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*Published in:*  
Journal of Environmental Chemical Engineering

*Link to article, DOI:*  
[10.1016/j.jece.2018.10.064](https://doi.org/10.1016/j.jece.2018.10.064)

*Publication date:*  
2018

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Hitzl, M., Mendez, A., Owsianiak, M., & Renz, M. (2018). Making hydrochar suitable for agricultural soil: A thermal treatment to remove organic phytotoxic compounds. *Journal of Environmental Chemical Engineering*, 6(6), 7029-7034. <https://doi.org/10.1016/j.jece.2018.10.064>

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Hitzl, M.; Mendez, A.; Owsianiak, M.; Renz, M. Making hydrochar suitable for agricultural soil: A thermal treatment to remove organic phytotoxic compounds. *J. Environ. Chem. Eng.* 2018, 6, 7029–7034, doi:10.1016/j.jece.2018.10.064.

Making hydrochar suitable for agricultural soil: a thermal treatment to remove organic phytotoxic compounds

Martin Hitzl,<sup>a</sup> Ana Mendez,<sup>b</sup> Mikołaj Owsianiak,<sup>c</sup> Michael Renz\*<sup>d</sup>

<sup>a</sup>Ingelia, S.L., C/Jaime Roig 19, 46010 Valencia, Spain

<sup>b</sup>Departamento de Ingeniería Geológica y Minera. E.T.S.I. Minas y Energía. Universidad Politécnica de Madrid, C/Ríos Rosas, nº21, 28003, Madrid

<sup>c</sup> Division for Quantitative Sustainability Assessment, Department of Management Engineering, Technical University of Denmark, Bygningstorvet, Building 116B, DK-2800 Kgs. Lyngby, Denmark

<sup>d</sup> Instituto de Tecnología Química (UPV-CSIC), Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 Valencia, Spain; E-mail: mrenz@itq.upv.es

## Abstract

Unlike biochars, hydrochars often have initial phytotoxic effects that prevent their being directly applied to soil, an undesirable property thought to be due to the volatile organic compounds they contain. Thermal treatment in the 200 to 600 °C temperature range was proposed for mitigation purposes and it was shown that at a temperature of 275 °C phytotoxicity is eliminated from the carbonaceous solids. The phytotoxic property was “recovered” or maintained in the separated liquid, which can be used to

generate heat in the HTC process, thereby achieving the safe disposal of harmful compounds at no additional cost. The post-treatment unlocks the potential of transforming the organic fraction of municipal solid waste into a soil amendment product in a zero-waste process.

The absence of phytotoxicity was confirmed by the Zucconi method on seed germination. A gas-chromatographic method was also developed, based on the quantification of the total amount of substances detected by desorption, for a rough but quick estimation of hydrochar phytotoxicity. It was shown that the absence of these volatile compounds is in line with the absence of phytotoxicity as evaluated by the Zucconi method.

#### Keywords

Circular economy; hydrothermal carbonization; OFMSW; waste treatment.

## 1. Introduction

Carbon derived from renewable biomass, the so-called *biochar*, has been recommended as a climate change mitigation tool [1–4]. Biochar is considered to sequester carbon from the atmosphere into the soil. This carbon is the carbon dioxide taken from the atmosphere during plant growth. It can then be “fixed” in the solid residue during a thermochemical transformation of the biomass at temperatures between 180 and 700 °C. Removing carbon dioxide from the atmosphere reduces the concentration of greenhouse gas (GHG) in the medium term and thus has a mitigating effect on climate change, while adding biochar to soil induces carbon sequestration, thanks to its stability [5].

Applying carbon to soil improves soil health and fertility, which is advantageous for agricultural production. As soils containing charcoal, such as *terra preta de Indio*, are known for their high levels of soil fertility [4], it was considered that biochar would have the same effect and this gave rise to studies on using it to enrich soils.

Many studies have now proved this hypothesis to be true: biochar improves the composition and water retention and increases nutrient uptake and crop yields [6–9] and also modifies soil microbial habitats and supply nutrients to soil microbes [10]. It has been said that biochar can be considered “as a slow releasing reservoir of nutrients in soils” [2,11]. However, at the same time warnings have also been given that its composition depends largely on the feedstock and that contamination may occur due to the presence of heavy metals and toxic compounds [9].

Hydrochar is a particular type of biochar with a unique feature: it is produced in an aqueous atmosphere by hydrothermal carbonization (HTC) [12–14]. The presence of water during the process makes it suitable for the transformation of residual wet lignocellulosic biomass, whereas drier feedstocks are preferred for other thermochemical transformations, such as torrefaction or pyrolysis. Prior to these latter processes, the biomass has to be dried thermally, i.e. the water must be removed, with serious disadvantages for the economic and ecological balance, which increase in proportion to the amount of water it contains.

Due to their significant impact, wet feedstocks are in themselves a serious concern for climate change: during composting or uncontrolled decomposition (e.g. in landfills) greenhouse gases are emitted, especially methane [15–18]. Using these feedstocks in a different way would avoid these GHG emissions, for example, applying HTC to wet lignocellulosic feedstocks to be used as a soil conditioner would have a threefold mitigation effect on climate change: carbon sequestration, improved crop yields (which in a system perspective is seen as a benefit through, for example, reducing fertiliser inputs) and avoiding the GHG emissions released during bio-degradation of wet resources.

However, using pristine hydrochar to improve crop yields is not as straightforward as it seems at first glance [11]. Unfortunately, with some exceptions, pristine hydrochars have a phytotoxic effect on plant growth. For instance, it has been found that the hydrochar water content is highly phytotoxic and has negative effects on seed germination and plant growth [19]. Hydrochar was considered to be unsuitable as a

soilless medium for tomato cultivation due to its negative effects on plant growth and fruit yield [20]. The same negative influence was also confirmed in cress germination tests for gaseous phytotoxic emissions, in barley germination and salad germination growth tests and in earthworm avoidance tests for toxic substances [21]. Although a number of examples of the poor performance of hydrochar *versus* biochar derived from pyrolysis can be found in the literature, there are also cases which permit a more optimistic view.

In one study phytotoxicity was only found to be relevant during the initial period of application. When barley was regrown after harvesting, positive results were observed in plant growth instead of the negative results found in the first cultivation cycle [21]. Although this was unexpected, it stimulated the search for a remedy for hydrochar's phytotoxic effects, and it was found that simply washing with nitric acid was enough to eliminate the negative effects on plant growth. When employed as a soilless growth medium it was found to stimulate seedling growth, unlike in the control experiment [19]. Co-composting of hydrochar also eliminated organic pollutants [22]. These procedures confirmed that hydrochar also has beneficial effects in soil amendment, although a removable component masks the benefit due to its predominantly phytotoxic properties.

The main problem related to the attenuation of its undesirable properties is that the detrimental substances have not been identified and it is not known if the effect is due to a single highly phytotoxic substance or, which is more likely, to the accumulation of various harmful substances. In addition, the classical contaminants, such as heavy

metals, dioxins or polyaromatic hydrocarbons (PAH), were only detected in low concentrations [22]. Single substances, phenolics (e.g. guaiacol or 3-methoxyphenol) have been identified and used as markers of phytotoxicity in HTC process water [23]. Short chain aldehydes, ketones and furanics have been detected by headspace thermal desorption from the solid, coupled to gas chromatography-mass spectrometry (GC-MS) [24,25]. There is thus a need for a quick but reliable wide-ranging analysis to evaluate hydrochar phytotoxicity. A second drawback related to the cost of removing toxic substances is that even though the procedures are simple they involve additional costs. Washing hydrochar produces a wastewater stream that poses environmental risks due to the presence of these phytotoxic substances. Although these compounds are thought to degrade during composting, this process requires a large area of land since it is relatively slow and can last for months, in addition to which it may also give off unpleasant smells.

From the above it can be concluded that hydrochar has a great potential for climate change mitigation when applied to soil, and this has even been quantified by a life cycle assessment [26]. However, intrinsic phytotoxicity requires post-treatments which are easy to carry out but further increase production costs. The purpose of the present work was thus to make hydrochar suitable for soil application by means of a simple post-treatment.

We here describe a novel moderate temperature post-treatment of hydrochar (<300 °C) that eliminates undesired properties and allows the use of residual wet biomass for soil amendment. Using the detection principle of a new analysis method based on the



soft desorption of the potentially toxic compounds, a procedure based on thermal treatment was developed for producing refined non-toxic hydrochar suitable for soil amendment material. The absence of phytotoxicity was confirmed by Zucconi tests on seed germination [27]. We also show that this undesirable property is “maintained” in the eliminated liquid. The side stream of the hydrochar upgrading is quite concentrated and as it contains mainly organic material it can be used directly for heat generation, with benefits for the energy balance of the process and avoiding additional disposal costs.

## 2. Materials and Methods

### 2.1 Thermal finishing treatment

A nitrogen down-flow (approx. 100 mL/min) was applied to hydrochar pellets (20 to 30 g) placed on a porous glass frit in a tubular quartz reactor. The reactor was heated to the desired temperature in the range from 200 to 600 °C at a rate of 3 K/min and the temperature was maintained for 0 or 1 hour. The sample was then allowed to cool down to room temperature while maintaining the nitrogen flow. The solid obtained was labelled as refined or advanced hydrochar. During the treatment a liquid can be condensed, consisting of an aqueous and an organic phase, which separate slowly on standing. Mass yields for the solid (refined hydrochar) and for the liquid depend on the temperature of the treatment and are specified in Table 1.

For the treatment of hydrochar (30.7 g) at 275 °C, a liquid was condensed at the reactor outlet at –78 °C. The amount collected (6.79 g) accounted for 22% of the mass yield and 1.01 g (16% of the liquid and 3.2% of the initial starting material) was water. In this case, 22.5 g of refined hydrochar remained (73.5% mass yield).

The thermal treatments of the GP-1 and GP-2 samples were carried out on smaller scale, with 15.3 g and 9.10 g, respectively. Recovery of the solid carbon material was in the same range as previously, with 77.2% and 81.8% mass yield, respectively.

### 2.2 Evaluation of phytotoxicity by chromatographic means

This analytical procedure indirectly estimates the phytotoxicity of hydrochar samples with the aim of obtaining a faster response than it is possible with germination tests,

which may last for days. The procedure is based on the hypothesis that the phytotoxic substances are volatile compounds at temperatures up to 200–300 °C. Their presence is thus quantified by chromatographic means, whatever their degree of phytotoxicity.

The hydrochars were analysed by means of a CDS 5000 Series Analytical Pyroprobe equipped with a ¼" Pt coil filament. 1 mg of the sample was placed in a quartz probe tube and heated to 120, 140, 160, 180, or 200 °C for 2 h, employing hydrogen as the carrier gas. The pyrolyzer was connected to a two-dimensional Agilent 7890 gas chromatograph in which the products were analysed online. The GC apparatus was equipped with an HP Innowax column (30 m x 0.250 mm x 0.25 µm) as the first column and a DB-5 as the second (5 m x 0.250 mm x 0.25 µm, placed in an LTM oven) with a capillary-flow modulator connecting both columns. The system incorporates two detectors, one fast detection FID for quantification and one Agilent Technologies 5977A mass selective detector to identify single compounds. The results of the analyses were visualised and handled by means of GC image software.

### 3. Results and Discussion

#### 3.1 Chromatographic estimation of the presence of potential phytotoxic substances

Estimating the phytotoxic effects of materials is indispensable, although somewhat time-consuming due to the long plant response time, which means that analyses can last several days, even for relatively fast seed germination experiments. A novel, chromatographic prediction method was thus required to provide the maximum

information on as many compounds as possible. For this end an analysis was carried out to detect any water soluble and volatile substances that could hinder plant growth.

Although the volatile content of carbons is generally determined by a standard method, its results are better suited to predicting or characterising combustion properties, since the analyses temperatures can reach 900 °C, which cause undesirable pyrolysis reactions in the case of volatile adsorbed molecules. The simplest method of quantifying a volatile content in a lower temperature range is by thermogravimetric analysis (TG), however this method provides no information on the substance removed from the solid. This method was therefore discarded in favour of a combination of desorption together with a gas chromatographic analysis.

An analytical pyrolyzer desorption technique was used to treat 1-mg samples in the 120–200 °C temperature range, connected to a gas chromatograph with a micro-fluidal modulator to provide two-dimensional images (Figure 1). This system facilitated the grouping of similar compounds for a deeper evaluation of the compounds at a later stage. To start with, all the organic compounds were considered as target compounds, regardless of their toxicological properties, for two reasons: the worst contaminants had not yet been identified, and the phytotoxic properties of some of the identified compounds were unknown.

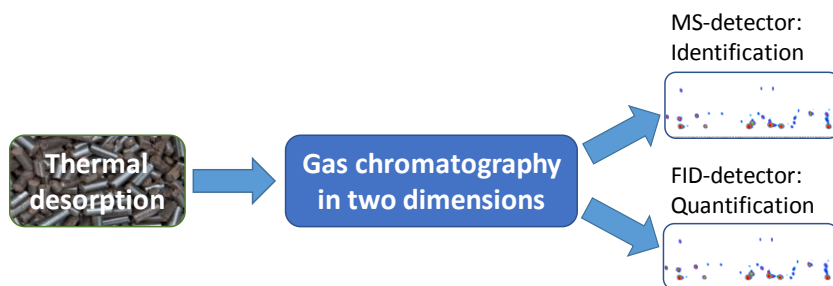


Figure 1. Schematic description of the analysis procedure.

To select the best desorption temperature, the analysis started at 120 °C and rose in 20-K steps. The hydrochar studied was the organic fraction of municipal solid waste (see Supplementary Material). The total number of compounds detected increased with a pronounced gain from 180 to 200 °C. At 200 °C a higher number of higher weight compounds was detected, together with new lower weight substances, due to the fragmentation reactions induced by pyrolysis in the solid material of the more labile moieties. These reactions eliminated the higher weight material and produced highly volatile substances. As these thermal modifications at 200 °C were undesirable, the desorption temperature was set at 180° C for the entire study.

In the first attempt to validate the analytical method, comparative samples were prepared by washing pristine hydrochar at different pH (pH 3.5, pH 6.0, pH 9.5 and deionized water) to remove the phytotoxic substances. The subsequent analysis confirmed that on average 50% of the initial volatile compounds had been eliminated (see Supplementary Material) and validated the analysis procedure, although the efficiency of the washing method had not been confirmed or optimised. However, the results showed that it was necessary to test whether desorption of the volatile

substances would eliminate the phytotoxic substances, as suggested by the results of the proposed analytical method.

### 3.2 Thermal elimination of substances hindering plant growth

With the aim of developing a simple general method of eliminating phytotoxic compounds from pristine hydrochar, the carbonaceous material was treated at different temperatures in the range from 200 to 600 °C to remove increasing amounts of gases and liquids. At 200 °C 12% of the mass was lost and 40% at 300 °C (Table 1, Entries 2 and 5). The standard analysis of volatile content for carbon, although carried out at higher temperature (900 °C), confirmed that this part had been clearly reduced. A value close to zero was not reached, since the pyrolysis reactions still removed labile, higher weight content during the procedure. As the volatile content diminished, the fixed carbon content increased with increasing temperatures. For instance, after treatment at 300 °C the fixed carbon value had increased by 60% over the pristine hydrochar value, by 30.7% versus 18.8%, respectively (Table 1, Entry 5). Inorganic elements, especially Ca, Al, Fe, and Si, were concentrated successively within the carbon material when the treatment temperature was raised (see Table S1, Supplementary Material). This is due to the elimination of volatile matter, as occurs in biochar produced from sewage sludge at different temperatures [28,29].

Table 1. Physico-chemical properties of hydrochar treated at different temperatures.

Entry	Hydrochar treatment temp. [°C]	Mass loss [wt%]	Volatile Matter <sup>b</sup> [wt%] <sup>e</sup>	Ash Content <sup>c</sup> [wt%] <sup>e</sup>	Fixed Carbon <sup>d</sup> [wt%] <sup>e</sup>
1 <sup>a</sup>	--		68.2	13.2	18.8
2	200	12.3	63.9	14.5	21.7
3	250	26.8	57.3	17.4	25.4
4	275	28.3	55.3	17.4	27.3
5	300	39.6	47.7	21.6	30.7
6	400	57.6	26.5	29.9	43.6
7	600	64.3	12.8	35.9	51.3

<sup>a</sup> Parent sample (pristine hydrochar). <sup>b</sup> Determined by heating to 900 °C for 7 min in a closed vessel. <sup>c</sup> Ash determined by heating to 815 °C for 1 h in air. <sup>d</sup> Calculated as dry hydrochar minus Ash and Volatiles. <sup>e</sup> Based on dry solid.

After the treatment, the refined hydrochar had lost its characteristic smell, even at the lowest treatment temperatures. Compounds like guaiacol and its methylated and methoxylated derivatives, which smell smoky and vanilla-reminiscent, were detected by GC-MS in the condensed liquid. The treatment can thus be said to reduce hydrochar's characteristic smells and can be considered as facilitating the use of hydrochar as a solid fuel, since the smell of pristine hydrochar can be unpleasant and may involve health issues.

The effluent obtained was a relatively concentrated organic stream which could be used to produce energy. This has two advantages for the entire HTC process: first, a waste stream is avoided, which is of paramount interest, as the separated compounds probably involve environmental issues. In contrast, treatments such as washing create wastes that have to be disposed of. Secondly, the plant's energy balance can be improved and made independent of external energy sources (provided that the heat demand of the second process can be supplied by the flue gas from the central heating unit). The power available for this purpose should be estimated roughly.

The liquid products' energy was estimated on the basis that the heating energy of the pristine solid is maintained within the solid product and effluents, so that the energy balance was determined with the mass balance and the heating values of the refined hydrochars (see Figure 2). It can be seen that in the finishing temperature range of 250 – 300 °C, 30 – 40% of the energy contained in pristine hydrochar is eliminated from the solid. This can thus be utilized to generate heat for the HTC process and finishing, which was estimated to be approximately 25% of the energy contained in pristine hydrochar [30]. This rough estimation confirmed that the finishing process can be implemented in the traditional HTC process and that interesting synergies could be created. A graphical description of the production process of advanced hydrochar with the proposed energy management system is depicted in Figure 3.



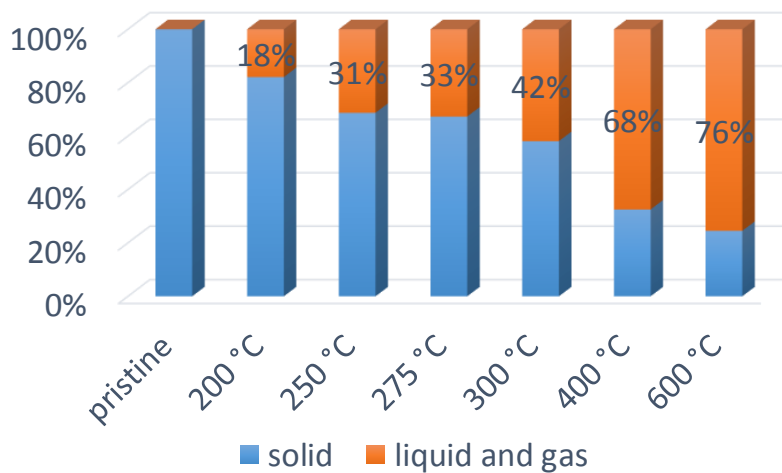


Figure 2. Energy distribution between solid and liquid/gaseous effluent of the finishing process, based on the higher heating value (HHV) of the solid and mass balance.

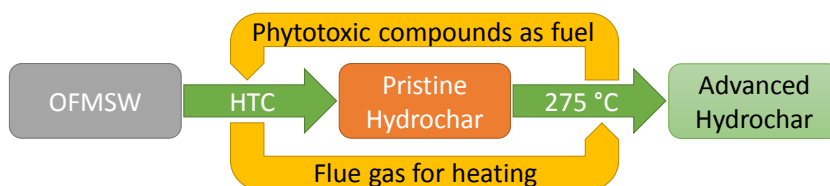
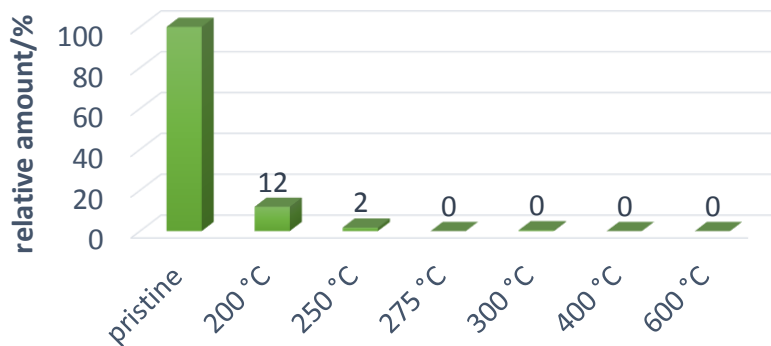


Figure 3. Scheme of the production process for advanced hydrochar without phytotoxic properties. In the first step lignocellulosic biomass such as the organic fraction of municipal solid waste is transformed by hydrothermal carbonization to produce pristine hydrochar and then treated thermally (in the absence of water) to obtain advanced hydrochar. The co-produced liquid stream, involving phytotoxic and malodorous substances can be used to generate heat for the HTC process. The second thermal process can be powered by the flue gas from the first.

As the finishing process was designed to eliminate phytotoxic substances, its efficacy should be evaluated by the chromatographic method, involving desorption in a pyrolyzer and subsequent gas chromatographic analysis. Figure 4 shows that, as

expected, the treatment effectively removes the volatile organic substances. After the treatment at 200 °C almost 90% of the compounds had been desorbed and at 250 °C this proportion was 98%. At higher desorption temperatures no further volatile compounds were detected, so that 275 °C was considered as the standard temperature for the production of refined hydrochar.



*Figure 4. Relative amounts of organic compounds desorbed during analysis at 180 °C and a heating ramp of 20 K/ms. Temperatures are those of the thermal treatment to produce advanced hydrochar samples.*

Once having optimised the removal of potentially phytotoxic organic compounds, it only remained to confirm the success of the process by tests on plant seeds.

### 3.3 Evaluating the phytotoxic properties of hydrochar samples

The Zucconi test was applied to determine the phytotoxic properties of the hydrochar samples. The numbers of germinated seeds exposed to aqueous extracts of the samples were counted, the length of the roots were compared to a blank experiment

and the germination index (GI) was calculated. In general, the GI values were classified into high (GI < 50), moderate (50 < GI < 80) and non-confirmed phytotoxicity (80 < GI < 100). The material can be considered as phytonutrient or phytostimulant when these values are over 100.

The results of the test are given in Figure 5. The high phytotoxic potential of pristine hydrochar was considerably reduced after the treatment at 200 °C. For the treatments at higher temperatures, phytotoxicity was completely absent and different degrees of phytostimulation were detected in all cases, i.e. in the 250 – 600 °C temperature range. When the liquid waste was tested for phytotoxic properties it was found to be highly phytotoxic and prevented any germination, confirming that the thermal treatment did not destroy the phytotoxicity but transferred this property to the waste.

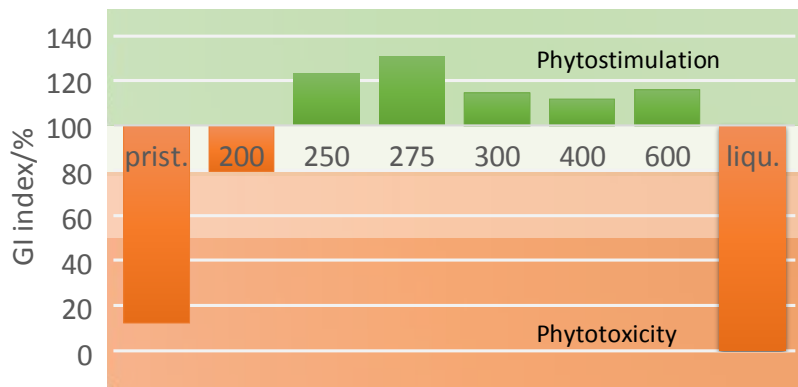


Figure 5. Results of the Zucconi test applied to hydrochar samples and the liquid effluent of the treatment at 275 °C. Classification: < 50% high phytotoxicity, 50–80 moderate phytotoxicity, 80–100 absence of phytotoxicity, >100 phytostimulation. Temperatures are those applied during the thermal treatment to produce advanced hydrochar.

A range of desorbed compounds was identified by mass spectrometry (see Supplementary Material) and they were similar to those identified by Berge et al. in HTC process water [31]. This effluent consisted of either aldehydes, cyclic ketones (e.g. 2,3-dimethyl-2-Cyclopenten-1-one or 2-Cyclopenten-1-one) or monoaromatic compounds with aliphatic moieties and were similar to other compounds known to be ecotoxic to various freshwater organisms [32].

The phytotoxic properties of the different hydrochar samples had already been evaluated by a chromatographic procedure and predicted a very low amount (2% of the initial amount) in the sample treated at 250 °C and the complete absence of phytotoxicity for higher treatment temperatures. The Zucconi test results fit well with these predictions and validate the suitability of this analysis for predicting the phytotoxicity level of hydrochar samples.

In order to extrapolate the thermal treatment to other types of hydrochar samples, two samples of garden pruning biomass (GP-1 and GP-2) were treated at 275 °C, giving phytotoxicity levels of 41 and 48, respectively, for pristine hydrochar. After the treatment, these values rose to 89 and 83, indicating absence of phytotoxicity.

#### 3.4. Implications for environmental performance and energy balance

The production of advanced hydrochar requires an additional energy supply for the thermal treatment, which increases the potential environmental impact, including climate change. A previous life cycle assessment study on hydrochar use in agriculture showed that from a climate change perspective the benefits of carbon sequestration and temporary storage outweighed the impacts of hydrochar production, transport

and application to soils [26]. In Spain, the difference between climate change benefits and climate change impacts is equal to 1 kg CO<sub>2</sub>, achieved with the application and temporary storage of 1 kg of biogenic HTC carbon for a temperate agricultural soil (or treatment of 6 kg of wet green waste with a 70% water content). This difference of 1 kg CO<sub>2</sub> is equal to the production of 26 MJ of electricity in Spain (using the current Spanish electricity mix), which is twelve times higher than the additional energy needed for thermal treatment (1.15 MJ/kg of pristine hydrochar). The additional energy requirements for the thermal post-treatment are therefore not expected to significantly change the climate impact of advanced hydrochar systems. In fact, as argued below, full scale implementation of the thermal treatment is expected to optimise energy use and to reduce the impact on climate change. We now plan to carry out a full life cycle assessment of advanced hydrochar production to determine the environmental performance of advanced hydrochar for other types of environmental impact than climate change, plus the potential environmental benefits of increasing crop yields.

The optimised process as described in Figure 3 consists of two steps. Using the organic side stream and the flue gases from the HTC heat generation unit, the energy demand of the overall process should be in the range of the bare HTC process, or only slightly higher. However, the process could be intensified by changing the process-type to one-step torrefaction at 275 °C. This has not yet been studied in detail, but two fundamental differences can be expected: the HTC process involves a reaction sequence of hydrolysis, chemical transformation and subsequent polymerization. This sequence clearly changes the macromolecular structure of the material, so that

different material properties can be expected for the carbonaceous product. On the other hand, HTC avoids the evaporation of approximately 66 to 75% of the feedstock moisture, which should be beneficial for the energy balance. In short, although a one-step torrefaction cannot be ruled out at this stage, it does not seem a likely alternative to the two-step HTC with subsequent “dry” thermal treatment.

#### 4. Conclusions

Even though hydrochar has significant potential as soil amendment material it also involves an initial phytotoxic effect. It has been shown here that a simple finishing procedure by thermal treatment at an optimum temperature of 275 °C is able to eliminate all its phytotoxic substances and thus produce refined hydrochar suitable for application to agricultural soils. The absence of phytotoxic properties was confirmed by subsequent seed germination tests.

A fast analysis procedure was designed to predict hydrochar’s phytotoxic potential and was shown to be valid, as the amount of volatile compounds detected by gas chromatography after thermal desorption at 180 °C was proportional to the phytotoxic activity of the material.

The thermal treatment thus unlocks the high potential for the conversion of the organic fraction of municipal solid waste into a soil amendment product, while the analytical procedure allows the careful application of the material with rigorous real-time control.

## Acknowledgements

M.O. and M.R. are grateful for the financial support received from the European Commission under the CharM and AdvCharM of the Climate-KIC Programme.

## Supplementary Material

The Supplementary Material associated with this paper can be found in hydrochar production in an industrial reactor, in the phytotoxicity evaluation (Zucconi test), in the determination of the energy balance, inorganic elements content after thermal treatments and in the chromatographic analyses in the online version.

## References

- [1] N.A. Qambrani, M.M. Rahman, S. Won, S. Shim, C. Ra, Biochar properties and eco-friendly applications for climate change mitigation, waste management, and wastewater treatment: A review, *Renew. Sustain. Energy Rev.* 79 (2017) 255–273. doi:10.1016/j.rser.2017.05.057.
- [2] P. Brassard, S. Godbout, V. Raghavan, Soil biochar amendment as a climate change mitigation tool: Key parameters and mechanisms involved, *J. Environ. Manage.* 181 (2016) 484–497. doi:10.1016/j.jenvman.2016.06.063.
- [3] M. Verma, N. M'hamdi, Z. Dkhili, S.K. Brar, K. Misra, Thermochemical Transformation of Agro-biomass into Biochar: Simultaneous Carbon Sequestration and Soil Amendment BT - Biotransformation of Waste Biomass into High Value Biochemicals, in: S.K. Brar, G.S. Dhillon, C.R. Soccol (Eds.), Springer New York, New York, NY, 2014: pp. 51–70. doi:10.1007/978-1-4614-8005-1\_3.

- [4] K. Lorenz, R. Lal, Biochar application to soil for climate change mitigation by soil organic carbon sequestration, *J. Plant Nutr. Soil Sci.* 177 (2014) 651–670. doi:10.1002/jpln.201400058.
- [5] J. Lehmann, Bio-energy in the black, *Front. Ecol. Environ.* 5 (2007) 381–387. doi:10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2.
- [6] B.B.M. Salim, Influence of biochar and seaweed extract applications on growth, yield and mineral composition of wheat (*Triticum aestivum* L.) under sandy soil conditions, *Ann. Agric. Sci.* 61 (2016) 257–265. doi:https://doi.org/10.1016/j.aoas.2016.06.001.
- [7] K.E. Brantley, K.R. Brye, M.C. Savin, D.E. Longer, Biochar Source and Application Rate Effects on Soil Water Retention Determined Using Wetting Curves, *Open J. Soil Sci.* 5 (2015) 1–10. doi:10.4236/ojss.2015.51001.
- [8] P. Weisberg, M. Delaney, J. Hawkes, Carbon Market Investment Criteria for Biochar Projects, *Public Interes. Energy Res. Progr.* (2010). [http://www.biochar-international.org/sites/default/files/WestCARB\\_Biochar\\_Report\\_DRAFT.pdf](http://www.biochar-international.org/sites/default/files/WestCARB_Biochar_Report_DRAFT.pdf).
- [9] R. Subedi, C. Bertora, L. Zavattaro, C. Grignani, Crop response to soils amended with biochar: Expected benefits and unintended risks, *Ital. J. Agron.* 12 (2017) 161–173. doi:10.4081/ija.2017.794.
- [10] X. Zhu, B. Chen, L. Zhu, B. Xing, Effects and mechanisms of biochar-microbe interactions in soil improvement and pollution remediation: A review, *Environ. Pollut.* 227 (2017) 98–115. doi:https://doi.org/10.1016/j.envpol.2017.04.032.



- [11] G. Duman, A.T. Tag, S. Ucar, J. Yanik, Comparative evaluation of dry and wet carbonization of agro industrial wastes for the production of soil improver, *J. Environ. Chem. Eng.* 6 (2018) 3366–3375.  
doi:<https://doi.org/10.1016/j.jece.2018.05.009>.
- [12] M.M. Titirici, R.J. White, C. Falco, M. Sevilla, Black perspectives for a green future: Hydrothermal carbons for environment protection and energy storage, *Energy Environ. Sci.* 5 (2012) 6796–6822. doi:10.1039/c2ee21166a.
- [13] M.M. Titirici, A. Thomas, S.-H. Yu, J.-O. Mueller, M. Antonietti, A Direct Synthesis of Mesoporous Carbons with Bicontinuous Pore Morphology from Crude Plant Material by Hydrothermal Carbonization, *Chem. Mater.* 19 (2007) 4205–4212.  
doi:10.1021/cm0707408.
- [14] M.M. Titirici, A. Funke, A. Kruse, Hydrothermal Carbonization of Biomass, in: *Recent Adv. Thermochem. Convers. Biomass*, 2015: pp. 325–352.  
doi:10.1016/B978-0-444-63289-0.00012-0.
- [15] S. Brown, Greenhouse gas accounting for landfill diversion of food scraps and yard waste, *Compost Sci. Util.* 24 (2016) 11–19.  
doi:10.1080/1065657X.2015.1026005.
- [16] A. Sánchez, A. Artola, X. Font, T. Gea, R. Barrena, D. Gabriel, M.Á. Sánchez-Monedero, A. Roig, M.L. Cayuela, C. Mondini, Greenhouse gas emissions from organic waste composting, *Environ. Chem. Lett.* 13 (2015) 223–238.  
doi:10.1007/s10311-015-0507-5.

- [17] J.K. Andersen, A. Boldrin, T.H. Christensen, C. Scheutz, Mass balances and life cycle inventory of home composting of organic waste, *Waste Manag.* 31 (2011) 1934–1942. doi:10.1016/j.wasman.2011.05.004.
- [18] J.K. Andersen, A. Boldrin, T.H. Christensen, C. Scheutz, Greenhouse gas emissions from home composting of organic household waste, *Waste Manag.* 30 (2010) 2475–2482. doi:10.1016/j.wasman.2010.07.004.
- [19] F. Fornes, R.M. Belda, Acidification with nitric acid improves chemical characteristics and reduces phytotoxicity of alkaline chars, *J. Environ. Manage.* 191 (2017) 237–243. doi:http://dx.doi.org/10.1016/j.jenvman.2017.01.026.
- [20] F. Fornes, R.M. Belda, P. Fernández de Córdova, J. Cebolla-Cornejo, Assessment of biochar and hydrochar as minor to major constituents of growing media for containerized tomato production, *J. Sci. Food Agric.* 97 (2017) 3675–3684. doi:10.1002/jsfa.8227.
- [21] D. Busch, C. Kammann, L. Grünhage, C. Müller, Simple biotoxicity tests for evaluation of carbonaceous soil additives: Establishment and reproducibility of four test procedures, *J. Environ. Qual.* 41 (2012) 1023–1032. doi:10.2134/jeq2011.0122.
- [22] D. Busch, A. Stark, C.I. Kammann, B. Glaser, Genotoxic and phytotoxic risk assessment of fresh and treated hydrochar from hydrothermal carbonization compared to biochar from pyrolysis, *Ecotoxicol. Environ. Saf.* 97 (2013) 59–66. doi:10.1016/j.ecoenv.2013.07.003.

- [23] R. Becker, U. Dorgerloh, E. Paulke, J. Mumme, I. Nehls, Hydrothermal carbonization of biomass: Major organic components of the aqueous phase, *Chem. Eng. Technol.* 37 (2014) 511–518. doi:10.1002/ceat.201300401.
- [24] K.A. Spokas, J.M. Novak, C.E. Stewart, K.B. Cantrell, M. Uchimiya, M.G. DuSaire, K.S. Ro, Qualitative analysis of volatile organic compounds on biochar, *Chemosphere.* 85 (2011) 869–882. doi:10.1016/j.chemosphere.2011.06.108.
- [25] R. Becker, U. Dorgerloh, M. Helmis, J. Mumme, M. Diakit , I. Nehls, Hydrothermally carbonized plant materials: Patterns of volatile organic compounds detected by gas chromatography, *Bioresour. Technol.* 130 (2013) 621–628. doi:10.1016/j.biortech.2012.12.102.
- [26] M. Owsianiak, J. Brooks, M. Renz, A. Laurent, Evaluating climate change mitigation potential of hydrochars: compounding insights from three different indicators, *GCB Bioenergy.* 10 (2018) 230–245. doi:10.1111/gcbb.12484.
- [27] F. Zucconi, A. Monaco, M. Forte, M. De Bertoldi, Phytotoxins during the stabilization of organic matter, in: J.K.R. Gasser (Ed.), *Compost. Agric. Other Wastes*, Elsevier, London, 1985.
- [28] G.Q. Lu, J.C.F. Low, C.Y. Liu, A.C. Lua, Surface area development of sewage sludge during pyrolysis, *Fuel.* 74 (1995) 344–348.  
doi:[https://doi.org/10.1016/0016-2361\(95\)93465-P](https://doi.org/10.1016/0016-2361(95)93465-P).
- [29] J. Zhang, F. L , H. Zhang, L. Shao, D. Chen, P. He, Multiscale visualization of the structural and characteristic changes of sewage sludge biochar oriented towards

potential agronomic and environmental implication, *Sci. Rep.* 5 (2015) 9406.  
<http://dx.doi.org/10.1038/srep09406>.

- [30] P. Burguete, A. Corma, M. Hitzl, R. Modrego, E. Ponce, M. Renz, Fuel and chemicals from wet lignocellulosic biomass waste streams by hydrothermal carbonization, *Green Chem.* 18 (2016) 1051–1060. doi:10.1039/c5gc02296g.
- [31] N.D. Berge, K.S. Ro, J. Mao, J.R. V Flora, M.A. Chappell, S. Bae, Hydrothermal carbonization of municipal waste streams, *Environ. Sci. Technol.* 45 (2011) 5696–5703. doi:10.1021/es2004528.
- [32] R.K. Rosenbaum, T.M. Bachmann, L.S. Gold, M.A.J. Huijbregts, O. Jolliet, R. Juraske, A. Koehler, H.F. Larsen, M. MacLeod, M. Margni, T.E. McKone, J. Payet, M. Schuhmacher, D. Van De Meent, M.Z. Hauschild, USEtox - The UNEP-SETAC toxicity model: Recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment, *Int. J. Life Cycle Assess.* 13 (2008) 532–546. doi:10.1007/s11367-008-0038-4.