89	94
30 %	92	81	93
1			
0.9			n.s
0.8		[- T T
0.7	n.s		
0.6	Ī	T	
0.5	T	n.s	
0.7 0.6 0.5 0.5 0.4			
0.3			
0.2			
0.1 —			
0			
control 5%	10% 20% 30% 5%	10% 20% 30% ^{control}	5% 10% 20% 30%
		Podzol	Gleysol

No seed germination inhibition

Higher application rates did not reduce biomass production

Fresh HC can contain organic contaminants $_{36,37,39}$ – not evident here

Adverse HC impacts reduced by:

- HTC process conditions (temp. & reaction time)₃₅
- Free gas exchange at soil-atmosphere interface₃₆
- Microbial decomposition of phytotoxic compounds₃₇
- Age and storage time of HC₃₆

End of the experiment (t_2)



Conclusions



Hypotheses:

Higher HC application rates will result in:

1) Greater pH changes



- Shifted the pH of the soil toward the pH of the hydrochar stabilized over time
- Most pronounced at higher application rates
- 2) Increased nutrient content (PO₄-P and K) and microbial activity
 - PO₄-P content increased with increasing application rates surplus remains
 - · K content increased with application rate sustained at higher rates
 - · Microbial activity initially increased stimulus limited to labile C availability
- 3) Germination inhibition and reduced plant growth



Supported plant growth, especially at higher application rates

HC from biogas digestate is suitable for soil amelioration, preferably in smaller regular applications









Chapter 4:

The stability of carbon from a maize-derived hydrochar as a function of fractionation and hydrothermal carbonization temperature in a Podzol

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Chapter 4



Background



HC less effective tool for C sequestration

- Higher H:C and O:C ratios_{49,50}
- Labile C fraction_{15,51}

Dependent on HTC conditions and feedstock,

Means to improve HC effectiveness

- Higher HTC production temperatures₁₃
 - Condensed C structure → recalcitrant_{8,52}
- Interactions and association with primary soil organic matter (SOM)
 - Protection against degradation_{53,54}
 - Increased stability



Limited knowledge available about HC – SOM interactions



Methodology



Hydrochar:

- Maize silage feedstock
- 190, 210 and 230 °C
- 5 % application rate
- C,H,N,S,O and ash content





Methodology:

- Density fractionation procedure₅₅
- Flash 2000 Elemental CN Analyzer coupled via a ConFlo III Interface to a Delta V Advantage IRMS₅₆
- Euro Elemental Analyzer
- Kruskal-Wallis H Test (SPSS, ver. 26)

Soils:

- Podzol (sandy loam)
- Pot experiments for ~ 1 year
- Homogenously mixed with hydrochars
- Control (no HC)

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Methodology



Measured parameters:

- Weight proportions of:
 - Initial free particulate organic matter ($iPOM_F$) at the beginning
 - Free particulate organic matter (POM_F)

 - Organic matter bound to clays (OM_{CI})
- C and N accumulated OC, TOC
- δ ¹³C (‰) % HC-derived C in SOM fractions_{57,58}
 - Distinct δ ¹³C signatures of different plants tissues₆₂



$$C_{HC-derived} \left[\%\right] = \left(\left(\delta^{13}C_{sample} - \delta^{13}C_{control}\right) / \left(\delta^{13}C_{HC} - \delta^{13}C_{control}\right)\right) \times 100$$

Share of HC-C and native SOC per fraction







- 1) How much HC-C is lost (decomposed) from the free-POM fraction of the soil after approx. 1 year (i.e. how stable is the HC-C in its initial free-POM form)?
- 2) Is the level of HC-C decomposition from the free-POM fraction controlled by the HTC production temperature?
- 3) Do the remaining products of HC decomposition become incorporated within the relatively stable SOM structures of the occluded-POM fraction and organic matter bound to clay particles?
- 4) Are the interactions and associations of the HC decomposition products with the relatively stable SOM fractions (POM_O and OM_{Cl}) controlled by the HTC production temperature?


Results and discussion: HC properties



Table 4.1: The elemental composition (CHNS, O), ash content and calculated atomic ratios of the hydrochars produced at increasing HTC temperatures.

Hydrochars	С	Н	Ν	S	0	Ash content	Atomic ratio		_	
				wt %			C/N	H/C	O/C	
190 $^{\circ}$ C HC	57.9	7.1	1.2	n.d	31.1	2.7	56.3	1.5	0.4	
210 °C HC	60.7	7.3	1.7	n.d	26.2	4.1	41.6	1.4	0.3	Increasing stability
230 °C HC	70.5	6.9	2.5	n.d	15.3	4.8	39.2	1.2	0.2	

n.d: not detected

- Increased C and decreased O with HTC temperature₅₉
- Increased degradability of HC = high H/C (≥ 0.6) and O/C (≥ 0.4) ratio_{19,40,60}



Figure 4.1: Scanning electron microscope (SEM) high resolution micrographs of the hydrochars produced at increasing HTC temperatures.

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Chapter 4



Results and discussion: C stocks of SOM fractions



The total organic carbon (TOC) content of the bulk soil (including sand and silt fractions (data not shown)) in g kg⁻¹ at the beginning of the study (shortly after HC addition) and after 1 year of soil incubation, and the percentage (%) lost over the 1 year period.

	Bulk soil TOC*				
	After HC addition	After 1 year			
	(g kş	% loss			
Control	18.1	21.2			
HC190	47.1	36.7	22		
HC210	48.5	38.5	21		
HC230	53.4	40.9	23		

*Bulk soil TOC was determined as the sum of accumulated OC of all SOM fractions (including silt and sand).





	Bulk soil TOC*			
	After HC addition	After 1 year		
	(g kg	% loss		
Control	18.1	21.2		
HC190	47.1	36.7	22	
HC210	48.5	38.5	21	
HC230	53.4	40.9	23	

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*Bulk soil TOC was determined as the sum of accumulated OC of all SOM fractions (including silt and sand).



Source: Lehmann 2019₆₈

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The average percent of total organic carbon (TOC) derived from the hydrochars (HC-C) and native soil organic carbon (SOC) at the beginning of the study (as iPOM_F), and after approx. 1 year (as POM_F, POM_O and OM_{CI})

Results and discussion: HC-derived C in SOM fractions universität OLDENBURG

VON





The average percent of total organic carbon (TOC) derived from the hydrochars (HC-C) and native soil organic carbon (SOC) at the beginning of the study (as iPOM_F), and after approx. 1 year (as POM_F, POM_O and OM_{CI})

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68 - 81 % HC-C lost from POM_F

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51 – 72 % SOC lost from POM_F

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Positive Priming Effect

Results and discussion: HC-derived C in SOM fractions universität OLDENBURG



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Hydrochars	Atomic ratio				
	C/N	H/C	O/C		
190 $^{\circ}$ C HC	56.3	1.5	0.4		
210 °C HC	41.6	1.4	0.3		
230 °C HC	39.2	1.2	0.2		

Interreg

North Sea Region

EUROPEAN UNION

BIOCAS

$H/C \ge 0.6$: higher degradability_{19.60}



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HC-C and SOC increased in POM_o fraction

Results and discussion: HC-derived C in SOM fractions

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Chapter 4

Interreg

North Sea Region

EUROPEAN UNIO

BIOCAS

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OM_{CI} fraction – slow reactivity_{8.64.65}





1) How much HC-C is lost from the POM_F fraction after approx. 1 year?

- 68 81 % HC-C and 51 72% native SOC was lost from the POM_F fraction
- Positive priming effect was temporary

2) Is the level of HC-C decomposition from the POM_F fraction controlled by the HTC production temperature?

- No significant differences in losses between different temperature HCs

3) Does HC-C incorporate within the relatively stable POM_o and OM_{cl} fractions?

- Yes, HC-C present in POM_O and OM_{CI} fractions after 1 year

4) Are these interactions controlled by the HTC production temperature?

- Influenced HCs physico-chemical and structural properties
- No significant differences in HC-C content of POM_O and OM_{CI} fractions



Conclusion



Despite large C contribution from the maize-derived HCs, its effectiveness is reduced by positive priming effect. Therefore, more research is required on reducing initial priming losses and promoting long-term stabilization in stable SOM fractions







Chapter 5:

Major Conclusions and Future Perspectives

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Chapter 5





- Hydrochar from biogas digestate effective soil amendment
 - Repeated addition of finer grained HC at 5 10 % application rates

- Hydrochar from maize silage low suitability for C stabilization over short-term
 - Longer-term research required to verify C sequestration potential





- Field studies using recommended grain size and application rate
- Influence of recommended HC parameters on other soil properties, e.g. Nmin, Ca, Mg, Al and Fe
- Long-term research (> 2 years) required on C balance in SOM fractions
- More soil types and textures beneficial HC interactions







Thank you for your attention!

Danke für Ihre Aufmerksamkeit!

Questions?





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