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Toxicity screening of biochar-mineral composites using germination tests

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Abstract

This study assessed the properties and toxicity (water cress germination trials) of 38 waste-derived, novel biochar-mineral composites (BMCs) produced via slow pyrolysis and hydrothermal carbonization (hydrochars). The biochars were produced from sewage sludge and compost-like output (CLO) by varying the type of mineral additive (zeolite, wood ash and lignite fly ash), the mineral-to-feedstock ratio and the carbonization process. While pure hydrochars completely inhibited germination of water cress, this effect was ameliorated by mineral additives. Seedlings grew best in pyrolysis chars and while wood ash addition decreased plant growth in many cases, 1:10 addition to CLO doubled germination rate. The factors responsible for the phytotoxicity can be attributed to pH, salinity and organic contaminants. Importantly, while pure minerals inhibited germination, conversion of minerals into BMCs reduced their inhibitory effects due to buffered release of minerals. Overall, mineral wastes (e.g., combustion ashes) and waste biomass can be used safely as sources of nutrients and stable organic carbon (for soil carbon sequestration) when converted into specific biochar-mineral composites, exploiting synergies between the constituents to deliver superior performance.

Keywords: Biochar; Hydrochar; Pyrolysis; HTC; Ash; BMC

Abbreviations¹

¹ EC, electric conductivity; BMC, biochar mineral composites; CLO, compost-like output; HTC, hydrothermal carbonization

1 Introduction

Biochar is the solid, carbon-rich fraction obtained from thermochemical conversion of biomass in an oxygen-limited environment (International Biochar Initiative, 2011).

Biochars can be differentiated into chars from pyrolysis, which is a process that takes place at temperature of 350-750°C, and hydrochars formed at temperatures of 180-250°C at elevated pressures in subcritical, liquid water (Lehmann and Joseph, 2015; Libra et al., 2011). During the last decade, a growing interest in the use of biochar surfaced, ranging from soil amendment for higher crop productivity (Lehmann and Joseph, 2015; Liu et al., 2013), carbon sequestration (Wang et al., 2015) and environmental remediation (Xie et al., 2015) to the support of chemical (Zhu et al., 2015) and biological (Mumme et al., 2014) processes.

Biochar represents a highly heterogenic group of materials and its properties depend on the nature of feedstock and production conditions. When applied to soil its value derives mainly from its chemical stability, high surface area, cation exchange capacity, high pH, nutrient provision (P, K, Ca, Mg) and sorption capacity. However, biochar has also been reported to exhibit adverse effects on plant growth, water and soil organisms in a number of studies caused by sorption of N, organic/inorganic contaminants and high pH and salinity levels (Bargmann et al., 2013; Busch et al., 2013; Buss et al., 2016b; Buss and Mašek, 2014; Gell et al., 2011; Kołtowski and Oleszczuk, 2015; Lucchini et al., 2014; Oleszczuk et al., 2013; Prommer et al., 2014; Smith et al., 2013).

A way to influence the physical and chemical properties of biochar, such as stability or carbon retention, is the addition of minerals prior to the production of pyrolysis chars (Li et al., 2014; Xu et al., 2017) or hydrochars (Mumme et al., 2015). The addition of minerals to biochar before or after thermal treatment creates a new product called

biochar mineral composites (BMC). Apart from the potential of influencing the physical and chemical properties, minerals add plant nutrients to the resulting product.

Overall, BMC's have been studied in only a few articles which in most cases used existing biochars to produce BMCs (Blackwell et al., 2015; Chia et al., 2014; Lin et al., 2013). In our study, as previously conducted by Mumme et al. (2015) the feedstocks and minerals were mixed before thermal treatment. This study is the first to screen waste-derived BMCs produced by both HTC and pyrolysis for potentially phytotoxic effects and general properties. Seed germination and early seedling growth are very sensitive to the influence of external factors and therefore, germination trials in a controlled, soil-free environment were conducted to assess BMC's toxicity.

Overall, 38 different biochars were produced from two different feedstocks with different production technologies / conditions and three different minerals added in different ratios. The objective was to investigate the effects of BMCs on seed germination and early seedling growth of watercress as model organism as the first step towards evaluating the safety of BMCs. Properties, such as pH, electric conductivity (EC), ash content and elemental content (CHN, nutrient and potentially toxic elements) were assessed. Furthermore, the aim was to investigate whether potential inhibitory effects of pure minerals are reduced by incorporation into BMCs.

2 Materials and methods

2.1 Origin and properties of organic feedstocks and minerals

To demonstrate economic feasibility, we decided that the minerals and the feedstocks for thermochemical conversion should both be waste materials (marginal biomass). Therefore, in this study, compost-like output (CLO), a byproduct from composting made of partially degraded residues that is often landfilled (Donovan et al., 2010) and sewage sludge were used as feedstocks.

The sewage sludge was obtained from Daldowie wastewater treatment site (Glasgow, Scotland), where it was first mechanically dewatered using a centrifuge, then dried and pelletized. The CLO was obtained as a waste product from a compost facility in Ireland from the mechanical separation of mixed municipal solid waste (fraction < 20 mm).

The organic feedstocks were mixed with three different minerals: wood ash, fly ash and, for reference, zeolite. The wood ash was retrieved from a manually-fed 50 kW log wood boiler with flue gas venting (Atmos, Czech Republic), which was fed with a 70:30 mixture of dry oak and robinia wood. The fly ash was obtained from AHG Industry GmbH & Co. KG and derived from lignite coal burning in HKW Chemnitz, Germany.

A natural hydrated zeolite with particle size 0-100 μm mainly composed of clinoptilolite (90-92%), cristobalite (5-7%), feldspar (2-4%), mica (1-2%), and quartz (traces) was obtained from Zeolithversand LTD (Germany). Further information about the zeolite can be obtained from Mumme et al. (2015).

2.2 Production of BMCs

CLO and sewage sludge were mixed with a definite amount of minerals prior to thermochemical conversion in ratios of 10:1 (100 g source material and 10 g mineral) and 1:1

(50 g and 50 g). The ratios are based on dry matter (TS 105°C). Overall, 28 different hydrochars were produced and 10 different pyrolysis chars. An overview of all samples is shown in Table 1 and SI Table 1.

2.2.1 HTC

All HTC experiments were performed in a one-liter stir reactor (Parr Instruments, Moline, IL, USA, model 4520) with the respective mixtures and addition of distilled water to a volume of 700 mL. The reactor was heated with a performance of 2°C min⁻¹ to the initialized holding temperature of 190°C or 230°C regulated by the software SpecView. Over the whole timespan the stirrer was turning with 90 rpm and at the end of the holding time (120 minutes) the heaters were switched off. The samples were left to cool to room temperatures for 3 hours. The HTC product (slurry) was filtered through a 5-8 µm paper filter via -0.200 mbar vacuum filtration; the solids were dried at 105°C for 24 hours.

2.2.2 Pyrolysis

Prior to pyrolysis the feedstocks were homogenized. A swing mill of type RS 200 from Retsch and a grinding application made of 98% pure iron was used for grinding the materials at 1400 rpm for 90 seconds. The mixture ratios were identical to the HTC experiments, however, lignite fly ash was not tested. An overview of all the treatments and produced biochars is shown in Table 1. The mixtures were filled in a fireclay crucible made of ceramic with a capacity of 30 g. The holding time at highest treatment temperature (HTT) for CLO was set to 20 minutes. Because of a different reaction behavior of sewage sludge in pyrolysis (initial endothermic reaction) the holding time at HTT was 25 minutes to guarantee complete carbonization. The crucibles were inserted and removed at the HTT of 550°C to prevent a temperature drift. The atmosphere in the

furnace was kept inert through a nitrogen flow of 12 L h^{-1} . The pyrolysis chars were left to cool at room temperature closed with a lid to prevent ashing of the char.

2.3 Germination tests

All materials tested in this study are typically used as soil amendments and therefore, instead of applying pure materials, a 1% application rate in sand was tested. This is a comparably high concentration applied to a material with very low buffering capacity compared to soil. The results, therefore, will indicate realistic, but still worst-case scenario effects of the materials on germination and early seedling growth. An adapted version of the EN 16086-2 2011 method was used with sand as control instead of peat allowing for direct comparisons.

Hydrochars and pyrolysis chars were stored in closed containers for around two months at room temperature between production and testing in the germination assays. All additives were mixed with sand at a 1% rate (dry base) and the sand was wetted before with DI water to reach 80% of its water holding capacity (WHC). The medium sand used for the germination test contained particles of 50 – 70 mesh (210-297 μm) (Sigma-Aldrich Company Ltd., UK). The petri dishes used for the trial contained a filter paper and an amount 0.9 g de-ionized water which is equivalent to 80% of the WHC of the filter paper. The WHC of the sand was determined by soaking 5 g of sand in water for 1 h which was first drained for 18 h and subsequently dried in an oven at 80°C.

The BMC's were weighed into plastic bags, mixed with sand, water was added and they were mixed again. Each petri dish was filled with $36.6 \text{ g} \pm 0.1 \text{ g}$ of the wet mix and 10 seeds of *Nasturtium officinale* (watercress) were spread. The experiment was replicated four times per treatment. As per method, the petri dishes were sealed with parafilm. The

dishes were stored in a temperature control room at around 25°C in an angle of 50 degrees for seven days to germinate. A schematic of the test can be found in SI Figure 2.

The treatments were assessed in two germination batches (SI Table 1). Seeds were considered to have germinated if the radicle had emerged. Root and shoot length were determined by image analysis using software ImageJ version 1.50i.

2.4 Analysis of biochar properties

2.4.1 Electric conductivity (EC) and pH

For EC and pH measurements 1 g of biochar was mixed with distilled water in a ratio of 1:20 and the mixture was shaken for 1.5 h (12 h and 54 h) on a bench-top shaker according to Rajkovich et al. (2012) which is the method recommended by the International Biochar Initiative (IBI, 2014) for analysing biochar. The EC and pH were measured using a HM digital EC probe (model COM-100) and a Mettler Toledo FE 30, respectively.

2.4.2 Elemental content via ultimate analysis

The CHNS elemental content was determined using a Vario EL III elemental analyzer (Elementar Analysensysteme GmbH, Germany).

2.4.3 Elemental content via ICP-OES

The feedstocks and biochars were digested using modified dry ashing which is a method that has been optimized for biochar (Enders and Lehmann, 2012). The digested samples were analyzed using an iCAP 6000 Series Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) (Thermo Fisher Scientific, Waltham, MA, USA). Overall 23 elements were analyzed and nutrient concentrations are reported in Table 2,

167 2.5 *Statistics*

168 Germination test results were analyzed using one-way ANOVA, followed by Tukey
169 post hoc tests with a significance level of 0.05 was applied.

3 Results and discussion

3.1 Material properties of Biochar and BMCs

Compared to pyrolysis, during HTC less dehydration and aromatization reactions take place and hence more carbon is conserved in relation to the mineral content which results in higher carbon and hydrogen contents in hydrochars (Table 1 and Table 2) (Libra et al., 2011). Additionally, while minerals dissolve into the HTC liquor to some degree (Libra et al., 2011), during pyrolysis most minerals are retained in the pyrolysis char (Buss et al., 2016a). This results in lower ash contents of hydrochars compared to pyrolysis chars which along with formation of organic acids also lowers the pH values of hydrochars. This is particularly apparent for hydrochars from sewage sludge and less so in the CLO-derived samples. Pyrolysis, increased the pH compared to the raw materials (Table 1 and Table 2) as reported in other studies (Cantrell et al., 2012; Jindo et al., 2014; Ronsse et al., 2013).

Thermo-chemical conversion and mineral addition had a stronger influence on pH, ash and elemental composition of biochar from sewage sludge than it had on CLO-biochars. This can be attributed to the already high ash content in the untreated CLO of 55.0% (ash₅₅₀, Table 2) compared to 29.7% in raw sewage sludge. Consequently, e.g. the content of ash₅₅₀ of hydrochars produced at 190°C changed with 1:1 wood ash addition from: 39.4% to 71.7% for sewage sludge but only from 66.6% to 84.3% for CLO (Table 1 and Table 2). Addition of minerals decreased the C, N, H and S contents of the biochars as expected because the ash fraction is mostly inert and hence increases proportionally (Table 1 and Table 2). The 1:1 mineral additions resulted in biochars with ash contents in the range of 70-90%.

Wood ash addition to the biomass feedstocks in the ratio of 1:1 resulted in EC values in the pyrolysis BMCs of only 1/4 (sewage sludge) and 1/3 of the EC of pure wood ash (Table 1 and Table 2). The ECs are expected to be $>1/2$ of the wood ash EC value due to enrichment of the ash fraction during pyrolysis and addition of ash from the biomass feedstocks. This clearly shows that addition of biomass and conversion into biochar buffers the release of minerals and reduces the EC. With the addition of wood ash and lignite fly ash, the BMCs contained exceptionally high concentrations of the macronutrients, P, K, Ca, Mg, S and N which could make them an ideal compound fertilizer (Table 1, Table 2, Table 3, Table 4). However, it is important that they do not exhibit any phytotoxic effects which is investigated in the following sections.

3.2 Germination and seedling growth in feedstock materials and minerals

Compared to the sand-only controls, watercress seed germination was significantly inhibited by all unpyrolysed feedstock amendments (Fig. 1). The inhibition ranged from around 50% (sewage sludge, zeolite) to 100% (wood ash).

The complete inhibition of germination caused by wood ash can clearly be attributed to its high pH (12.78, Table 1) and osmotic potential/salinity, here approximated by measuring the EC ($16,100 \mu\text{S cm}^{-1}$, Table 1) which were the most relevant factors in other studies, such as Etiegni et al. (1991). More specifically Etiegni et al. (1991) and Buss et al. (2016b) attributed the toxic effects mostly to the exceptionally high potassium (K) concentration in wood ash / biochars, which we do see in our wood ash as well: more than 7.5% of the wood ash sample is potassium (Table 3). Fly ash has a very similar pH (12.54) to wood ash and zeolite has the second highest concentration of K of the materials (Table 3) which very likely were the reasons for the low germination

rates in these treatments (Fig. 1). It is unlikely that heavy metals caused toxicity directly although they will have contributed to the high osmotic potential (Buss et al., 2016b).

Salinity / K concentration and pH, however, does not explain the low germination rate caused by addition of CLO and sewage sludge. Ramírez et al. (2008) reported that fresh sewage sludge applied to artificial soil in similar concentrations as in our study (~1%) reduced the germination rate in seeds of various plant species and the toxicity correlated well with total N and NH_4^+ contents. Fresh compost can also result in phytotoxic effects due to the presence compounds such as NH_4^+ (Wong, 1985). In our study, pure CLO (N 2.49%, Table 2) and sewage sludge (N 4.28%, Table 1) had the highest N contents of the materials by far which indicates that indeed NH_4^+ was responsible for the germination inhibition caused by the two raw materials (Fig. 1).

After germination, the seedlings grown in sand amended with sewage sludge and CLO showed significantly longer shoots and roots compared to the sand-only controls (Fig. 1). Similar to this result, in Ramírez et al. (2008), despite inhibition of germination, sewage sludge did not affect shoot growth negatively and in some cases even stimulated growth. After germination, the macronutrient N (NH_4^+) (Monaco et al., 2003), K (Penny et al., 1976) and P (Jaworski and Valli, 1964) demonstrate positive effects on shoot growth in the early seedling development which explains the effects in our trial. While sewage sludge and CLO both have high N contents (Table 1 and Table 2), additionally sewage sludge has a high concentration of P (1.1%, Table 3) and CLO a high content of K (0.8%, Table 4).

Overall, application of the untreated amendments is problematic for various reasons (e.g., osmotic potential, high pH, NH_4^+). Yet, the amendments also resulted in positive

effects on seedling growth after germination due to their high nutrient contents. This shows the need for mixing different materials and using treatments, such as thermochemical conversion, to mitigate the inhibitory effects and improve the growth stimulating effects of the materials.

3.3 Germination and seedling growth in pure biochars

Pyrolysis mitigated the germination inhibition caused by pure sewage sludge completely and increased the germination rate of seeds grown in CLO from 10 to 45%. Yet, HTC treatment increased the toxicity of both materials (Fig. 2).

During thermo-chemical conversion, nitrogen (N) vaporizes or is washed into the HTC liquor readily (Antal and Grønli, 2003; Libra et al., 2011), resulting in lower N concentrations in biochar compared to its parent material (Table 1 and Table 2). Furthermore, high-temperature treatment converts N-containing compounds into heterocyclic (unavailable) N-structures (Yao et al., 2010). Consequently, the seeds exposed to pyrolysed sewage sludge and CLO germinated mostly unhampered of the influence of excess N (Fig. 2).

Pyrolysed compost still only showed a germination rate of 46% with a high standard deviation indicating borderline toxicity. This can be explained by the elevated pH of 8.95 (Table 2) which is the lower range where germination inhibition can occur (Henig-Sever et al., 1996; Singh et al., 1975). Seed germination decreases exponentially with pH as described in Buss et al. (2016b) and therefore, only some seeds reacted to the high of pyrolysed compost. The shoot and root length of seedlings in the sewage sludge treatment increased significantly after pyrolysis, however, no improvement was visible

in the pyrolysed CLO treatment which already displayed very high shoot and root length prior to pyrolysis (Fig. 1 and 2).

During HTC, mobile organic compounds that are formed during the process are not separated from the char as effectively as during pyrolysis which can result in elevated concentrations of potentially toxic organics, such as phenols and organic acids (organics not measured in this study but reported in Bargmann et al. (2013)). Consequently, fresh hydrochars can cause inhibitions on germination and during early seedling growth (Bargmann et al., 2013; Busch et al., 2013). Our hydrochars were stored in closed containers for around two months before testing in germination assays which does not enable volatilization of organic compounds from the char. Therefore, inhibition by organic compounds originated from the HTC process is the most probable cause for the hydrochar effects in the germination tests. Different post-treatment measures were successful in reducing the toxicity of fresh hydrochars (Bargmann et al., 2013; Busch et al., 2013) and would also need to be implemented prior to application of our hydrochars.

3.4 *Impact of HTC-derived BMCs on germination and seedling growth*

The interactions of feedstock type, treatment method/temperature and mineral addition were very complex; some of the key features are discussed in the following.

Zeolite addition increased germination rate compared to the non-amended treatments.

Zeolite has the ability to adsorb metals and organic compounds such as those present in HTC char, which have the potential for inhibitory effects, and this could explain the increased germination rate of zeolite-amended chars (Bargmann et al., 2013; Chao et al., 2012).

The highest germination rates for mineral-amended sewage sludge-derived hydrochars were in the range of 30-60% (for all 1:1 mineral additions and 1:10 fly ash addition treated at 190°C) which is similar to untreated sewage sludge (Fig. 1) and higher than unamended sewage sludge-derived hydrochars (Fig. 3).

Ash addition also affected shoot and root growth. With 1:1 wood ash addition the shoots of seedlings grown in sewage sludge hydrochar increased from 12 mm for 190°C (no germination at 230 °C) to 35 / 36 mm (190° / 230°C) (and 18 / 16 mm for the 10:1 addition). This is higher than the length of the seedlings grown in the pure sewage sludge treatment (20 mm) and similar to the shoot length of seedlings in sewage sludge pyrolysed at 550°C (38 mm) (Fig. 2) (highest shoot length of all sewage sludge treatments. Therefore, when the seedlings germinated, they grew unhampered. The organic contaminants only inhibited or delayed germination and did not completely suppress plant growth as observed previously (Bargmann et al., 2013).

Overall, wood and fly ash addition increased the germination rate and growth of shoots and roots for sewage sludge and CLO significantly, while the shoot/root ratio was

barely influenced by any of the minerals (Fig. 3, SI Table 5). The most probable reason for the lower toxicity of hydrochars amended with minerals is the smaller organic fraction in the feedstocks and subsequently fewer precursors for the formation of potentially toxic organics, such as phenols and organic acids.

Not all of the phytotoxic effects, mitigation of toxic effects and beneficial effects can be explained here. It is likely that a combination of various factors, mostly EC, pH, concentration of nutrients and, most important for hydrochars, the concentration of organic contaminants has caused the effects. The highest germination rates were observed in the range of 40-60% with many in the range of 0-20%. This demonstrates that hydrochar-BMCs still caused significantly phytotoxic effects and should be post-treated before use as soil amendment.

The addition of 1% BCMs to sand is a high application rate if applied mostly to supply nutrients and tested as a worst-case scenario of effects on plant growth. Application in lower rates some time before sowing of the seeds is likely to give enough time for vaporization of the volatile organics which could be sufficient for post-treatment. The results show that mineral addition does increase the germination rate and shoot and root length compared to non-amended treatments. In addition, minerals incorporated into hydrochars resulted in better plant performance than pure minerals. Hence, mixing minerals with feedstock prior to thermo-chemical conversion brings advantages over applying both products separately.

3.5 *Impact of pyrolysis-derived BMCs on germination and seedling growth*

Generally, the seeds performed best when grown in the pyrolysis chars (Fig. 4, SI Table 5). Zeolite addition to sewage sludge and CLO did not affect germination or seedling growth (Fig. 4). Wood ash addition reduced the germination rate when mixed with compost in both ratios and reduced the germination rate when blended with CLO in the ratio 1:1, however, increased the germination rate when blended 1:10 compared to the control (SI Table 5).

Pyrolysis-derived BMCs amended with wood ash most likely caused toxic effects due to the high pH and the high osmotic potential (salinity) of the BMCs (Table 1 and Table 2). This is presented in SI Fig. 1 with a line of linear regression between germination rate and pH of the pyrolysis chars. SI Fig. 1 also demonstrates that the hydrochars with 1:1 mineral addition exhibited stronger toxic effects than pyrolysis chars with comparable pHs which is attributed to additional adverse effects from organic contaminants. The remaining 20 hydrochars are not shown in SI Fig. 1, their germination rates were even less well correlated with pH because their toxicity was nearly exclusively caused by organic contaminants. Under normal circumstance, the production of pyrolysis chars results in very low concentration of organic contaminants (Buss et al., 2015) and pH and osmotic pressure (salinity) are the factors that affect plant growth adversely (Buss et al., 2016b) resulting in the linear correlation between germination rate and pH (SI Fig. 1).

Despite some reduction of germination rate, the seedlings grown in pyrolysis chars performed best. Typically, pyrolysis chars neither contain high concentrations of easily available N-containing compounds as the raw material do, nor do they contain mobile organic contaminants as the hydrochars. Although some pyrolysis chars reduced

germination rate, once germinated all pyrolysis char treatments increased the shoot and root growth significantly by a factor of 2-5 compared to the sand only control, most probably due to nutrient supply (SI Table 5). As described in 3.1, the wood-amended BMCs showed lower ECs than would be expected considering the amount of wood added (and the volatilization of organics).

This clearly demonstrates that pyrolysis-derived BMCs can increase plant growth and are promising nutrient providers and liming agents.

4 Conclusions

Cress seeds grown in many pyrolysis-derived BMCs exhibited better growth performance than the sand-only control and can be used safely. Raw materials (ash, compost, sewage sludge), several pyrolysis chars and most hydrochars decreased germination rate compared to the control. Pure mineral application resulted in reduced plant growth, however, the phytotoxicity was reduced when the minerals were incorporated into biochar due to buffered release of minerals (lower EC). A combination of pH, EC/potassium, N-containing compounds and organic contaminants (not measured) was responsible for the observed inhibitions. When BMCs are applied to soil of low-buffering capacity, soil pH and EC have to be monitored closely to avoid toxicity. BMCs derived from hydrothermal carbonization need to be post-treated to reduce their concentrations of toxic organics. Taking these recommendations into account, BMCs produced from mineral wastes (e.g., combustion ashes) and waste biomass can be applied safely and can be great sources of nutrients and stable organic carbon.

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Table 1 Bulk properties of feedstocks, pure biochars and BMCs derived from sewage sludge (n = 1).

mineral type	mineral ratio	process	pH (H ₂ O)	EC μS cm ⁻¹	Ash ₅₅₀ %dry	C %dry	N %dry	H %dry	S %dry
	Zeolite		6.79	19.9	100	0.004	0	1.32	0.037
	Wood ash		12.78	16100	99.50	6.60	0	0.37	1.11
	Fly ash		12.54	8170	99.78	0.42	0	0.19	3.00
	Raw sewage sludge		6.76	388	29.65	39.74	4.28	6.20	0.66
Without mineral		HTC190	4.40	149	39.36	38.33	2.08	5.25	0.57
		HTC230	4.70	50.3	45.20	38.82	2.11	4.79	0.52
		Pyro550	6.73	31.6	57.49	31.80	3.87	2.21	0.63
Zeolite	1:10	HTC190	5.54	134	52.38	32.77	2.21	4.43	0.72
		HTC230	5.16	208	50.53	35.27	2.19	4.84	0.63
		Pyro550	6.95	114	63.45	27.47	3.33	2.04	0.55
	1:1	HTC190	4.94	182	74.40	15.93	1.17	2.71	0.30
		HTC230	5.27	125	83.33	12.08	1.26	2.36	0.29
		Pyro550	7.75	45.3	84.10	11.57	1.54	1.53	0.26
Wood ash	1:10	HTC190	6.63	593	43.38	34.74	1.93	5.03	0.66
		HTC230	6.46	208	50.11	33.87	1.80	4.56	0.71
		Pyro550	9.71	470	62.25	27.48	2.97	2.17	0.93
	1:1	HTC190	10.66	1050	71.69	20.18	0.57	2.70	0.57
		HTC230	9.32	232	83.46	14.56	0.27	1.87	0.56
		Pyro550	11.31	4040	83.66	13.84	0.74	0.99	1.11
Lignite fly ash	1:10	HTC190	5.81	334	44.77	33.96	1.95	5.10	0.82
		HTC230	5.43	388	51.99	34.36	1.91	4.71	0.92
	1:1	HTC190	9.12	354	71.07	17.55	0.68	2.71	1.79
		HTC230	7.88	244	71.61	19.58	0.62	2.74	1.56

Table 2 Bulk properties of feedstock, pure biochars and BMCs derived from CLO
(n = 1).

mineral type	mineral ratio	process	pH (H ₂ O)	EC $\mu\text{S cm}^{-1}$	Ash ₅₅₀ %dry	C %dry	N %dry	H %dry	S %dry
	Raw CLO		8.31	1980	55.03	24.03	2.49	3.14	1.45
Without mineral		HTC190	7.00	758	66.62	23.75	1.20	2.17	0.80
		HTC230	7.21	745	67.72	26.30	1.29	2.24	0.94
		Pyro550	8.95	1420	69.77	21.43	1.50	1.58	1.16
Zeolite	1:10	HTC190	6.83	781	59.07	26.85	1.52	3.07	0.92
		HTC230	7.20	706	68.55	23.63	1.23	2.35	0.90
		Pyro550	8.28	834	70.56	21.50	1.46	1.63	1.16
	1:1	HTC190	6.58	491	81.71	12.98	0.77	1.99	0.44
		HTC230	6.95	473	85.28	10.98	0.75	1.80	0.38
		Pyro550	8.57	711	84.83	10.45	0.77	1.48	0.53
Wood ash	1:10	HTC190	7.69	791	63.98	25.30	1.22	2.48	0.94
		HTC230	7.56	794	65.36	25.31	1.19	2.39	1.10
		Pyro550	9.74	2280	72.43	20.36	1.13	1.18	1.34
	1:1	HTC190	10.96	1290	84.32	13.36	0.25	1.29	0.42
		HTC230	11.16	1320	87.41	12.26	0.18	1.09	0.46
		Pyro550	11.76	5710	87.63	11.79	0.37	0.67	1.16
Lignite fly ash	1:10	HTC190	6.98	991	65.83	23.61	1.25	2.49	1.26
		HTC230	7.53	784	65.83	24.33	1.16	2.42	1.34
	1:1	HTC190	10.02	684	81.43	11.82	0.41	1.76	2.31
		HTC230	9.97	574	83.84	10.35	0.30	1.28	2.06

Table 3 Plant nutrient concentrations (mg kg^{-1}) in the feedstocks and their resulting hydrochars produced at 190 and 230°C and pyrolysis chars produced at 550°C from pure and mixed materials derived from sewage sludge ($n = 1$).

mineral type	mineral ratio	process	P mg kg^{-1}	K mg kg^{-1}	Ca mg kg^{-1}	Mg mg kg^{-1}	Mn mg kg^{-1}	S mg kg^{-1}	B mg kg^{-1}
	Zeolite		58.5	14051	7346	348	20.8	113	2.66
	Fly ash		178	1221	194884	11855	795	27199	162
	Wood ash		7697	75652	272484	19250	4322	9246	243
	Raw sewage sludge		11152	1520	9342	3185	386	4120	19
Without mineral		HTC190	16262	1083	11704	4065	516	3496	38.2
		HTC230	18732	1570	14514	5100	626	3763	24.1
		Pyro550	24282	2970	17909	6602	792	4923	9.47
Zeolite	1:10	HTC190	16782	2970	15029	4630	528	4140	3.28
		HTC230	17012	3207	15219	4759	535	3825	3.26
		Pyro550	19712	5516	16804	5420	615	4154	9.16
	1:1	HTC190	5298	8483	7417	1260	134	1159	33.5
		HTC230	8149	7752	11459	2087	201	2076	52.3
		Pyro550	6897	11861	11939	2276	188	1529	60.4
	1:10	HTC190	15212	3262	30839	5287	841	4223	8.39
		HTC230	17292	3374	40499	6663	1036	5544	11.3
		Pyro550	20382	14892	57679	8181	1303	7854	35.2
Wood ash	1:1	HTC190	11072	12446	174434	14055	3096	4353	177
		HTC230	7451	10121	165534	12355	2740	4748	114
		Pyro550	10042	51129	181484	14165	3180	9859	186
Lignite fly	1:10	HTC190	15332	1640	25464	4653	541	5038	4.66

ash		HTC230	17082	1794	32039	5826	628	6622	5.14
	1:1	HTC190	736	996	127584	9095	716	24979	96.7
		HTC230	3564	923	113534	8462	702	20976	63.5

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Table 4 Plant nutrient concentrations (mg kg^{-1}) in the feedstock and their resulting hydrochars produced at 190 and 230°C and pyrolysis chars produced at 550°C from pure and mixed materials derived from CLO (n = 1).

mineral type	mineral ratio	process	P mg kg^{-1}	K mg kg^{-1}	Ca mg kg^{-1}	Mg mg kg^{-1}	Mn mg kg^{-1}	S mg kg^{-1}	B mg kg^{-1}
Without mineral	Raw CLO		4250	7788	64309	5255	484	10446	33.85
		HTC190	4297	1735	65609	5335	523	7498	9.31
		HTC230	4786	1737	65874	5063	506	7887	11.2
Zeolite	1:10	Pyro550	5376	9697	79224	6230	584	12356	35.7
		HTC190	4129	5048	59584	5070	466	7003	8.22
		HTC230	5006	6662	65499	5862	557	9369	9.76
	1:1	Pyro550	4648	10394	69729	5324	485	10098	56.5
		HTC190	1689	9323	33309	2076	184	3107	4.01
		HTC230	1993	9198	36774	2793	198	3113	5.81
Wood ash	1:10	Pyro550	1644	14739	36169	2419	200	4338	16.3
		HTC190	5093	3830	100764	6593	932	7930	22.7
		HTC230	5194	4129	93484	7408	888	7097	27.2
	1:1	Pyro550	5938	19276	115184	8885	1106	12794	84.9
		HTC190	4073	11726	169984	11745	2166	3149	151
		HTC230	5273	12336	171484	12735	2360	3813	154
Lignite fly ash	1:10	Pyro550	6364	53659	210284	14535	3176	10776	171
		HTC190	4861	2037	85534	6534	630	13299	19.7
	1:1	HTC230	4500	2079	88599	6428	580	11721	17.6
		HTC190	2029	1375	110584	7217	763	18666	75.6
		HTC230	2055	1488	119434	8181	692	19656	80.8

Fig. 1 Cross vitality parameters of Controls, raw feedstocks and pure minerals. Means and standard deviations of four replicates. Different letters indicate statistically significant differences ($P < 0.05$).

Fig. 2 Impact of HTC and pyrolysis treatment of sewage sludge (a-d) and CLO (e-h) on cress vitality parameters (without mineral addition). Means and standard deviations of four replicates. Different letters indicate statistically significant differences ($P < 0.05$). N.A. = not applicable.

536 **Fig. 3** Impact of HTC-derived BMCs from sewage sludge (Sew) and CLO with zeolite (Zeo), wood ash (W-ash) and lignite fly ash (F-ash)
537 on cress vitality parameters. Means and standard deviations of four replicates. Different letters indicate statistically significant differences
538 ($P < 0.05$) and asterisk indicate single measurement values. N.A. = not applicable..

Fig. 4 Impact of pyrolysis-derived BMCs from sewage sludge (Sew) (a-d) and CLO (e-h) on cross vitality parameters. Means and standard deviations of four replicates. Different letters indicate statistically significant differences ($P < 0.05$). N.A. = not applicable.

Highlights

- Effects of biochar-mineral composites on water cress germination were studied
- Addition of minerals can reduce the toxicity of HTC products
- Wood ash addition to pyrolysed compost can improve cress germination rate
- Wood ash addition to pyrolysed sewage sludge reduced cress germination rate
- Many pyrolysis-derived BMCs increased plant growth