Bioresource Technology 183 (2015) 163–174

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Reverse engineering of biochar

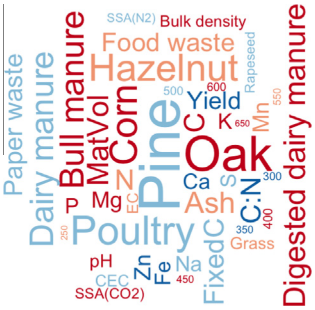
Verónica L. Morales [a,*], Francisco J. Pérez-Reche [b], Simona M. Hapca [a], Kelly L. Hanley [c], Johannes Lehmann [c], Wei Zhang [d]

[a] SIMBIOS Centre, Abertay University, Dundee DD1 1HG, UK
[b] Institute for Complex Systems and Mathematical Biology, SUPA, Department of Physics, University of Aberdeen, Old Aberdeen AB24 3UE, UK
[c] Department of Crop and Soil Sciences, Cornell University, Ithaca, NY 1453, USA
[d] Department of Plant, Soil and Microbial Sciences, Environmental Science and Policy Program, Michigan State University, East Lansing, MI 48824, USA

HIGHLIGHTS

- Starting biomass and peak pyrolysis temperature jointly affect biochar properties.
- 19 different physico-chemical properties of biochar were properly modeled by GLM.
- Models reveal complex relationships between biochar properties and predictors.
- Ubiquitous non-Gaussian and non-linear attributes were accounted for in GLMs.
- Proposed correlation networks, models and web-tool can be used to engineer biochar.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 December 2014
Received in revised form 9 February 2015
Accepted 10 February 2015
Available online 18 February 2015

Keywords:
Physico-chemical properties
Slow-pyrolysis
Correlation networks
Generalized Linear Models
Web-tool

ABSTRACT

This study underpins quantitative relationships that account for the combined effects that starting biomass and peak pyrolysis temperature have on physico-chemical properties of biochar. Meta-data was assembled from published data of diverse biochar samples ($n = 102$) to (i) obtain networks of intercorrelated properties and (ii) derive models that predict biochar properties. Assembled correlation networks provide a qualitative overview of the combinations of biochar properties likely to occur in a sample. Generalized Linear Models are constructed to account for situations of varying complexity, including: dependence of biochar properties on single or multiple predictor variables, where dependence on multiple variables can have additive and/or interactive effects; non-linear relation between the response and predictors; and non-Gaussian data distributions. The web-tool *Biochar Engineering* implements the derived models to maximize their utility and distribution. Provided examples illustrate the practical use of the networks, models and web-tool to engineer biochars with prescribed properties desirable for hypothetical scenarios.

1. Introduction

Biochar, the product of biomass thermochemical conversion in an oxygen depleted environment, has gained increasing recognition as a modernized version of an ancient Amerindian soil management practice, with at times wide-ranging agronomic and

---

* Corresponding author at: Inst. of Environmental Engineering, ETH Zürich, Zürich 8093, CH.

E-mail address: morales@ifu.baug.ethz.ch (V.L. Morales).

http://dx.doi.org/10.1016/j.biortech.2015.02.043
0960-8524/

environmental gains (Lehmann et al., 2003; Atkinson et al., 2010; Novak et al., 2013). Some of the most commonly acclaimed benefits of biochar application to soils include: increased long-term C storage in soils (Atkinson et al., 2010; Joseph et al., 2010; Cross and Sohi, 2011; Ennis et al., 2011; Karhu et al., 2011; Novak et al., 2013), restored soil fertility (Glaser et al., 2002; Lehmann et al., 2003; Gaskin et al., 2008; Novak et al., 2009; Atkinson et al., 2010; Laird et al., 2010; Beesley et al., 2011; Lehmann et al., 2011; Enders et al., 2012; Spokas et al., 2012b; Novak et al., 2013), improved soil physical properties (Novak et al., 2009; Joseph et al., 2010; Ennis et al., 2011; Karhu et al., 2011; Lehmann et al., 2011; Novak et al., 2013), boosted crop yield and nutrition (Novak et al., 2009; Major et al., 2010; Lehmann et al., 2011; Rajkovich et al., 2012; Spokas et al., 2012a; Novak et al., 2013), enhanced retention of environmental contaminants (Cornelissen et al., 2005; Loganathan et al., 2009; Cao and Harris, 2010; Beesley et al., 2011), and reduced N-emission and leaching (Spokas et al., 2012b; Novak et al., 2013). Examples of the specific biochar properties responsible for these benefits are summarized in Table 1.

Biochar quality can be highly variable, and its performance as an amendment – whether beneficial or detrimental – is often found to depend heavily on its intrinsic properties and the particular soil it is added to (Lehmann et al., 2003; Novak et al., 2009; Atkinson et al., 2010; Major et al., 2010; Lehmann et al., 2011; Spokas et al., 2012a). As has been previously concluded, biochar application to soil is not a "one size fits all" paradigm (Spokas et al., 2012a; Novak et al., 2013). Consequently, detailed knowledge of the biochar properties and the specific soil deficiencies to be remediated is critical to maximize the possible benefits and minimize undesired effects of its use as a soil amendment. While soil deficiencies must be identified on a site-by-site basis, it is conceivable that biochar properties can be engineered through the manipulation of pyrolysis production parameters and proper selection of parent biomass type (Zhao et al., 2013). The capacity to produce biochars with consistent and predictable properties will, first, enable efficient matching of biochars to soils, and second, facilitate the deployment of this soil management strategy at large and commercial scales. Although the properties and effects of biochar samples produced from a variety of methods and starting biomasses have been intensively studied, as yet, the analytical techniques for characterization and effect quantification are not standardized. This creates a challenge when comparing biochar properties and effects across studies. At the same time, making such comparisons is imperative to gain a comprehensive understanding of alterable biochar properties.

The prevailing hypothesis in the literature is that the selection of peak pyrolysis temperature and parent biomass – as two key production variables – fundamentally affects resulting biochar properties. Identification of relationships between production variables and biochar properties has been pursued by many investigators, but has been limited to the small number of samples produced and analyzed for each study (e.g., Karaosmanoğlu et al., 2000; Zhu et al., 2005; Gaskin et al., 2008; Nguyen and Lehmann, 2009; Cao and Harris, 2010; Joseph et al., 2010; Keiluweit et al., 2010; Cao et al., 2011; Cross and Sohi, 2011; Hossain et al., 2011; Mukherjee et al., 2011; Enders et al., 2012; Rajkovich et al., 2012; Zhao et al., 2013), with few reports combining measurements from more than one source (Cordero et al., 2001; Glaser et al., 2002; Atkinson et al., 2010; Ennis et al., 2011; Spokas et al., 2012a). The knowledge gained from the above studies does not provide a quantitative understanding of the relationships between production variables and biochar properties. The shortcomings responsible for such lack of systematic insight include: (i) reported trends that are primarily qualitative with respect to the independent effect of parent biomass or temperature (e.g., decrease in labile carbon with increasing pyrolysis temperature for selected samples (Cross and Sohi, 2011)), (ii) trends that are often in conflict with similar samples of other studies (e.g., positive effect (Rajkovich et al., 2012) vs. negligible effect (Nguyen and Lehmann, 2009) of temperature on pH for oak biochar), and (iii) correlations that are not convincing (e.g., correlation $r = 0.5$ between volatile matter content and microporous surface area (Mukherjee et al., 2011)). A recent study by Zhao et al., 2013 reports, for the first time, a quantitative evaluation of the individual influence of feedstock source and production temperature on various biochar properties. The authors classified a variety of physical and chemical biochar properties as predominantly

Table 1
Benefits from specific biochar properties.

Biochar property	Agronomic and environmental benefits
BulkD [$\mathrm{Mg\ m^{-3}}$]	Low bulk density biochar can reduce the density of compacted soils, thereby improving root penetration (Atkinson et al., 2010; Ennis et al., 2011; Novak et al., 2013), water drainage and aeration (Joseph et al., 2009; Laird et al., 2010). The latter may mitigate green house gas emissions (Karhu et al., 2011).
SSA(N_2), SSA(CO_2) [$\mathrm{m^2\ g^{-1}}$]	High nanopore and micropore specific surface area, respectively, may increase the sorptive affinity of organic compounds to biochars (Cornelissen et al., 2005; Beesley et al., 2011), and improve water holding capacity (Karhu et al., 2011).
Yield [%]	Yield reflects the quantity of biochar material produced from the pyrolysis process.
EC [$\mathrm{mS\ m^{-1}}$]	Electrical conductivity indicates the quantity of salt contained in the biochar. High EC can stabilize soil structure (Joseph et al., 2009; Hossain et al., 2011).
CEC [Av ($\mathrm{mmol_c\ kg^{-1}}$)]	Increased cation exchange capacity can improve the soil's ability to hold and exchange cations (Chapman, 1965; Glaser et al., 2002).
pH_w [–]	Soil solution pH directly affects soil surface charge, which determines the type of exchangeable nutrients and mineral ions it attracts (Mukherjee et al., 2011). Additionally, the buffering capacity of biochar can neutralize acidic soils, redude aluminum toxicity and change the soil microbial community structure (Abe, 1988; Lehmann et al., 2011).
Ash [%]	Ash may improve the sorption capacity of biochar for organic compounds and metals (Cao et al., 2011).
MatVol [%]	Volatile matter affects biochar longevity in soil (Lehmann et al., 2011; Enders et al., 2012). Residual volatiles can also impact organic substance sorption by blocking pores and changing surface chemical interactions (Sander and Pignatello, 2005; Zhu et al., 2005; Novak et al., 2013).
C [$\mathrm{mg\ g^{-1}}$]	Total carbon in organic matter benefits the soil.
N [$\mathrm{mg\ g^{-1}}$]	Total nitrogen in the biochar supplies a macronutrient, but its availability is limited. Biochar may strongly sorb ammonia and act as a nitrogen-rich soil amendment (Spokas et al., 2012b).
C:N [–]	Carbon to nitrogen ratio influences the rate of decomposition of organic matter and release of soil nitrogen (Novak et al., 2009).
FixedC [%]	Fixed carbon is non-labile and therefore is a property attributed to biochar stability (Keiluweit et al., 2010; Enders et al., 2012; Rajkovich et al., 2012).
P, S [Total ($\mathrm{mg\ kg^{-1}}$)]	Macronutrients provided by biochar, which can improve soil fertility.
Ca, K, Mg, Na, Fe, Mn, Zn [Total ($\mathrm{mg\ kg^{-1}}$)]	Micronutrients provided by biochar, which can improve soil fertility.

Notes: BulkD = bulk density, SSA = specific surface area, EC = electrical conductivity, CEC = cation exchange capacity, MatVol = volatile matter, FixedC = fixed carbon.