PHYTOTOXICITY OF SEWAGE SLUDGE BIOCHARS PREPARED AT DIFFERENT PYROLYSIS CONDITIONS

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Pyrolysis of sewage sludge was carried out at three different lab-scale reactors and conditions: an Auger reactor for sewage sludge pyrolysis at low temperature (300ºC), a stirred batch reactor (530ºC) and a fluidised bed reactor (530ºC). The starting material is anaerobically digested and thermally dried sewage sludge from a wastewater treatment plant located in Spain. A preliminary study to assess the feasibility of application to soil of the three biochars was performed using two germination tests and a greenhouse experiment. Water soluble compounds from biochar did not affect seed germination, but volatile compounds reduced germination of more sensitive seeds. Biochar applied to soil at agricultural rates (20 t/ha) reduced growth and development of a corn crop. No differential effects of the three pyrolysis conditions were found.
Keywords: Phytotoxicity, sewage sludge, pyrolysis, biochar.

1 INTRODUCTION

Sewage sludge production has been continuously increasing in the EU. Consequently, adequate management and valorisation pathways are required for treating this residue. Land application has been used extensively in agricultural lands; however, the high amount of leachable metals and organic compounds in sewage sludge impose a limit to this practice [1]. As a carbonaceous material, sewage sludge can be pyrolysed to yield liquid and gaseous fractions that could be used as fuels, and a solid residue (biochar) that could be used as soil amendment [2]. Several authors have presented promising results in this direction; for instance, a very recent work by Zielińska and Oleszczuk reported a reduction in the PAH content of sewage sludge after pyrolysis, and a decrease in the toxicity of biochars, with certain exceptions [3]. Méndez et al. observed a reduction in the risk of heavy metal leaching if biochar was applied to soil instead of sewage sludge [4]. Hossain et al. reported a 64% improvement of tomato cherry production by applying sewage sludge biochar at 10 t·ha^{-1} [5]; however, Li et al. found (also for tomato) plant damage at higher rates due to a U-shaped dose response relationship between biochar dosage and seed germination/seedling growth [6]. Thus, biochar from sewage sludge may still inherit some of the undesirable characteristics (high metal, nitrogen and sulphur content, presence of hazardous organic compounds, amongst others) that may affect plant growth negatively. The physic-chemical characteristics of sewage sludge biochar have been extensively studied, taking into account the effects of pyrolysis temperature, reactor and type of sludge [7–11]. Also, studies dealing with metal content of biochars and its evolution during pyrolysis are available in the literature [12] It is known that heavy metal availability decreases after sewage sludge pyrolysis [13]; nevertheless, the heavy-metal content of sewage sludge and its biochar can severely limit its use as a soil amendment due to imposed legal limits [14]. However, information on the phytotoxicity of sewage sludge biochars has been scarce until very recently [3, 5–6], and to the best of our knowledge, none has studied the possible influence of the pyrolysis reactor on plant germination. Also, no studies on the toxicity of gaseous emissions from sewage sludge biochars can be found.

The aim of this preliminary study is to evaluate the phytotoxicity of several biochars prepared in three different pyrolysis reactors. Germination tests of corn seedlings were performed according to the procedure used by Rogowska et al. [15]. Gaseous emissions toxicity tests were carried out following the procedure described by Kamann et al. from other types of biochar [16].

2 EXPERIMENTAL

2.1 Materials: Sewage sludge

Table I: Sewage sludge characteristics

		Standard	mass fraction %
Proximate analysis	Dry matter	ISO-589-1981	93.5
	Ash	ISO-1171-1976	39.0
	Volatiles	ISO-5623-1974	50.1
	Fixed Carbon	[a]	4.4
Ultimate analysis	Carbon	[b]	29.5
	Hydrogen	[b,c]	4.7
	Nitrogen	[b]	5.3
	Sulphur	[b]	1.3
	Oxygen	[d]	20.2
HHV (MJ·kg^{-1})		ASTM D-3286-96	12.8
Ash mineral composition[e]	Al	[f]	5.1
	Ca	[f]	6.5
	Fe	[f]	18.6
	K	[f]	1.4
	Mg	[f]	1.7
	Na	[f]	0.4
	P	[f,g]	7.6
	Si	[f]	12.2
	Ti	[f]	0.4

[a] By difference. [b] Using a Carlo Erba 1108. [c] Includes hydrogen from moisture. [d] O (mass fraction %) = 100 – C (mass fraction %) - H (mass fraction %)- N (mass fraction %) – S (mass fraction %) - Ash (mass fraction %). [e] Ash was obtained at 815 °C. [f] Analyzed by ICP-AES. [g] Measured in dry sewage sludge.

Anaerobically digested and thermally dried sewage sludge was supplied from a wastewater treatment plant located in Madrid, Spain. After grinding and sieving, the fraction with particle size between 250 µm and 500 µm was selected for pyrolysis experiments. Table I shows the proximate and ultimate analyses, the higher heating value and the metal content of the sludge.

2.2 Pyrolysis experiments

Three different laboratory scale systems were used, namely Auger Reactor (AR), Fluidized Bed Reactor (FBR) and Stirred Batch Reactor (SBR).

Low temperature pyrolysis (i.e., torrefaction) was performed in the AR at 300 ºC. This experimental system was operated at a feed rate of 1 kg·h^{-1}, which corresponds to a solid residence time of around 35 min in the reaction zone. A nitrogen flow of 1 L$_{(STP)}$·min^{-1} was used as purge gas. Further details about the experimental system can be read elsewhere [17].

Fluidised bed pyrolysis was done using the ~1 kg·h^{-1} experimental system (FBR) previously used by Atienza-Martínez et al. [18, 19]. The pyrolysis temperature was 530 ºC and the average residence time of the solids was 5.7 min. A nitrogen flow of 4.5 L$_{(STP)}$·min^{-1} was used as fluidising gas.

Fixed bed batch pyrolysis was performed in the SBR. The experimental system is shown in Figure 1. Around 1 kg of sewage sludge was pyrolysed to a final temperature of 530 ºC at a heating rate of around 8 ºC·min^{-1}. Once reached, the final temperature was held for 30 minutes. A nitrogen flow of 1 L$_{(STP)}$·min^{-1} was used as purge gas.

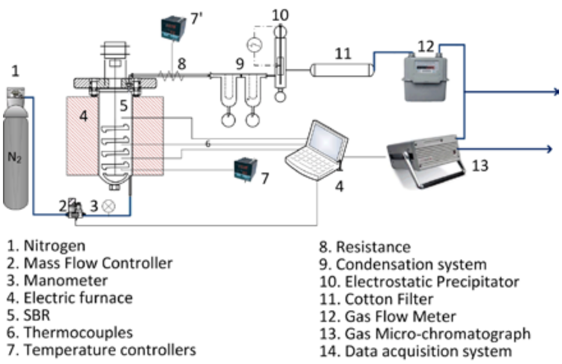

Figure 1: Diagram of the SBR pyrolysis plant

Three repetitions were made for each experimental system, for the sake of reproducibility and to ensure the production of sufficient amounts of biochar in order to perform the germination and gas phytotoxicity assays.

Ash content, higher heating value and elemental composition of chars were determined using the methods previously shown in Table I**.**

2.3 Corn germination assays

To evaluate the effects of biochar on seedling growth, corn seeds (*Zea Mays* L.) were germinated in aqueous extracts of the produced biochars, as described by Rogovska et al. [15]. Firstly, biochar extracts (BS) were prepared using 20 g of biochar and adding water to a 1:30 dilution. Each solution was shaken for 5 minutes, equilibrated during 24 hours and then filtered. For each extract, pH, electrical conductivity and nutrient compositions were measured.

Nutrient solutions (NS) were prepared reproducing the measured nutrient content of each one of the biochar extracts, in order to distinguish the specific effects of inorganic compounds and pH on seedling growth.

Germination tests were carried out using BS, NS and distilled water (DW, control) as moistening medium. In each test, 12 corn seeds were placed between two sheets of germination paper in a Petri dish and moistened with approximately 5 mL of solution. The dishes were sealed and placed for 7 days in in a germination chamber which was maintained dark and at a constant temperature of 25 ºC. Every 48 hours, additional solution or distilled water was added. Each test was replicated 4 times. Germination was considered successful if the length of both shoot and radicle was at least 5 mm.

2.4 Gaseous phytotoxic emissions test

Additional germination and growth tests were made to assess the effect of gaseous phytotoxic emissions from biochar. The system used in this work is similar to the one described by Busch et al. [16]: 130 g of biochar were put in an aluminium container and water was added to 50% of its maximum water holding capacity (WHC). The char container was hung in the middle of a 500 mL vessel. Fifty Cress seeds (*Lepidium Sativum* L.) were placed in a piece of cotton above the char compartment, and constantly moistened by connecting the pad (by means of strips of cotton) to a distilled water reservoir at the bottom of the vessel. The setup is shown in **Figure 2**.

The system was sealed, introduced in a germination chamber (SCLAB PGA-180) and maintained for 10 days at 18-20 ºC and 3000 lux in a 12h day cycle. Due to the high amount of biochar needed, the tests were only replicated twice. It was considered that no toxic effects were detected if fresh weight was at least 80% of the one corresponding to control treatment.

Additional tests were also made with corn seeds (6 seeds per test), using the same procedure.

Figure 2: Setup of the gaseous emission tests.

2.5 Pot experiments with corn

Greenhouse experiments using 1 L pots (10 corn seeds per pot) and soil taken from the experimental facilities at CITA, Zaragoza, were conducted applying a biochar rate of 20 t·ha^{-1}. The three types of sewage sludge biochar (AR, FBR and SBR) were tested, and a control experiment without biochar was also performed. The soil was air dried and then mixed thoroughly with biochar. Corn was watered regularly every 2 days, and grown during three weeks. Afterwards, it was harvested, oven-dried at 45 °C during 48 hours, and weighed.

3 RESULTS AND DISCUSSION

3.1 Pyrolysis yields and product characteristics

The three pyrolysis systems gave different biochar yields with the compositions shown in Table II. As expected, torrefaction in AR produced the highest biochar yield, lowest ash content and highest C content. Pyrolysis at 530 ºC in FBR and SBR produced similar biochar yields, ash percentages and higher heating values (HHV), but significant differences mainly in C and O content (although the latter was determined by difference).

BET surface areas (not shown) were below 20 $m^2 \cdot g^{-1}$ for all biochars.

Table II: Biochar characteristics

		AR	FBR	SBR
Char yield (mass %)		63.8	49.0	51.0
Ash (mass %)		58.6	74.7	74.0
Ultimate analysis	Carbon	27.90	17.48	21.00
	Hydrogen	2.68	1.14	0.90
	Nitrogen	3.82	2.31	2.50
	Sulphur	1.08	1.30	1.30
	Oxygen (diff.)	5.92	3.07	0.30
HHV (MJ/kg)		12.50	7.30	7.81

As explained in the previous section, aqueous solutions (BS) were prepared from each biochar. Their pH, electrical conductivity and nutrient composition (dissolved inorganic content) are shown in Table III. These values were used as a reference for the preparation of the nutrient solutions (NS).

Table III: Characteristics of the nutrient solutions.

		AR	FBR	SBR
pH		7.20	7.30	8.30
EC	(mS/cm)	0.20	0.36	0.18
NH_4^+	(mg/L)	10.0	4.5	0.1
Na^+	(mg/L)	3.6	9.5	4.3
K^+	(mg/L)	4.8	9.3	3.2
Ca^{2+}	(mg/L)	21.8	38.4	15.0
Mg^{2+}	(mg/L)	2.0	6.2	3.9
Cl^-	(mg/L)	10.1	20.6	24.2
CO_3^{2-}	(mg/L)	n.d.	n.d.	n.d.
HCO^{3-}	(mg/L)	45.8	47.0	42.7
PO_4^{3-}	(mg/L)	0.6	0.6	1.1
SO_4^{2-}	(mg/L)	49.4	92.5	n.d.
NO_3^-	(mg/L)	<0.1	0.6	0.5

3.2 Germination tests

Figure 3 shows the results of the corn seed germination tests performed with the aqueous biochar extracts (BS) and nutrient solutions (NS). Control tests produced 83.3% ± 9.58% germination. Results using BS from either AR, FBR or SBR are not statistically different from the control results; thus, no negative effects of these extracts have been observed on corn germination.

Regarding the NS prepared, the high variability within the results of NS-AR does not allow to draw a conclusion about its effect on germination. In contrast, a statistically significant, positive effect was observed for NS-FBR and NS-SBR. This fact suggests that the nutrients leached from sewage sludge biochars might positively impact germination. However, comparison with BS results suggests a counter effect of other compounds present in these extracts that offsets the positive effect of nutrients. It has been previously shown that heavy metals and organic compounds can be leached from sewage sludge biochars [20] (although their amount of is dramatically lower than that from sewage sludge).

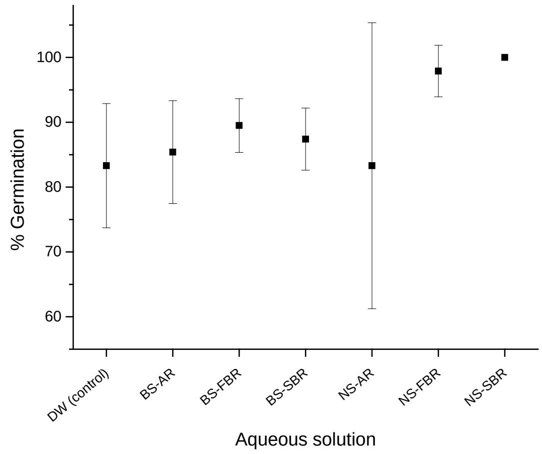

Figure 3: Germination results (% of corn seedlings with radicle & shoot over 5 mm) using BS and NS.

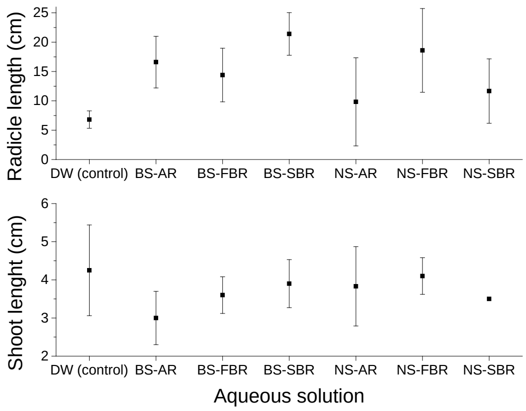

Figure 4: Germination results (radicle and shoot length) using BS and NS.

The average lengths of shoots and radicles from these tests are presented in Figure 4. It is worth noting that the application of all the BS extracts produces a statistically significant, positive effect on radicle length; whereas for the NS laboratory-made nutrient solution, only NS-FBR shows a noticeable improvement in this parameter. Thus, the AR and SBR biochars produce an improvement in radicle length that is not attributable to the leached nutrients. The reason for this behaviour might be in the presence of low concentrations of several metals or organic compounds that induce growth and resistance to stress (Hormesis effect), whereas high concentrations lead to harmful effects. This effect was hypothesised in similar works with other types of biochars [6, 21].

Phenols, other aromatic compounds, PAHs and heavy metals, amongst others, are mentioned as a possible cause. Heavy metals tend to concentrate in biochar after pyrolysis [3, 14], and some of them may be leached (although the leaching toxicity decreases with pyrolysis, compared to raw sewage sludge [13]); whereas a wide range of organic compounds are condensed in sewage sludge bio-oil [17–19, 22], part of which may remain in biochars and may be leached afterwards.

Regarding shoot length, none of the extracts produced a distinguishable effect, either positive or negative, in this parameter. Thus, the mentioned Homesis effect may only have significant impact in radicle growth.

Figure 5: An example of germination tests: one of the runs using BS-FBR, showing shoot and radicle growth.

3.3 Gaseous emissions tests

Results from the germination tests carried out with cress and corn seeds to assess possible phytotoxic gaseous emissions are presented in Figure 6.

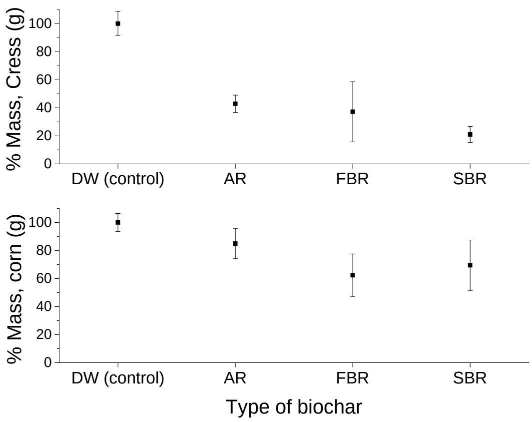

Figure 6: Gaseous emissions results (mass of germinated seeds).

Interestingly, it was observed that germination of both types of seeds under these conditions was rather poor. In most cases, the final mass was clearly lower than the control treatment and germination was also worsened. This was especially true for cress seeds (Figure 7), with around a two-fold decrease, whereas corn seeds showed a less dramatic mass difference.

The different germination behaviour, compared to the previous tests with aqueous extracts, deserves further consideration. The aqueous biochar extract solutions were prepared and let 24 h to equilibrate (see Section 2.3). During this long time at ambient temperature, several volatile compounds might have leached from the chars and evaporated. Thus, the aqueous extracts might be free of these hypothetic compounds. In contrast, any volatile evolution in the gaseous emission tests would have started at the beginning of the experiment (at the moment that the char is wetted), so these volatiles would have been in contact with the seed pad placed just above the biochar compartment.

Figure 7: Some gaseous emissions experiments using cress seeds: (a) control, (b) AR biochar, (c) FBR biochar, (d) SBR biochar.

3.4 Pot experiments

After three weeks, the percentage of corn seeds germinated in the pot experiments was similar to the previously reported values from germination tests in Petri dishes (see Section 3.2).

Results of the greenhouse experiments using pots are shown in Figure 8. At the mentioned application rate of 20 $t \cdot ha^{-1}$, corn above-ground biomass was significantly lower than control experiments when any of the tested biochars were used. As can be seen in the Figure, only around 40-50% of the reference mass was achieved in the biochar tests. Comparing between biochar types, a small but statistically relevant difference was found between FBR and AR biochars, the former being less detrimental for corn above-ground biomass.

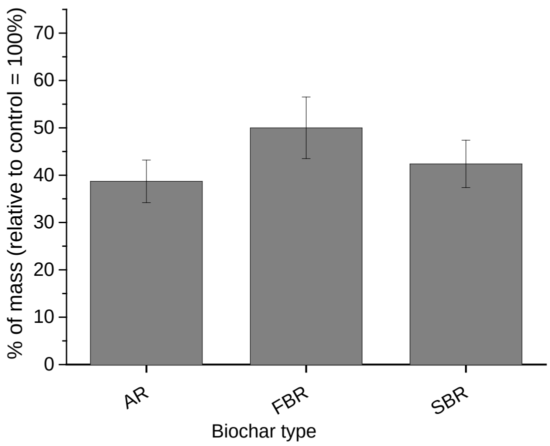

Figure 8: Biomass mass reduction in pot experiments using biochars (100% mass = control experiment)

The negative effect on plant growth might suggest an excessive biochar application rate. However, other authors have reported increased plant growth with sewage sludge biochar rates as high as 216 $t \cdot ha^{-1}$ [23]. The leaching of volatile compounds, as explained in the gaseous emissions Section, could also play a role in the observed biomass decrease. Further research, including varying the biochar application rates, would be necessary in order to assess soundly the possible use of these biochars in agriculture.

4 CONCLUSIONS

A preliminary study on the phytotoxicity of sewage sludge biochars has been conducted with simple and easily repeatable tests available in the literature. Corn seed germination in aqueous solutions prepared from biochars did not show significant differences against the nutrient solutions and the control test (distilled water). Thus, germination of corn was not negatively affected by any of the biochars. However, gaseous emissions from biochars affected significantly corn and cress germination. The negative effect was clearly greater in the more sensitive cress seeds, and might be attributed to the release of volatile compounds right after leaching with water. On the germination tests, no statistical differences amongst the three types of pyrolysis conditions were detected. Finally, a first laboratory test on application of biochars to soil (20 tons per hectare) showed negative effects on corn growth, with a significant decrease in plant weight of more than 50% regardless of the biochar type.

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7 LOGO SPACE

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