

Patrick Maloney

From: Sent: To: Subject: Attachments: E-000002-17-0138



Forest Bioenergy Docket 55-uses-of-Biochar.pdf; Biochar.pdf; 3 D 4 Meiler.pdf; 2017_Hagemann_PLOS ONE Biochar nitrate capture.pdf; Compost_biochar_IBI_final.pdf

Dear Commissioner Dunn,

Mr. Patrick Rappold from the Arizona Department of Forestry and Fire Management made me aware of the above mentioned Docket you opened.

Carsten <pioneerlogusdiv@aol.com>

Saturday, July 01, 2017 12:29 PM

Dunn-Web

I am working on opening a new company BIOCHAR AZ LLC with business partners from Germany. We have a small plant concept that converts about 24 tons of woody biomass into 6 tons of high quality (90 % +)Biochar.

While operating the plant generates about 1 MW of Electric and 2 MW of Thermal Energy.

We are ready to build the first plant here in Arizona looking into financing options and possible partnerships.

Just as an example :

If we could install a plant at one of the City of Phoenix's Landfills we would be able to divert woody biomass and other material that is negative for composting e.g. Palm Fronds and Oleander and process it into Biochar. The Biochar can be sold for agricultural and other applications.

Best case scenario that would support the City's Circular Economy Concept would be to apply the Biochar to the compost at the City's new composting facility. Please see attached article about the effects of Biochar in Composting.

Please let me know if you have any further questions and/or suggestions to whom I may talk to.

Sincerely

Carsten Heyer

Arizona Corporation Commission DOCKETED

JUL 3 2017

DOCKETED I

сл



Carsten Heyer pioneerlogusdiv@aol.com Cell: 1-805-350-2915 3006 E Posey Ct., Payson, Az. 85541 Phone 928 468 0996



Pioneer Floor Plans Photo Gallery

ithakajournal

viticulture ecology climate-farming 112012

55 Uses of Biochar by Hans-Peter Schmidt Please cite the article as follows: Schmidt HP 55 Uses of Biochar 11 (thaka Journal 1/2012: 286–289 (2012) www.ithaka-journal.net Editor: Delinat-Institute for Ecology and Climatefarming. CH-1974 Arbaz www.delinat-institut.org, www.ithaka-journal.net. 158N 1663–0521

55 Uses of Biochar

by Hans-Peter Schmidt

Initially only used in agriculture, the range of uses for biochar now covers a wide range of different fields, giving this plant-based raw material the chance to make the most of its positive properties. Wherever biochar is specifically used even for industrial purposes, the carbon taken from the atmosphere in the form of CO_2 can be stored for long periods or at least used to replace fossil carbon sources. Biochar is much too valuable and expensive for any farmer to be able to afford to spread 10 tonnes or more per hectare on his fields. Whereas a hectare will normally provide an annual benefice of EUR 1000, the EUR 8000 needed to purchase and spread the biochar would need to be amortised over several decades. The CO_2 certificates favoured by so many outside the trade would be of no much help either.

Does it really make sense to work biochar into fields?

These economic considerations are not so different from what the natives in the Amazon delta and Australia had to face when they used biochar to improve their soils, and where you will still find some places with over 100 tonnes of biochar buried into just one hectare of soil. Even if no money existed back in those days, it would have made no economic sense to cut down some 300 to 400 huge rain forest trees and then use ancient charcoal kilns to make some 100 tonnes of biochar

Delinat Institute for Ecology and Climate-farming 1 www.delinat-institut.org 1 Ithaka Journal

286

from 2000 tonnes of wood – just to bury the biochar in the soil. And don't forget: all this would have been done without any chainsaws or axes and no animals to pull the logs close to the field.

The idea of applying dozens of tonnes of biochar to fields can only come from scholars who, on the basis of a right observation (50 t biochar per hectare) have arrived at a false conclusion completely without any practical relevance – i.e. the massive one-time application of biochar. And this is quite apart from the fact that no soil becomes Terra Preta just because tonnes of char have been ploughed in.

Example of Terra Preta Cultures

The char used back then was probably created in the typical hearths of the natives, in which not just ash but also relatively large amounts of charcoal were produced at relatively low heat (Smith 1999). This char, basically a waste product, was then apparently used as a way of preventing infectious diseases. This was done by regularly adding char to faeces and other waste in the large jungle settlements, thus sterilising them (see Terra Preta – Model of a Cultural Technique. Schmidt 2011). Once the organic waste had been stabilised through composting or fermenting it with added char, it was then used as a fertiliser on the fields. These methods led to the char being loaded with nutrients and its surface achieving

55 Uses of Biochar I Hans-Peter Schmidt 1 Ithaka Journal 112012: 286-289 1 ISSN 1663-0521

sequence that, once worked into the soil, the char was able to the char- stabilised organic waste of some 500 people must use of biochar for recycling organic wastes. In other words, it took centuries to bring the biochar content of the soil up to greater binding capability through oxidisation, with the concan be up to 500 times higher. Different to carbon and nitroplant growth, but mainly through the manual addition of exhave been worked into every hectare of soil over a period of 1000 years to gain such Terra Preta nutrient contents. Terra Preta has been created over centuries through the secondary According to investigations carried out by Bruno Glaser and colleagues (Birk et al 2007), the amount of phosphor in Terra Preta soils compared to natural soils in the immediate vicinity gen, phosphor can not be accumulated in the soil through crement, (fish-)bones and ash. A rough estimate shows that fully unfold its function as a nutrient store and humus stabiliser (through the creation of char-clay-humus complexes). over 100 tonnes per hectare.

The many uses of biochar

Biochar is much too valuable for it to be just worked into the Biochar is much too valuable for it to be just worked into the soil without having it used at least once for more beneficial purposes – whether as storage for volatile nutrients, as an adsorber in functional clothing, as insulation in the building industry, as energy storage in batteries, as a filter in a sewage plant, as a silage agent or as a feed supplement. Such uses can be followed by use in a farmer's slurry pit or in a sewage plant. before being composted. It should only be worked into the soil at the end of this "cascade", helping to create Terra Preta.

at the end of this "cascade", helping to create Jerra Preta. The following list of 55 possible uses of biochar is by no means complete. In fact it has only just been started. In the medium term biochar will (or must) replace oil as the main raw mate-

rial of our industrial society, insofar as mankind is willing to maintain living conditions on the planet in the long term (see: Biochar – a key technology for the planet, Schmidt 2012).

We will initially just comment shortly on each usage of the list, as we intend to devote in-depth articles to some of them, highlighting in particular the use of biochar in agriculture and cattle farming and supporting the articles with the latest research findings. Biochar is without doubt one of the decade's most exciting fields of research, with findings and their practical implementation increasing exponentially from year to year. Nevertheless, however much we enthuse over our field of research and the importance of our findings, it's the real world that decides about its success.

The cascaded use of biochar in animal farming

 Silage agent, 2. Feed additive l supplement, 3. Litter additive, 4. Slurry treatment, 5. Manure compositing, 6. Water treatment in fish farming

At present some 90% of the biochar used in Europe goes into animal farming. Different to its application to fields, a farmer will notice its effects within a few days. Whether used in feeding, litter or in slurry treatment, a farmer will quickly notice less smell. Used as a feed supplement, the incidence of diarrhoea rapidly decreases, feed intake is improved, allergies disappear, and the animals become calmer. For in-depth articles on the use of biochar in cattle and poultry farming, see: Treating liquid manure with biochar, Schmidt 2012; Biochar in poultry farming, Gerlach & Schmidt 2012; The use of biochar in cattle farming, Gerlach are currently being surveyed with the aim of creating a statistic on the effects of biochar in animal farm. First results are expected in Mai 2013.

Delinat Institute for Ecology and Climate-farming 1 www.delinat-institut.org 1 lthaka Journal 287

Use as a soil conditioner

 Carbon fertiliser, 8. Compost, 9. Substitute for peat in potting soil, 10. Plant protection, 11. Compensatory fertiliser for trace elements

fects on soil fertility were seen when applying untreated bioto have a humus content of over 1.5%, meaning that such tion of plant nutrients released in the soil can instead often have – at least in the short and medium term – a negative effect on plant growth. These are the reasons why in temperate climates biochar should only be used when first loaded with nutrients and when the char surfaces have been actiing nutrients is to co-compost the char. This involves adding 10–30% biochar to the biomass to be composted (see: Ways of Making Terra Preta: Biochar Activation, Schmidt 2012). The co-composting of biochar results not only in a valuable soil conditioner. The compost can be used as a highly efficient substitute for peat in potting soil, greenhouses, nurseries and In certain very poor soils (mainly in the tropics), positive efter, aeration of the soil and the release of nutrients through vated through microbial oxidation. The best method of loadchar. These include the higher capacity of the soil to store waraising the soil's ph-value. In temperate climates, soils tend effects only play a secondary role. Indeed the high adsorpother special cultures.

When biochar is used as a carrier for plant nutrients, efficient mineral and organic long-term fertilisers can be produced. Such fertilisers prevent the leaching of nutrients, a negative aspect of conventional fertilisers. The nutrients are available as and when the plants need them. Through the stimulation of microbial symbiosis, the plant takes up the nutrients from the porous carbon structure. Through mixing biochar with such organic waste as wool, molasses, ash, slurry and pomace, organic carbon-based fertilisers can be produced. These

Delinat institute for Ecology and Climate-farming 1 www.delinat-institut.org 1 Ithaka Journal 288	 20. Treating pond and lake water [Biochar is good for adsorbing pesticides and fertilizers, as well as for improving water aeration.] Biogas production 21. Biomass additive, 22. Biogas slurry treatment First tests show that, through adding biochar to a fermenter's biomass (especially heterogeneous biomasses), the methane and hydrogen yield is increased, while at the same time decreasing CO₂ and ammonia emissions (Inthapanya et al. 2012; Kumar et al. 1987). Through treating biogas slurry with lacto-ferments and biochar, nutrients are better stored and emissions prevented (see (in German): The sustainable production of biogas through climate farming, Schmidt 2012) 	 The treatment of waste water 23. Active carbon filter, 24. Pre-rinsing additive, 25. Soil substrate for organic plant beds, 26. Composting toilets, The treatment of drinking water 27. Micro-filters, 28. Macro-filters in developing countries 27. Micro-filters, 28. Macro-filters in developing countries 27. Micro-filters, 28. Macro-filters in developing countries Divers other uses Exhaust filters (29. Controlling emissions, 30. Room air filters) Industrial materials (31. carbon fibres, 32. plastics) Electronics (33. semiconductors, 34. batteries) Metallurgy (35. metal reduction) Cosmetics (36. soaps, 37. skin-cream, 38. therapeutic bath additives) Paints and colouring (39. food colorants, 40. industrial paints) Energy production (41. pellets, 42. substitute for lignite) Medicines (43. detoxification, 44. carrier for active pharmaceutical ingredients)
Delinat Institute	gies, but also dampness through air condensing on the out- side walls, which can lead to mould developing (see Biochar as building material for an optimal indoor climate, Schmidt 2013). Such biochar-mud plaster adsorbs smells and toxins, a prop- erty not just benefiting smokers. Alongside their use in hous- ing, biochar-mud plasters are particularly good for warehous- es, factory and agricultural buildings as well as in schools and other rooms frequented by people. Biochar is a very efficient adsorber of electromagnetic radia- tion, meaning that biochar-mud plaster is very good at pre- venting "electrosmog". Biochar can also be applied to the outside walls of a building by jet-spray technique mixing it with lime. Applied at thick-	nesses of up to 20 cm, it is a substitute for styrofoam. Houses insulated this way become carbon sinks, while at the same time having a more healthy indoor climate. Should such a house be demolished at a later date, the biochar-mud plaster can be recycled as a valuable compost additive. Together with the German company Casadobe, the Delinat Institute is currently developing a range of biochar-mud plas- ters, expected to be available on the market in mid-2013. Decontamination 17. Soil additive for soil remediation [for use in particular on for- mer mine-works, military bases and landfill sites.] 18. Soil substrates [highly adsorbing, plantable soil substrates for use in cleaning waste water; in particular urban waste wa- ter contaminated by heavy metals] 19. A barrier preventing pesticides getting into surface water [Sides of field and ponds can be equipped with 30-50 cm deep barri- ers made of biochar for filtering out pesticides.]
	are at least as efficient as conventional fertilizers, and have the advantage of not having the well-known adverse effects on the ecosystem. The biochars contain all trace elements originally contained in the pyrolised biomass. During pyrolysis, the crucial trace elements (over 50 metals) become part of the carbon struc- ture, thereby preventing them being leached out and making them available to plants via root exudates and microbial sym- biosis. This feature can be used specifically when certain trace elements are missing in a certain regional soil or in soil-free intensive cultures such as "Dutch tomatoes". A range of by-products are produced during pyrolysis. These remain stuck to the pores and surfaces of the biochar and in many cases have the ability to mobilise plant's internal im-	mune systems, thereby increasing its resistance to pathogens (Elad et al. 2011). This potential use is however only just now being developed and still requires a lot of research effort. Use in the building sector 12. Insulation, 13. Air decontamination, 14. Decontamination of earth foundations, 15. Humidity regulation, 16. Protection against electromagnetic radiation ("electrosmog") Two of biocchar's properties are its extremely low thermal conductivity and its ability to absorb water up to 6 times its weight. These properties mean that biocchar is just the right material for insulating buildings and regulation and forchar: biochar can be added to sand at a ratio of up to 50%. This creates indoor plasters with excellent insulation and breathing properties, able to maintain humidity levels in a room at 45–70% in both summer and winter. This in turn prevents not just dry air, which can lead to respiratory disorders and aller-

•

•

55 Uses of Biochar I Hans-Peter Schmidt 1 Rhaka Journal 112012: 286–289 1 ISSN 1663-0521

Textiles

45. Fabric additive for functional underwear, 46. Thermal insulation for functional clothing, 47. Deodorant for shoe soles

In Japan and China bamboo-based biochars are already being woven into textiles (Lin et al. 2008) to gain better thermal and breathing properties and to reduce the development of odours through sweat. The same aim is pursued through the inclusion of biochar in inlay soles and socks.

Wellness

48. Filling for mattresses, 49. Filling for pillows Biochar adsorbs perspiration and odours, shields against electromagnetic radiation (electrosmog), and removes negative ions from the skin. Moreover, it acts as a thermal insulator reflecting heat, thereby enabling comfortable sleep without any heat build-up in summer. In Japan, pillows have been filled with biochar for a long time. This is supposed to prevent insommia and neck tension.

50. Shield against electromagnetic radiation

Biochar can be used in microwave ovens, television sets, power supplies, computers, power sockets, etc. to shield against electromagnetic radiation. This property can also be used in functional clothing as protection for parts of the body particularly sensitive to radiation.

All of the proposed biochar uses except nos. 35, 41, 42 are carbon sinks. After its initial or cascading use, the biochar can be recycled as a soil conditioner. Fully depreciated when finally returned to the soil, the black carbon will slowly build up in the soil – and over a few generations the soil's biochar content could easily reach 50 to 100 t per ha.

We have listed 50 possible uses of biochar. But the title refers to 55 uses ... This is to be seen as an indication of our intention to keep on adding to the list over the conning weeks and years, as experience builds up. We can also be sure that the author has missed out a number of uses already available today (the first version of this article only contained 44 possible uses)

References

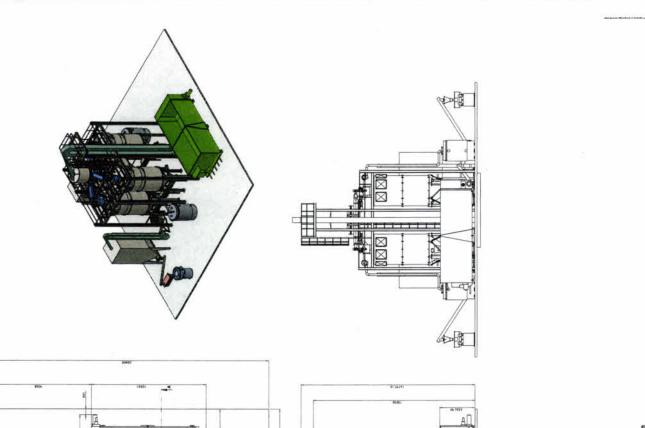
- Birk J, Grosch H, Neves E, Teixeira W, Glaser B (2007): Rekonstruktion von Bestedlungsmuster und -intensität einer Terra Preta anhand der kleinräumigen Nährstoffverteilung, Mitteilungen der Deutschen Bodenkundlichen Gesellschaft 110:643 – 644
- Elad, Y. D RDavid, Y M Harel, M Borenshtein, H B Kalifa, A Silber, and E R Graber. 2010. Induction of systemic resistance in plants by biochar, a soil-applied carbon sequestering agent. Phytopathology 100 (9): 913-921
 - Gerlach A: The use of biochar in cattle farming. Ithaka Journal 2012:281-285 (2012)
- Gerlach H, Schmidt HPP, Biochar in poultry farming. Ithaka Journal 2012: 262-264 (2012)
- Inthapanya, Sangkhom, Preston T R, und Leng R A. 2012. Biochar increases biogas production in a batch digester charged with cattle ma
 - nure. http://www.lrtd.org/lrtd24/12/sang24212.htm Kumar, S., M. C. Jain, und P. K. Chhonkar. 1987. A note on stimulation of biogas production from cattle dung by addition of charcoal. Biologi
 - cal wastes 20 (3): 209–215. Lin, C M, und C W Chang. 2008. Production of thermal insulation composites containing bamboo charcoal. Textile Research Journal 78 (7): posites containing bamboo charcoal. Textile Research Journal 78 (7):
- 555 560 Schmidt HP: Pflanzenkohle – eine Schlüsseltechnologie zur Schließung der Stoffkreisläufe Thaka Iournal 2012: 75...79 (2012)
 - Stoffkretsläufe, Ithaka Journal 2012: 75–79 (2012) Schmidt HP: Treating liquid manure with biochar. Ithaka Journal 2012, 273–276 (2012)

Schmidt HP: Biogas durch Klimafarming nachhaltig produzieren, Ithaka Journal 2012: 61-66 (2012) Schmidt HP: Ways of Making Terra Preta: Biochar Activation, 2012,

- chimidt HP: Ways of Making Terra Preta: Biochar Activation, 2012, http://bit.ly/XIKASI
- Schmidt HP: Terra Preta Modell einer Kulturtechnik, Ithaka Journal 2011: 117–121 (2011)
 - Schmidt HP: Biochar as building material for an optimal indoor climate, Ithaka Journal 2013: x y (2013)
 - Smith NJH (1980) Anthrosols and human carrying capacity in Amazonia. Ann Assoc Am Geogr 70:553 – 566
- Smith NJH (1999) The Amazon River forest: a natural history of plants, and people. Oxford University Press, New York

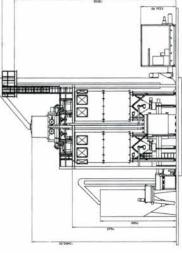
55 Uses of Biochar I Hans-Peter Schmidt 1 Ithaka Journal 112012: 286-289 1 ISSN 1663-0521

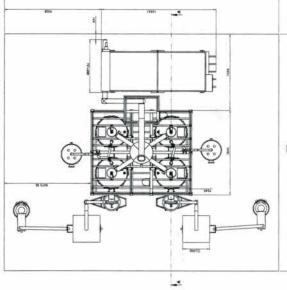


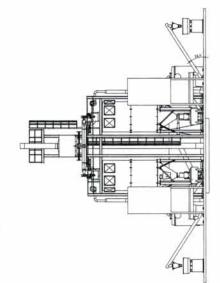


908

SECTION A.A.







Alle Tellen und Abmessungen in diese Zeichnung sind vorbehaltlich und nicht endgultig!! 4.Mejer.Vatkohlungsahbga 1. Bonnasoburker Sham mari waiking floor⁴ 1. Bevorota fur Hochschnitzel 1. Evologar fur Hochschnitzel 2. Konsenburker (Hochschnitzel) 5. na int intweitee 4. Obserschnecke fur Mideridizklung 2. Kuhhenecke fur Kuhing von Kohlediekte Kuhing) 2. Kuhhenecker fur Kuhing von Kohlediekte Kuhing) 2. Wechenburker (Kohling von Kohlediekte Kuhing) 2. Wechenburker (Kohling von Kohlediekter Kuhing)



G OPEN ACCESS

Citation: Hagemann N, Kammann CI, Schmidt H-P, Kappler A, Behrens S (2017) Nitrate capture and slow release in biochar amended compost and soil. PLoS ONE 12(2): e0171214. doi:10.1371/journal. pone.0171214

Editor: Jorge Paz-Ferreiro, RMIT University, AUSTRALIA

Received: November 3, 2016

Accepted: January 18, 2017

Published: February 15, 2017

Copyright: © 2017 Hagemann et al. This is an open access article distributed under the terms of the <u>Creative Commons Attribution License</u>, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Data Availability Statement: Original data (amount of N released during each step of extraction from each replicate of each treatment) is available through PANGAEA database (<u>https://doi. pangaea.de/10.1594/PANGAEA.867498</u>).

Funding: NH was financially supported by a BMBF PhD scholarship provided by the Rosa Luxemburg Foundation, Berlin, Germany. The composts used in this experiments were produced during a "Short Term Scientific Mission" (STSM) granted to NH by EU COST Action TD1107 "Biochar as option for sustainable resource management". CK gratefully **RESEARCH ARTICLE**

Nitrate capture and slow release in biochar amended compost and soil

Nikolas Hagemann¹*, Claudia I. Kammann², Hans-Peter Schmidt³, Andreas Kappler¹, Sebastian Behrens^{4,5}*

1 Geomicrobiology, Center for Applied Geoscience, University of Tuebingen, Sigwartstrasse 10, Tuebingen, Germany, 2 Working group Climate Change Research for Special Crops, Department for Soil Science and Plant Nutrition, Hochschule Geisenheim University, Geisenheim, Germany, 3 Ithaka Institute for Carbon Strategies, Ancienne Eglise 9, Arbaz, Switzerland, 4 Department for Civil, Environmental, and Geo-Engineering, University of Minnesota, Minneapolis, MN, United States of America, 5 BioTechonology Institute, 140 Gortner Labs, 1479 Gortner Avenue, St. Paul, Mn, United States of America

* nikolas@hagemann.at (NH); sbehrens@umn.edu (SB)

Abstract

Slow release of nitrate by charred organic matter used as a soil amendment (i.e. biochar) was recently suggested as potential mechanism of nutrient delivery to plants which may explain some agronomic benefits of biochar. So far, isolated soil-aged and composted biochar particles were shown to release considerable amounts of nitrate only in extended (>1 h) extractions ("slow release"). In this study, we quantified nitrate and ammonium release by biochar-amended soil and compost during up to 167 h of repeated extractions in up to six consecutive steps to determine the effect of biochar on the overall mineral nitrogen retention. We used composts produced from mixed manures amended with three contrasting biochars prior to aerobic composting and a loamy soil that was amended with biochar three years prior to analysis and compared both to non-biochar amended controls. Composts were extracted with 2 M KCl at 22°C and 65°C, after sterilization, after treatment with H₂O₂, after removing biochar particles or without any modification. Soils were extracted with 2 M KCl at 22°C. Ammonium was continuously released during the extractions, independent of biochar amendment and is probably the result of abiotic ammonification. For the pure compost, nitrate extraction was complete after 1 h, while from biochar-amended composts. up to 30% of total nitrate extracted was only released during subsequent extraction steps. The loamy soil released 70% of its total nitrate amount in subsequent extractions, the biochar-amended soil 58%. However, biochar amendment doubled the amount of total extractable nitrate. Thus, biochar nitrate capture can be a relevant contribution to the overall nitrate retention in agroecosystems. Our results also indicate that the total nitrate amount in biochar amended soils and composts may frequently be underestimated. Furthermore, biochars could prevent nitrate loss from agroecosystems and may be developed into slow-release fertilizers to reduce global N fertilizer demands.



acknowledges DFG grant KA-3442/1-1 and the FACCE-JPI project "DesignerChar4Food" that enabled her to work on nitrate capture. The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

Competing interests: The authors have declared that no competing interests exist.

Introduction

Biochar is defined as carbonized organic matter produced predominantly from agricultural residues [1] that can be applied in animal farming, manure treatment, as composting additive, and eventually as a soil amendment. Inspired by the global historic use of charcoal in agriculture [2–6], biochar is today mainly applied with the intention to increase crop yields. So far, this is done with mediocre success of just 18% grand mean yield increase across 60 studies around the world [7]. However, there are cases of up to three-[8] to fourfold crop yield increase [9], which need to be mechanistically understood to identify the factors that lead to plant growth promotion. The studies resulting in these remarkable yield increases both used low biochar application rates per hectare with high-dose root zone application together with a nitrogen source in planting basins. Biochar was either co-applied with inorganic NPKS fertilizer [8], or macerated in urine prior to co-application with compost [9].

The interaction of biochar with mineral and organic nitrogen species, specifically with nitrate, was recently suggested as one key mechanism of biochar plant growth promotion, as nitrate was shown to be slowly released from both soil-aged [10] and co-composted biochars [11]. The term "co-composted" refers to biochar which is mixed with compost feedstock (i.e. organic matter that is both rich in nutrients and labile organic carbon, e.g. manure) prior to aerobic composting [12]. This approach resulted in a compost of higher agronomic quality (superior plant growth promotion in pot trails) compared to the mixing of pristine/fresh biochar (no post-production treatment) into already matured compost [11].

Plant available nitrate in soil or compost is typically quantified by extraction with de-ionized water or 2 M KCl solution for 1 h [13]. Following up on the work of Kammann and colleagues [11], we define "slowly released nitrate" as nitrate that is only released in subsequent extractions, after an initial 1 h extraction. The underlying mechanisms of "nitrate slow release" are so far widely unknown and summarized as "nitrate capture".

Slow release of nitrate by biochar might prevent nitrate leaching $[\underline{10}]$ and provide nitrate to plants over a longer period of time compared to non-biochar-amended composts or fertilized soils $[\underline{11}]$. However, this effect has so far mostly described for isolated biochar particles, but has been hardly studied within the respective matrix, i.e. compost or soil. Thus, the relevance of slowly released nitrate by biochar can be questioned as also soil (clay, e.g. $[\underline{14}]$) and compost might not release all nitrate and ammonium within 30 min or 1 h of extraction.

Therefore the goal of this study was to quantify the release of nitrate and ammonium from three different biochar-amended manure composts and a biochar-amended loamy soil in comparison to unamended compost and soil. Nitrate and ammonium were quantified following repeated extractions with 2 M KCl in 5 to 6 steps over a period of 1 week of total extraction time. We used different extraction conditions to gain further insights into the mechanisms of nitrate capture and slow release.

Methods

Biochar amended composts

Three different biochars were aerobically co-composted at 4.3% (w/w) in windrows [15] (20 m³ feedstock per treatment) with mixed manures and green plant material (manure: green plant material = 20:1 by weight) at the Ithaka Institute at St. Léonard, VS, Switzerland from August to October 2014 (biochar-amended composts CB1, CB2, CB3). In biochar-amended compost CB1, we used a mixed woody waste biochar B1 (700°C, Pyreg[®] reactor [16]), in CB2 a sewage sludge char B2 (650°C, Pyreg[®] reactor) and in CB3 a wood waste/pruning residue biochar B3 quenched with water (700°C, flame curtain pyrolysis in a KonTiki [17, 18]). Biochar properties

were analyzed according to the requirements of European Biochar Certificate [1] by Eurofins Umwelt Ost GmbH, Halsbrücke-Tuttendorf, Germany and are listed in <u>Table 1</u>.

An additional control windrow (Con) was not amended with biochar. Frequent aeration (daily mechanical turning during the first three weeks, every three days thereafter) [<u>15</u>] resulted in composting temperatures of ~60°C for at least 2 weeks. After 63 days, composts contained <10 mg NH₄⁺-N kg⁻¹, had ambient temperature and were packaged in open plastic bags and stored frost-protected.

Tübingen biochar field trial

In June 2012, B1 type biochar (same manufacturer, same type of feedstock, different batch, and separate analysis in Table 1) was incorporated at a rate of 60 Mg ha⁻¹ into the upper 15 cm of a Terric Anthrosol (top- and subsoil of a Cambisol mixed by construction activities) at the Tübingen-Sand field site (lat. 48.5342, long. 9.0711). Before that, biochar was soaked in a diluted commercial fertilizer solution overnight (1:1 w/v, 1.25 g N kg⁻¹ biochar) and control plots (no biochar amendment) received an equivalent amount of fertilizer. There was no further fertilization during the experiment, which included cropping with Emmer wheat (*Triticum dicoccon*) in 2012 and winter vetch (*Vicia villosa*) in 2013 and green fallow thereafter. Soil from biochar-amended plots and biochar-free control plots was sampled from the upper 15 cm in September 2015.

Extraction procedures

Nitrate and ammonium were repeatedly extracted 1:10 (w/v) with 2 M KCl in 50 mL Falcon tubes in the dark on an end-to-end-shaker (HS501, IKA, Germany) at 150 rpm at room temperature (22±3°C), if not stated differently. After each step of extraction, Falcon tubes were centrifuged (4000 g, 10 min) and the supernatant was decanted into clean measuring cylinders to determine the volume of the decanted extractant. Aliquots were taken from the measuring cylinders for the quantification of nitrate and ammonium. Extractions were performed in triplicates. Composts without further modification were extracted both in February 2015, i.e. 6 months after beginning of the composting process, and in September/October/November 2015, i.e. after 12-14 months. After 6 months, composts were additionally extracted in a water bath at 70±1°C. After 12-14 months, composts were extracted additionally (i) after manually removing all biochar particles visible to the naked eye ("w/o biochar"), (ii) after γ -sterilization of the composts with 36.2 kGy by Synergy Health Allershausen GmbH, Germany, and extraction with autoclaved 2 M KCl under sterile conditions next to a Bunsen burner ("y-sterilized") and (iii) with a combined 2 M KCl + 3% H_2O_2 solution in the first step of extraction and 2 M KCl in the subsequent steps ("3% H₂O₂"). Biochar particles removed from the three biochar treatments were also analyzed and results were in line with previous studies [10, 11] showing slow release of nitrate by biochar. The results will be reported elsewhere [20].

Nitrate and ammonium quantification and data analyses

Nitrate was quantified by continuous flow analysis (SEAL Analytical, Germany) after reduction to nitrite with hydrazine, which was prepared according to SEAL's advice for soil extracts. Nitrite is quantified by UV-Vis absorption at 550 nm after reaction with N-1-naphtyl-ethylendiamin. Ammonium is quantified after reaction with sodium salicylate by UV-Vis absorption at 660 nm. The SEAL system is equipped with dialysis membrane, which removes any extraneous micro-particles to prevent side reactions or additional absorbance. We tested this system for artefacts due to the high content of dissolved organic carbon (DOC) and did not find any impact of DOC under relevant conditions. Detailed results are presented in the SI. Data were

	EBC basic treshold	B1	B1 used in soil	B2	B3
Manufacturer		SwissBiochar GmbH, Belmont-sur- Lausanne (VD), Switzerland	SwissBiochar GmbH, Belmont-sur- Lausanne (VD), Switzerland	Pyreg GmbH, Bingen. Germany	Ithaka institute, Arbaz (VS), Switzerland
Technology		Pyreg®	Pyreg®	Pyreg [®]	KonTiki-flame curtair pyrolysis
Feedstock		Mixed woody waste materials	Mixed woody waste materials	Sewage sludge	Vine wood
HTT" ["C]		700	700	650	750
BET surface [m²g` 200 232 ']		60	252		
Ash 550°C [% w/w]		18.2	19.4	76.5	18.4
Elemental Composition		A			
н	5.86	2.13	1.03	0.68	1.45
С	> 50	74.5	73.2	21.3	76.8
N		0.68	0.64	1.70	0.75
0	1.2	4.5	5.7	-2.7°	2.5
S		0.04	0.06	2.43	0.07
Molar ratios					
H/C	< 0.6	0.34	0.17	0.38	0.22
H/Corg	< 0.7	0.34	0.18	0.38	0.23
0/C	< 0.4	0.045	0.058	-0.01	0.024
pН	< 10	8.3	8.0	7.2	8.5
Salt [g kg ⁻¹]		3.83	4.3	8.41	4.71
Trace elements [mg kg ⁻¹]					
Pb	< 150	3	<2	27	4
Cd	<1.5	< 0.2	< 0.2	0.6	< 0.2
Cu	< 100	13	16	610	86
Ni	< 50	5	8	65	6
Hg	< 1	< 0.07	< 0.07	< 0.07	< 0.07
Zn	< 400	52	45	1290	200
Cr	< 90	6	10	110	9
В		24	36	74	41
Mn		190	310	1140	160
Nutrients [mg kg ⁻¹]	0-1/	Particular and the second s			
Р	6. D	870	1400	87000	2100
Mg		2700	3300	16000	4200
Ca		37000	49000	100000	40000
к		5800	8400	7200	4800
Na 740		740	830	6500	740
Fe		3900	2700	130000	3700
Si		28000	22000	36000	21000
S		230	400	230000	550
PAH [mg kg ⁻¹] ^b	12	4.60	6.70	2.40	6.90

Table 1. Origin of biochars and characterization according to the requirements of the European Biochar Certificate.

Bold numbers indicate that EBC basic threshold was exceeded (in B2 only).

^a Highest Treatment Temperature

^b Sum of 16 polyaromatic hydrocarbons as suggested by the US Environmental Protection Agency (EPA), extracted with toluene as recommended by the EBC [1, 19]

^c Oxygen content is calculated after thermal oxidation as follows: [O] = 100% - [C] - [H] - [N] - [S] - [ash]. Negative values are the result of both CO₂ precipitated as carbonate in the ash or reduced inorganic components of the biochar. The oxygen bound in the oxides of the inorganic compounds of the biochar increases the mass of the ash (pers. comm. Eurofins Umwelt Ost GmbH).

doi:10.1371/journal.pone.0171214.t001

corrected for the residual extractant that could not be removed by decanting (residual volume of extractant = water content of sample + added extractant-decanted extractant) which carries a small amount of already extracted nitrogen from one to the subsequent extraction. Initial water content was determined after drying separate aliquots of composts and soils at 105°C for 48 h. Data were normalized to the dry matter content of the composts and presented as the average of triplicate extraction ± standard error. Statistical analysis was conducted in ORIGIN PRO 8 (OriginLab, Northampton, MA, USA). Differences between the different composts were tested with one-way-ANOVAs and Tukey test, differences between soil and biochar amended soil were assessed with the paired *t*-test. The original data are available through PANGAEA database (doi.pangaea.de/10.1594/PANGAEA.867498).

Total nitrogen

Composts were freeze dried in March 2015, i.e. 7 months after setting up the composting windrows. After grinding in an agate mortar, samples were analyzed in triplicates in a CN element analyzer (vario EL, elementar, Hanau, Germany).

Results & discussion

Nitrate extraction at ambient temperature from compost after 6 months

Typically, a 1 h extraction with e.g. 2 M KCl is used to quantify the amount of extractable NO_3^- from soil or organic fertilizers such as compost [13]. After a total extraction time of 111 h (1 h + 1 h + 1 h + 18 h + 96 h), the amount of total extracted nitrate from the control compost did not differ considerably compared to the standard extraction procedure of 1 h only (0.64±0.07 vs. 0.60±0.06 g NO_3^- -N kg⁻¹, [total extraction] vs. [1h extraction], Fig 1A). The extracts from biochar-amended composts showed just 54–87% of the nitrate content of the control compost according to the 1 h standard extraction procedure (Fig 1A). However, for all biochar-amended composts, additional NO_3^- was released during the repeated extraction. Total NO_3^- content increased by 52% (CB1), 14% (CB2) and 21% (CB3) after a total of 5 extractions steps compared to the nitrate content according to first 1 h of extraction of the respective sample. Only the biochar-amended compost CB3 showed an extractable NO_3^- content comparable to the non-biochar-amended compost CB1 and sewage sludge char-amended compost CB2 was significantly lower, even after 1 week extraction time.

Nitrate extraction at elevated temperature

In order to potentially increase extraction efficiency and to accelerate the extraction of nitrate, repeated extractions were conducted at 70 ± 1 °C. These extractions resulted in the same amounts of NO₃⁻ released from non-biochar amended compost, biochar amended compost CB1 and sewage sludge char amended compost CB2. However, a total of 0.97 ± 0.21 g NO₃⁻-N kg⁻¹ were quantified by the extraction from CB3, i.e. 53% more compared to the extraction at 22 ± 3 °C on the shaker. This temperature-correlated increase of NO₃⁻ was only quantified for CB3 and thus was caused by additional NO₃⁻ release by biochar B3. B3, compared to B1 and B2, seems to have a greater capability to capture nitrate that is less accessible. Assuming that the difference of ~0.3 g N kg⁻¹ between control compost and biochar-amended compost CB3 was solely released from the biochar contained in the CB3 substrate, the biochar B3 contains at least 3 g N kg⁻¹, based on a final concentration of 10% biochar by weight. Initially, compost feedstock was amended with 4.3% biochar, but the composting process led to a



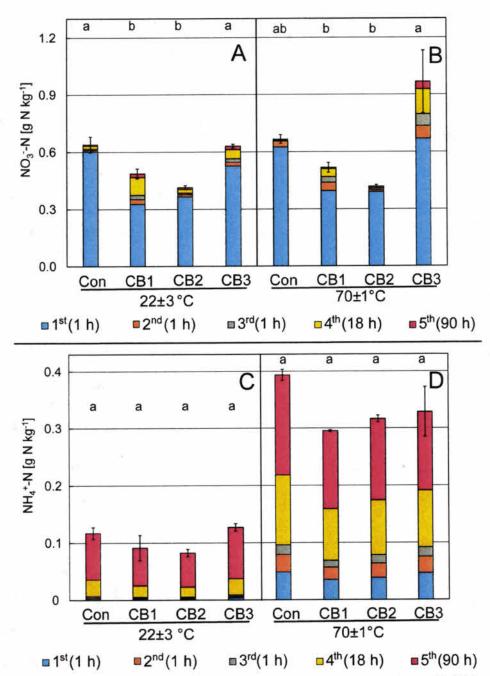


Fig 1. Mineral Nitrogen release during repeated extraction from 6 months old substrates. (A, B) Nitrate and (C, D) ammonium released from biochar-amended composts (Pyreg[®]—wood biochar amended compost CB1, Pyreg[®]—sewages sludge char amended compost CB2, Kon-Tiki—wood biochar amended compost CB3) and a non-amended control compost (Con) during consecutive, repeated extraction steps with 2 M KCl performed at ambient temperature on a shaker ("22±3'C", A, C) or in a water bath ("70±1'C", B, D). Extractions were performed 6 months after the beginning of the aerobic composting (2 months in aerobically managed windrows, 4 months storage in open plastic bags). Subsequent extraction steps with individual duration from 1 to 96 h are shown with increasing dark colors. Error bars indicate standard errors of triplicate extractions summated for 5 repeated extractions, lower case letters depict significant differences (0.05 level of an ANOVA) in total extracted amount of the respective N species with one set of extractions.

doi:10.1371/journal.pone.0171214.g001

mass loss due to oxidation of labile organic matter of the manure and thus to a relative increase of the biochar concentration to approximately 10% biochar [15].

Biochar nitrate capture

The term "nitrate capture" refers to uptake mechanisms of nitrate by biochar which are not yet fully understood. Up to 5.3 g NO3⁻N kg⁻¹ was captured in co-composted biochar particles as described by Kammann and colleagues [11]. They used a different wood biochar produced at 600-700°C (Carbon Terra GmbH, Wallerstein, Germany), but the same composting protocol with slightly different feedstocks (additional use of rock powder, different composition of manures, extractions ~2-3 years after composting process). Thus, despite differences in the type of wood biochar, nitrate capture (3 vs. 5 g NO3⁻-N kg⁻¹) was within the same range in our experiment. However, this capture of anionic nitrate by biochar cannot be fully explained by conventional anion exchange processes that are typically quantified as anion exchange capacity. Biochar is typically assumed to have a negative surface charge, which is responsible for its cation exchange capacity [21, 22]. Instead, non-conventional ion-water bonding/non-conventional hydrogen bonding have been suggested to be responsible for NO_3^{-1} retention by both cocomposted and soil-aged biochar [11, 23, 24]. However, non-conventional hydrogen bonding on inner porous biochar surfaces have generally not been subject to systematic investigation. Comparing potential key properties of biochars such as BET specific surface area, content of major elements, trace metals and nutrient contents as well as H/C and O/C ratios (Table 1) did not reveal major differences between biochars B1 and B3, at least not on the bulk scale. However, B2, a sewage sludge char, had considerably lower carbon content, elevated trace metal content and a lower BET specific surface area than B1 and B3, which might explain the observed lower nitrate capture.

Nitrate extraction after compost storage

Extractions after 12-14 months of compost maturation resulted in considerable higher extractable NO3⁻ contents for all composts (Fig 2A) compared to the extraction after 6 months. Compost maturing leads to biomass mineralization; ammonification and nitrification are probably responsible for this increase in NO_3^{-1} [25]. This increase was quantified exclusively with the first extraction and was similar for all three biochar amended composts as well as the notamended control. The absolute amount of NO3⁻ released from biochar amended composts in subsequent extractions (second to sixth extraction) did not differ from the results after 6 months. Thus, the relative contribution of slow nitrate release to the overall nitrate content of biochar-amended composts CB1, CB2 and CB3 decreased over time. Biochar was able to capture NO3⁻ released during the aerobic composting process in the windrows. After 2 months, the composting process was completed by conventional criteria (low NH4⁺ concentration, windrows cooled down to ambient temperature, very low CO₂ production) and packed into open plastic bags for storage. During this storage, water content was lower than during composting in windrows (wet/dry ratio of compost: 1.7-1.8 vs. 1.8-2.1) and the composts were not mixed anymore by mechanical aeration. Thus, nitrate produced during storage might not be captured by biochar due to water transport limitations for the nitrate, i.e. nitrate might not have reached the biochar surfaces.

Nitrate extraction from compost after removing biochar particles

After removing biochar particles, the effect of slow release of nitrate in subsequent extractions disappeared for biochar-amended compost CB2 (amount of slowly released nitrate < standard error of all extractions) (Fig 2B). B2 had a granular structure which was easy to manually

PLOS ONE

Biochar nitrate capture in compost and soil

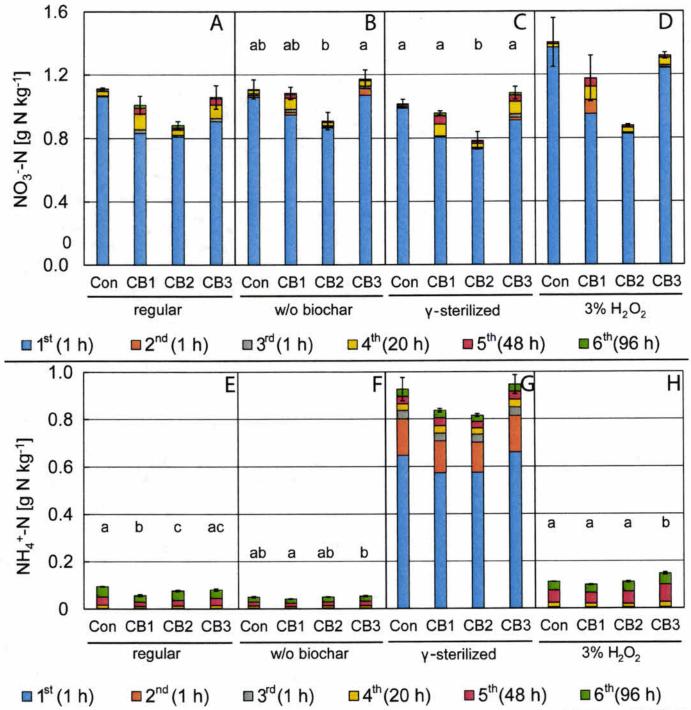


Fig 2. Mineral nitrogen release during repeated extraction from 12–14 months old biochar-amended composts. (A, B, C, D) Nitrate and (E, F, G, H) ammonium released from different biochar-amended composts (Pyreg[®]—wood biochar amended compost CB1, Pyreg[®]—sewages sludge char amended compost CB2, Kon-Tiki–wood biochar amended compost CB3) and a non-amended control compost (Con) during consecutive, repeated extraction steps with 2 M KCI (A, E) at ambient temperature on a shaker without further modification ("regular"), (B, F) after removing all biochar particles visible to the naked eye ("w/o biochar"), (C, G) after γ-sterilization of the composts ("γ-sterilized") or (D, H) with a combined 2 M KCI + 3% H₂O₂ solution ("3% H₂O₂") in the first extraction step. Extractions were performed 12 to 14 months after the beginning of the aerobic composting (2 months in aerobically managed windrows, subsequent storage storage in open plastic bags). Subsequent extraction steps with individual duration from 1 to 96 h are shown with increasing dark colors. Error bars indicate standard errors of triplicate extractions summated for 6 repeated extractions, lower case letters depict significant differences in total



extracted amount of the respective N species with one set of extractions. If no lower case letters are shown, the average values were not significantly different by the 0.05 level of an ANOVA.

doi:10.1371/journal.pone.0171214.g002

separate from the compost matrix. Biochar-amended composts CB1 and CB3 still showed slow release of nitrate even after removing all biochar particles visible to the naked eye, but to a lower extent (66–76% of slowly released nitrate in composts prior to biochar removal). Most likely, biochars B1 and B3 were not completely removed. Particle size distribution of CB1 and CB3 had a much larger spectrum with high amounts of micron size particles (data not shown). Additionally, Spokas and colleagues showed the physical disintegration of biochar in the presence of water resulting in biochar micro- and nanoparticles with the same chemical structure (approximated by O:C ratios) as the original biochar particles [26]. These particles also seem to contribute to the slow release of nitrate.

Nitrate extraction after compost sterilization

One batch of composts was γ -sterilized before the extraction to check if microbial ammonification and nitrification during the extraction (up to 167 h at 23°C) might cause slow release of nitrate. However, there were no considerable differences compared to the extraction of non- γ irradiated samples (<u>Fig 2C</u>). This was expected, as the activity of a soil or compost microbial community should be very low under the hypersaline conditions (2 M KCl = 149.1 g L⁻¹ salt) during extraction. Thus, slow release of nitrate is not a biotic process.

H₂O₂ as extractant

In order to test if nitrate was retained in a matrix of labile organic carbon, we combined 2 M KCl with 3% H_2O_2 solution during the first step of extraction. H_2O_2 induces abiotic oxidative mineralization of organic matter [27]. If nitrate was retained e.g. by an organic coating on the co-composted biochar particles [28, 29], oxidative mineralization could accelerate the rate of nitrate release by removing this organic matrix. Except for CB2, extraction with H_2O_2 -containing extractant resulted in increased total release of NO_3^- for all composts (Fig 2D), probably due to the mineralization and abiotic oxidation of compost organic nitrogen [27]. The elevated content of iron in B2 (Table 1, 130 g kg⁻¹) might have protected the biochar-amended compost CB2 from oxidation, as Fe(III) is known to catalyze the decomposition of H_2O_2 [30]. The amount of slowly released NO_3^- increased for CB1, but was not affected for CB2 and slightly decreased for CB3.

The increase for CB1 mainly happened during the second extraction, which is remarkably as the second extraction was not relevant during all other extractions (12 mg N kg^{-1} average release of NO₃⁻ during second extractions for all extractions after 12–14 months, here: 87 mg N kg⁻¹). Residual H₂O₂, e.g. retained by biochar B1, might have still reacted with the compost organic matter. However, it is not clear why this happened only in CB1.

Decreased amounts of slow released NO₃⁻ in CB3 show that captured nitrate on biochar B3 became partly accessible by the oxidative mineralization by H_2O_2 and thus was already extracted with the first step. This indicates that B1 and B3 may have different mechanisms to capture NO₃⁻. Organic coating of co-composted biochar [28, 29] might contribute to the nitrate capture of B3 as an additional reservoir for nitrate.

Nitrate extraction from soil

Unlike compost, the sandy loam soil showed a certain amount of slow release nitrate (Fig 3A) which comprised 70% of the total extracted nitrate. According to standard protocols, nitrate

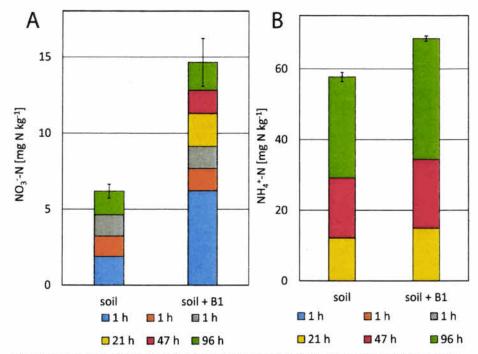


Fig 3. Mineral nitrogen release from soil without and with biochar. (A) Nitrate and (B) ammonium released from soil and biochar-(B1-type)-amended soil. Error bars indicate standard errors of triplicate extractions summed for 6 subsequent extractions. T-test revealed that the total amounts of extracted nitrate are significantly different (p = 0.0071), unlike the amounts of ammonium (p = 0.067) (B). The N content of some extracts was below detection limit, thus these sections are not visible in the tacked bar graphs.

doi:10.1371/journal.pone.0171214.g003

should be completely extractable with water or 2 M KCl within 1 h of incubation [13]. These protocols assume that nitrate moves freely within leachate in soils with predominantly negative surface charges [31] Nitrate retention has so far mainly been discussed in the context of highly weathered tropic soils with predominantly positive charged surfaces [31]. However, the soil used in this study was a temperate soil. The clay fraction of the soil, iron minerals or soil organic matter might be responsible for the slow release. Komarneni and colleagues developed a nitrate slow release fertilizer based on anionic clays that completely released NO_3 only after 3 to 7 days of extraction with an artificial soil solution [32]. Also Bhardwaj and colleagues produced a slow release fertilizer based on clay and zeolite [33]. However, nitrate retention and soil clay content do not necessarily correlate [34]. Klučáková showed that nitrate can sorb to humic acids by so far unknown mechanisms [35]. However, it is unknown how this effects the extractability of nitrate from soil. Klučáková used humic acids extracted from lignite. Additionally, the control compost used in this study, i.e. a material with very high organic matter content, did not show significant nitrate retention. Also other soil constituents have been suggested to sorb nitrate, including iron minerals and allophane [34]. Further studies comparing soils with different clay content, different types of clays, and different content of iron and organic matter are necessary to elucidate what mechanisms might be responsible for the retention of nitrate in non-biochar amended soil.

The amendment with 60 Mg ha⁻¹ biochar 3 years before the sampling for this study slightly decreased the relative amount of nitrate extracted during extractions steps 2 to 6 (58%). However, biochar amendment significantly (t-test, p = 0.007) increased the amount of total extractable nitrate by a factor of 2, although both treatments initially received the same amount of fertilizer and were managed identically over three years.

Release of ammonium

Considerable quantities of NH_4^+ have been released in all extractions (Figs <u>1C</u>, <u>1D</u>, <u>2E-2H</u> and <u>3B</u>). For both compost and soil extractions, the quantities of released ammonium rather seemed to depend on the duration of extraction than on the presence or absence of biochar. Elongated extractions with aqueous solutions have been used previously to estimate the amount of soil or compost organic N that can be mineralized. Cordovil and colleagues found that hot (100°C) extraction with 2 M KCl for 4 h could estimate the N mineralization from organic amendments during 4 weeks of incubation in soil [<u>36</u>]. Curtin and Campbell suggested "anaerobic incubation" of soil in distilled water (1:10) for 1 week at 40°C to estimate mineralizable nitrogen from subsequent NH_4^+ -N quantification [<u>37</u>]. In our experiments, all extractions showed that biochar had limited impact on the quantity of mineralizable N with CB2 having apparently the lowest mineralization rate. The highest quantities of NH_4^+ during the first step of extraction were found in γ -sterilized compost due to cell lysis, the subsequent abiotic ammonification and the absence of nitrifying bacteria. Still, ongoing ammonification during the extraction even after γ -sterilization strongly suggests an abiotic nature of this process.

Potential impact of biochar on the fate of N during composting

Elemental analysis (Table 2) showed that total N (N_{tot}) of the composts is one order of magnitude higher than the total amount of extracted mineral N, i.e. the sum of NO₃⁻ and NH₄⁺ (NO₂⁻ was negligible for all measurements). Biochar-amended composts CB2 and CB3 have the same N content as the non-biochar-amended control, although the initial N content before the composting was lower due to the "dilution" of the N rich manure by the 4.3% amendment with the biochar. CB1, however, had a lower total N content compared to all other substrates. Taking into account that the biochar amended composts had 4.3% less manure-N in the beginning, this indicates that biochar B1 could not reduce losses of nitrogen (leaching, gaseous losses) compared to the control compost, while B2 and B3 seem to improve the preservation of feedstock N. However, because the composting was performed in mechanically aerated windrow at sub-industrial scale, it was not possible to assess a holistic mass balance with C and N budgets. Thus, our conclusions on total nitrogen losses during the composting process have to be interpreted with care. We monitored pH during the composting process, as pH controls the losses of ammonia during composting (data not shown). However, we did not observe considerable differences.

Table 2. Mineral and total N content of non-amended control and biochar-amended composts.

		Control	CB1	CB2	CB3
Mineral N [NO3 ⁻] + [NH4 ⁺], [g kg ⁻¹]	6 months	0.8±0.1	0.6±0.0	0.5±0.0	0.8±0.1
	6 months, 70°C	1.1±0.1	0.8±0.0	0.7±0.0	1.3±0.2
	12 months	1.2±0.0	1.1±0.1	1.0±0.0	1.1±0.1
	12 months w/o biochar	1.2±0.1	1.1±0.0	1.0±0.1	1.2±0.1
	12 months sterilized	1.9±0.1	1.8±0.1	1.6±0.1	2.0±0.1
	12 months H ₂ O ₂	1.5±0.2	1.3±0.1	1.0±0.0	1.5±0.0
Total N [g kg ⁻¹]	elemental analysis	15.4±0.6	13.9±0.1	15.6±0.7	15.8±0.0

Amount of mineral N (= $[NO_3^-] + [NH_4^+]$) quantified in repeated extractions after 6 and 12 months. Amount of total N as quantified with elemental analysis of freeze dried compost.

doi:10.1371/journal.pone.0171214.t002

Agroecological relevance and future research

In this study we showed that biochar nitrate capture is a relevant process controlling total nitrate budgets of biochar-amended composts and soils. Even biochar micro- or nano-particles seemed to contribute to the nitrate capture and the resulting slow release of nitrate. Nitrate slow release was based on abiotic mechanisms because it was still observable after γ -sterilization of the composts. Non-biochar-amended compost did not show slow release of nitrate. Thus, biochar was the only component in a biochar-amended manure compost that caused nitrate capture and enabled its slow release. Soil, in our case a sandy loam, however, could retain nitrate beyond the conventional 1 h 2 M KCl extraction as well, because 70% of total extracted nitrate (6.2 mg N kg⁻¹) was only released during subsequent extractions, too. However, biochar did not further increase the relative contribution of slow release in biochar amended soil), but increased the total pool of extractable nitrate in soil (14.6 mg N kg⁻¹).

Increasing nitrate retention in agroecosystems is critical. Galloway and colleagues argue that the global production of reactive nitrogen species, which are predominately used as fertilizers, increased by 120% since 1970 due to a "pervasive inefficiency" [<u>38</u>] that promotes the formation of greenhouse gas nitrous oxide in agricultural soils [<u>39</u>]. Additionally, leached nitrate can be looked at as unintended fertilization of adjacent ecosystems and thus can lead to eutrophication and decrease the diversity of plant species e.g. in natural grasslands [<u>40</u>]. Ultimately, leached nitrate can be transported to the ocean and can cause eutrophication and the formation of hypoxic zones [<u>41</u>]. Overall, the anthropogenic alteration of global nitrogen cycling is considered the most urgent thread to maintaining the Earth in a resilient and habitable state [<u>42</u>]. Inefficient use of nitrogen fertilizers resulting in NO₃⁻ leaching to the groundwater is a major contributor to this situation [<u>43</u>]. Future research on biochar nitrate capture and slow release needs to aim at understanding the mechanisms of this so far hardly understood retention of nitrate. This might create the scientific basis for both a new generation of slow release fertilizers that also reduce nitrate leaching from agroecosystems on the long run. We suggest three complementary research strategies:

First, soil nitrate capture should generally be investigated in more detail. Our study showed that nitrate capture and slow release is not an exclusive characteristic of biochar, but can be an intrinsic feature of soils, too. However, it is unknown which soil constituents are responsible for this effect. So called "abiotic nitrate incorporation" into soil organic matter has been suggested in earlier studies [44-46]. Different types of clays have been successfully tested as basic constituents in slow release fertilizers [32, 47]. Thus, clays and biochars should be compared in sorption and desorption experiments to gain further mechanistic insights. Such experiments have been already performed with respect to N leaching in amended soils but not for slow release fertilizer development [14].

Second, **kinetics of biochar slow release of nitrate** [48] should be quantified for contrasting biochars and after nitrate sorption under contrasting conditions (pristine biochar vs. aged biochar, different nitrate sources, etc.). While a broad range of studies on the sorption of nitrate to biochar [49, 50] or on the effect of biochar on nitrate leaching from soil columns [51–53], have been performed, only few studies also focused on desorption of nitrate from biochar after sorption. Release kinetics under different conditions can reveal insights into strategies to maximize biochar nitrate capture, and the trade-off between plant availability and loss through leaching. For this purpose, it will be necessary to understand the underlying mechanisms on the molecular scale. New methods to quantify the amount of captured nitrate more rapidly could aid in this research. This study showed that the addition of 3% H₂O₂ to 2 M KCl or the increase of temperature during extraction (70°C) did not uniformly accelerate the extraction of captured

nitrate for all biochars, but revealed new mechanistic insights. Kammann and colleagues [11] used electro-ultrafiltration to gain mechanistic insights into the release characteristics. However, the method only released a fraction <50% of the nitrate that could potentially be released. This was confirmed by methodical investigations of Haider and colleagues [10]. Thus electro-ultrafiltration offers mechanistical insights but no means for quick and complete extraction of captured N from biochar particles. More methodical studies will be needed.

Third, release of organic N and C from (aged) biochar, biochar amended composts and soil should be quantified alongside with nitrate release. Organic N contributes to plant nutrition; Kammann and colleagues showed that co-composted biochar slowly released organic N in addition to low amounts of NH_4^+ , and dominantly NO_3^- [11]. They also showed an exponential rise-to-maximum correlation of the release of nitrate to the release of dissolved organic carbon with R^2 values of >0.99 that argue for a mechanistic physico-chemical relationship between nitrate and DOC [11]. The present study showed that H_2O_2 reduced the amount of slowly released nitrate at least for one biochar-amended compost (CB3), indicating a contribution of labile organic matter to nitrate capture, e.g. by an organic coating. Organic coatings on co-composted biochar particles have been proposed previously [28, 29] and might serve as an additional reservoir for nitrate.

The proposed research agenda could contribute to a more holistic understanding or biochar nitrate capture and slow release, which may facilitate the development of biochar-based slow release fertilizers. This will contribute to reducing the environmental impact of fertilization. Promoting the use of biochar as fertilizer carrier for anion retention in soils will contribute to the protection of our water bodies. So far, the widespread application of biochar in agriculture is considered desirable mainly due to its climate change mitigation potential [54– 57] and the hope to mimic the historic examples of extremely fertile anthropogenic soils [6, 58]. However, overall yield increase by biochar is just mediocre (+18%), while "high yield increases are more of an exception than the rule" as stated by Jeffery and colleagues [7].

Recent research suggests that biochar needs to be "loaded" with nutrients by e.g. co-composting [11], or by macerating in urine [9], or by co-application with mineral fertilizer directly in the rhizosphere [8] to result into remarkable yield increase. Thus, understanding the interaction of biochar and nutrients, particularly the mobile anion nitrate, is vital to achieve biochar-mediated growth promotion and thus provide an economic incentive for farmers to use biochar. Research on biochar nitrate capture mechanisms will provide the basic knowledge to develop slow release fertilizers into commercial products for routine application in sustainable agriculture.

Future studies on biochar and nitrogen transformations should always consider biochar nitrate capture as a potential pool of nitrogen, when data based on extraction are evaluated. Standard extraction procedures might underestimate the extractable nitrate content of biochar amended soils and fertilizers.

Supporting information

S1 File. Quantification of mineral N species in the presence of DOC. Introduction and results and discussion of a study on the potential impact of dissolved organic carbon (DOC) on the quantification of nitrate, nitrite and ammonium. (PDF)

Acknowledgments

We thank Ellen Röhm, Katharina Mayer, Patricia Riede and Anna Conrad for their support in the lab. We thank Kevin Friedrich and Pyreg GmbH, Dörth, Germany for providing biochar B2 and Johannes Harter for setting up and maintaining the Tuebingen-Sand biochar field experiment.

Biochar nitrate capture in compost and soil

Author Contributions

Conceptualization: NH CIK HPS AK SB.

Formal analysis: NH.

Funding acquisition: NH CIK.

Investigation: NH.

Methodology: NH CIK.

Resources: HPS AK SB.

Supervision: SB AK.

Visualization: NH.

Writing - original draft: NH.

Writing - review & editing: CIK HPS AK SB.

References

- European Biochar Foundation—European Biochar Certificate—Guidelines for a Sustainable Production of Biochar. Version 6.1 of June 19, 2015. [Internet]. European Biochar Foundation (EBC), Arbaz, Switzerland 2012.
- 2. Allen RL. Brief Compend of American Agriculture, 3rd Edition. New York: C.M. Saxton; 1847.
- Glaser B, Haumaier L, Guggenberger G, Zech W. The'Terra Preta'phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften. 2001; 88(1):37–41. PMID: <u>11302125</u>
- Wiedner K, Schneeweiß J, Dippold MA, Glaser B. Anthropogenic Dark Earth in northern Germany–The nordic analogue to Terra Preta de Índio in Amazonia? Catena. 2015; 132:114–25.
- Tryon EH. Effect of Charcoal on Certain Physical, Chemical, and Biological Properties of Forest Soils. Ecological Monographs. 1948; 18(1):81–115.
- Wiedner K, Glaser B. Traditional use of biochar. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science, Technology and Implementation. 2 ed. London: Routledge; 2015. p. 15–38.
- Jeffery S, Abalos D, Spokas K, Verheijen FGA. Biochar effects on crop yield. In: Lehmann J, Joseph SD, editors. Biochar for Environmental Management: Science, Technology and Implementation (2nd Edition). Florence, KY, USA: Taylor and Francis; 2015. p. 301–25.
- Cornelissen G, Martinsen V, Shitumbanuma V, Alling V, Breedveld GD, Rutherford DW, et al. Biochar effect on maize yield and soil characteristics in five conservation farming sites in Zambia. Agronomy. 2013; 3(2):256–74.
- Schmidt H-P, Pandit B, Martinsen V, Cornelissen G, Conte P, Kammann C. Fourfold Increase in Pumpkin Yield in Response to Low-Dosage Root Zone Application of Urine-Enhanced Biochar to a Fertile Tropical Soil. Agriculture. 2015; 5(3):723.
- Haider G, Steffens D, Müller C, Kammann CI. Standard extraction methods may underestimate nitrate stocks captured by field aged biochar. Journal of Environmental Quality. in press; 45(4).
- Kammann CI, Schmidt H-P, Messerschmidt N, Linsel S, Steffens D, Müller C, et al. Plant growth improvement mediated by nitrate capture in co-composted biochar. Scientific Reports. 2015; 5:1–12. http://www.nature.com/srep/2015/150609/srep11080/abs/srep11080.html#supplementary-information.
- Fischer D, Glaser B. Synergisms between Compost and Biochar for Sustainable Soil Amelioration. In: Kumar S, Bharti A, editors. Management of Organic Waste. 1. Rijeka: Intech; 2012.
- Maynard DG, Kalra YP, Crumbaugh JA. Nitrate and Exchangeable Ammonium Nitrogen. In: Carter MR, editor. Soil Sampling and Methods of Analysis: Taylor & Francis; 1993. p. 97–106.
- Dempster DN, Jones DL, Murphy DV. Clay and biochar amendments decreased inorganic but not dissolved organic nitrogen leaching in soil. Soil Research. 2012; 50(3):216–21.
- Kammann CI, Glaser B, Schmidt H-P. Combining Biochar and Organic Amendments. In: Shackley S, Ruysschaert G, Zwart K, Glaser B, editors. Biochar in European Soils and Agriculture: Science and Practice. 1. London: Routledge; 2016. p. 136–60.

- Sehn W, Gerber H, Siekmann K, Scherer J. Thermally mineralized: Pyreg—A process for the decentralized sewage sludge treatment. BWK—Das Energie-Fachmagazin. 2010; 62(3):55–8.
- Schmidt H-P, Taylor P. Kon-Tiki flame curtain pyrolysis for the democratization of biochar production. The Biochar Journal. 2014; 1:14–24.
- Cornelissen G, Pandit NR, Taylor P, Pandit BH, Sparrevik M, Schmidt HP. Emissions and Char Quality of Flame-Curtain "Kon Tiki" Kilns for Farmer-Scale Charcoal/Biochar Production. PLoS ONE. 2016; 11 (5):e0154617. doi: <u>10.1371/journal.pone.0154617</u> PMID: <u>27191397</u>
- Hilber I, Blum F, Leifeld J, Schmidt H-P, Bucheli TD. Quantitative determination of PAHs in biochar: a prerequisite to ensure its quality and safe application. Journal of Agricultural and Food Chemistry. 2012; 60(12):3042–50. doi: 10.1021/jf205278v PMID: 22397545
- Hagemann N, Conte P, Schmidt H-P, Kammann CI, Kappler A, Behrens S. Extent and kinetics of nitrate slow release by pristine, co-composted and soil-aged biochar. in prep.
- Pignatello JJ, Uchimiya M, Abiven S, Schmidt MWI. Evolution of biochar properties in soil. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management—Science, Technology and Implementation. 1. New York: Routledge; 2015. p. 195–233.
- Harvey OR, Herbert BE, Kuo L-J, Louchouarn P. Generalized Two-Dimensional Perturbation Correlation Infrared Spectroscopy Reveals Mechanisms for the Development of Surface Charge and Recalcitrance in Plant-Derived Biochars. Environmental Science & Technology. 2012; 46(19):10641–50.
- Conte P, Marsala V, De Pasquale C, Bubici S, Valagussa M, Pozzi A, et al. Nature of water-biochar interface interactions. GCB Bioenergy. 2013; 5(2):116–21.
- Conte P, Hanke UM, Marsala V, Cimò G, Alonzo G, Glaser B. Mechanisms of Water Interaction with Pore Systems of Hydrochar and Pyrochar from Poplar Forestry Waste. Journal of Agricultural and Food Chemistry. 2014; 62(21):4917–23. doi: <u>10.1021/jf5010034</u> PMID: <u>24814907</u>
- Eklind Y, Kirchmann H. Composting and storage of organic household waste with different litter amendments. II: nitrogen turnover and losses. Bioresource Technology. 2000; 74(2):125–33.
- Spokas KA, Novak JM, Masiello CA, Johnson MG, Colosky EC, Ippolito JA, et al. Physical Disintegration of Biochar: An Overlooked Process. Environmental Science & Technology Letters. 2014; 1(8):326– 32.
- McLean W. Effect of Hydrogen Peroxide on soil Organic Matter. The Journal of Agricultural Science. 1931; 21(02):251–61.
- Prost K, Borchard N, Siemens J, Kautz T, Séquaris J-M, Möller A, et al. Biochar Affected by Composting with Farmyard Manure. Journal of Environmental Quality. 2013; 42(1):164–72. doi: <u>10.2134/jeq2012</u>. <u>0064</u> PMID: <u>23673751</u>
- Joseph SD, Camps-Arbestain M, Lin Y, Munroe P, Chia CH, Hook J, et al. An investigation into the reactions of biochar in soil. Soil Research. 2010; 48(7):501–15.
- Haber F, Weiss J, editors. The catalytic decomposition of hydrogen peroxide by iron salts. Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences; 1934: The Royal Society.
- Wong MTF, Hughes R, Rowell DL. Retarded leaching of nitrate in acid soils from the tropics: measurement of the effective anion exchange capacity. Journal of Soil Science. 1990; 41(4):655–63.
- Komarneni S, Newalkar BL, Li D, Gheyi T, Lopano CL, Heaney PJ, et al. Anionic Clays as Potential Slow-Release Fertilizers: Nitrate Ion Exchange. Journal of Porous Materials. 10(4):243–8.
- Bhardwaj D, Sharma M, Sharma P, Tomar R. Synthesis and surfactant modification of clinoptilolite and montmorillonite for the removal of nitrate and preparation of slow release nitrogen fertilizer. J Hazard Mater. 2012; 227–228:292–300. doi: <u>10.1016/j.jhazmat.2012.05.058</u> PMID: <u>22683109</u>
- Tani M, Okuten T, Koike M, Kuramochi K, Kondo R. Nitrate adsorption in some andisols developed under different moisture conditions. Soil Science and Plant Nutrition. 2004; 50(3):439–46.
- Klučáková M. Adsorption of nitrate on humic acids studied by flow-through coulometry. Environmental Chemistry Letters. 2010; 8(2):145–8.
- Cordovil CMDS, Coutinho J, Goss MJ, Cabral F. Comparison of Chemical Methods of Assessing Potentially Available Organic Nitrogen from Organic Residues Applied to a Sandy Soil. Communications in Soil Science and Plant Analysis. 2007; 38(7–8):989–1006.
- Curtin D, Campbell C. Mineralizable nitrogen. In: Carter MR, Gregorich EG, editors. Soil sampling and methods of analysis. Boca Raton, FL: CRC Press; 2008. p. 599–606.
- Galloway JN, Townsend AR, Erisman JW, Bekunda M, Cai Z, Freney JR, et al. Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions. Science. 2008; 320(5878):889–92. doi: <u>10.1126/science.1136674</u> PMID: <u>18487183</u>

- Davidson EA. The contribution of manure and fertilizer nitrogen to atmospheric nitrous oxide since 1860. Nature Geoscience. 2009; 2(9):659–62.
- Stevens CJ, Dise NB, Mountford JO, Gowing DJ. Impact of Nitrogen Deposition on the Species Richness of Grasslands. Science. 2004; 303(5665):1876–9. doi: <u>10.1126/science.1094678</u> PMID: 15031507
- Diaz RJ, Rosenberg R. Spreading Dead Zones and Consequences for Marine Ecosystems. Science. 2008; 321(5891):926–9. doi: <u>10.1126/science.1156401</u> PMID: <u>18703733</u>
- Steffen W, Richardson K, Rockström J, Cornell SE, Fetzer I, Bennett EM, et al. Planetary boundaries: Guiding human development on a changing planet. Science. 2015; 347(6223):1259855. doi: <u>10.1126/science.1259855</u> PMID: <u>25592418</u>
- de Vries W, Kros J, Kroeze C, Seitzinger SP. Assessing planetary and regional nitrogen boundaries related to food security and adverse environmental impacts. Current Opinion in Environmental Sustainability. 2013; 5(3–4):392–402.
- Dail DB, Davidson EA, Chorover J. Rapid abiotic transformation of nitrate in an acid forest soil. Biogeochemistry. 2001; 54(2):131–46.
- Davidson EA, Chorover J, Dail DB. A mechanism of abiotic immobilization of nitrate in forest ecosystems: the ferrous wheel hypothesis. Global Change Biology. 2003; 9(2):228–36.
- Davidson EA, Dail DB, Chorover J. Iron interference in the quantification of nitrate in soil extracts and its effect on hypothesized abiotic immobilization of nitrate. Biogeochemistry. 2008; 90(1):65–73.
- Xi Y, Mallavarapu M, Naidu R. Preparation, characterization of surfactants modified clay minerals and nitrate adsorption. Applied Clay Science. 2010; 48(1–2):92–6.
- Chintala R, Mollinedo J, Schumacher TE, Papiernik SK, Malo DD, Clay DE, et al. Nitrate sorption and desorption in biochars from fast pyrolysis. Microporous and Mesoporous Materials. 2013; 179:250–7.
- Yao Y, Gao B, Zhang M, Inyang M, Zimmerman AR. Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. Chemosphere. 2012; 89(11):1467–71. doi: <u>10.1016/j.chemosphere.2012.06.002</u> PMID: <u>22763330</u>
- Kameyama K, Miyamoto T, Shiono T, Shinogi Y. Influence of Sugarcane Bagasse-derived Biochar Application on Nitrate Leaching in Calcaric Dark Red Soil. Journal of Environmental Quality. 2012; 41 (4):1131–7. doi: <u>10.2134/jeg2010.0453</u> PMID: <u>22751055</u>
- Alling V, Hale SE, Martinsen V, Mulder J, Smebye A, Breedveld GD, et al. The role of biochar in retaining nutrients in amended tropical soils. Journal of Plant Nutrition and Soil Science. 2014; 177(5):671– 80.
- Angst TE, Patterson CJ, Reay DS, Anderson P, Peshkur TA, Sohi SP. Biochar Diminishes Nitrous Oxide and Nitrate Leaching from Diverse Nutrient Sources. Journal of Environmental Quality. 2013; 42 (3):672–82. doi: <u>10.2134/jeq2012.0341</u> PMID: <u>23673933</u>
- Laird DA, Rogovska N. Biochar effects on nutrient leaching. In: Lehmann J, Joseph S, editors. Biochar for Environmental Management: Science, Technology and Implementation. 2 ed. London: Routledge; 2015. p. 521–42.
- Cayuela ML, van Zwieten L, Singh BP, Jeffery S, Roig A, Sánchez-Monedero MA. Biochar's role in mitigating soil nitrous oxide emissions: A review and meta-analysis. Agriculture, Ecosystems & Environment. 2014; 191:5–16.
- Kuzyakov Y, Bogomolova I, Glaser B. Biochar stability in soil: Decomposition during eight years and transformation as assessed by compound-specific 14C analysis. Soil Biology and Biochemistry. 2014; 70:229–36.
- Lehmann J, Abiven S, Kleber M, Pan G, Singh BP, Sohi SP, et al. Persistence of biochar in soil. In: Lehmann J, Stephen J, editors. Biochar for Environmental Management: Science, Technology and Implementation. 2 ed. London: Routledge; 2015. p. 233–80.
- Hagemann N, Harter J, Behrens S. Elucidating the Impacts of Biochar Applications on Nitrogen Cycling Microbial Communities. In: Ralebitso-Senior TK, Orr CH, editors. Biochar Application. 1. Amsterdam: Elsevier; 2016. p. 163–98.
- Glaser B. Prehistorically modified soils of central Amazonia: a model for sustainable agriculture in the twenty-first century. Philosophical Transactions of the Royal Society B: Biological Sciences. 2007; 362 (1478):187–96.



The Use of Biochar in Composting

By Marta Camps, Massey University; and Thayer Tomlinson, International Biochar Initiative February 2015; for more information, please see <u>www.biochar-international.org</u>. Reviewed by Mariluz Cayuela and M.A. Sánchez-Monedero

Both compost and biochar production are methods to utilize and recycle organic wastes. This paper provides information on the use of biochar in composting and highlights the potential benefits, which include the ability to accelerate the process of composting and reduce the loss of nutrients, among others.

 Composting is a technology for the treatment and disposal of biodegradable waste. Almost any food waste, industrial food waste, and sewage sludge can be composted. The main advantages of successful composting are a decrease in waste volume; the elimination of most organic toxic compounds, pathogens and pests (potentially present in the original



waste); the transformation of organic matter; and associated nutrients into a product that acts as a slow release fertilizer (referred to as 'stabilization' in the compost literature).

 Biochar is a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment. It has a greater persistence than the uncharred precursor biomass. Biochar can be used as a product itself or as an ingredient within a blended product, with a range of potential applications as an agent for soil improvement. When the right biochar is

1



added to the right soil, biochar can, among other benefits, improve resource use efficiency, remediate and/or protect soils against particular environmental pollution, and become an avenue for greenhouse gas (GHG) mitigation¹.

Compost and Biochar: In Competition for Feedstocks?

Although both biochar and compost use organic wastes as feedstocks, the two operations do not have to be an either/or option; instead, they can be combined for synergistic production and utilization. For example, many materials that make good compost, such as food waste and wet manures, are not easily used for biochar production since a large amount of heat would be needed to dry the materials prior to producing biochar. Ideal feedstocks for composting have from 60 - 70% moisture, high nutrient levels, and low lignin content². Ideal feedstocks for biochar have 10 - 20% moisture and high lignin content, such as field residues or woody biomass.

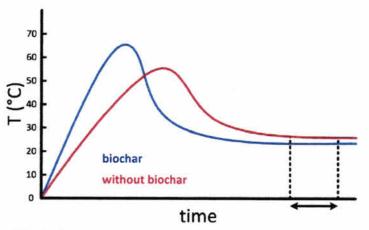
Biochar Benefits to the Composting Processes

Based on current findings, the benefits of adding biochar to the composting process may include shorter compost times; reduced rates of GHG emissions (methane, CH₄ and nitrous oxide, N₂O); reduced ammonia (NH₃) losses; the ability to serve as a bulking agent for compost; and reduced odor. For the biochar material itself, undergoing composting helps to charge the biochar with nutrients without breaking down the biochar substance in the process.

Adding biochar can enhance the composting process through:

- Accelerating the composting process
- Reducing GHG emissions
- Reducing ammonia loss
- Serving as a bulking agent for the compost
- Reducing odor

A wide range of biochar application rates to compost have been tested, from 5 - 10% to 50% (mass basis) or higher^{3, 4}. A biochar dose higher than 20 - 30% (mass basis) is not recommended as an excessive amount relative to the composting material could interfere with biodegradation. At adequate doses, biochar has been found to accelerate the composting process—mainly through improving the homogeneity and structure of the mixture and stimulating microbial



Biochar increases the temperature in a compost process, accelerating the time needed for material decomposition^{4, 6, 7}

activity in the composting mix. This increased activity translates to increased temperatures and a shorter overall time requirement for compost development⁵. This may have important economic implications since accelerated composting is a desirable effect.

2

One challenge to compost operations is the loss of nutrients and the emission of GHGs during the composting process—specifically CH4 and N2O. Adding biochar at 3% (mass basis) to a pig manure, wood chips, and sawdust compost mixture was found to reduce N2O emissions by 26%⁸. For methane, a recent study found that the addition of biochar reduced CH₄ emissions from poultry manure composting piles9. However, other studies have shown that biochar has no impact on the overall GHG emissions since these emissions were offset by the enhanced microbial activity on the composting mix containing biochar¹⁰. In those cases there may not be a net impact on GHG emissions.

The porous nature of biochar can reduce the bulk density of compost and facilitate aeration in the composting mix. For compost feedstocks that are high in nitrogen (N), such as animal manures, biochar offers the opportunity to reduce the overall N loss over the process, especially that of NH₃. The odor problems caused by NH₃ loss during composting are not only unpleasant, but can reduce the acceptance of a composting facility by a community. A 20% (mass basis) biochar addition to poultry litter reduced the NH3 concentration in the emissions by up to 64% and N losses by up to 52% without negatively influencing the composting process^{11, 12}.

A common problem during the composting of manure is the formation of big lumps upon drying that stops the process. The addition of 3% (mass basis) of wood biochar to poultry manure co-composted with straw was able to significantly reduce the formation of big lumps in the pile, improving the composting process and the overall structure of the final compost¹³.

Biochar and Compost: Looking Ahead for Wider Commercial Use

Although initial publications show measurable benefits on the impact of biochar on composting, the number of studies is still very limited. Many of the traditional indices used for evaluating the quality ('stability') of compost (e.g., the carbon/nitrogen, C/N, ratio) are not valid when biochar is included in the mixture (6), since biochars have very different properties than the rest of the composting material (e.g. high C/N ratio, which will not decrease during the composting process in contrast to the remaining organic material) and may even influence compost quality assays if controlled for biochar (e.g., water-soluble C may adsorb to biochar). Establishing compost quality indices that take the benefits of biochar into account could help increase the commercial use of this activity.

At this time there is not a significant industry for compost amended with biochar, even though many current biochar producers sell a biochar/compost blend. The 2013 IBI State of the Industry Report found that compost was the most common additive to biochar when biochar was sold as part of a blend¹⁴. There are a few companies that are actively taking a leading role in commercializing biochar-amended compost blends by producing biochar onsite and utilizing those feedstocks for biochar production which would be less ideal for composting.

Increasing the use of biochar in compost operations requires education on the benefits of biochar to producers, not only on emissions and odor reductions, but also on the potential economic benefits of accelerated composting time to offset the additional price of producing/purchasing biochar.

References

- 1. International Biochar Initiative (IBI) (2014a). Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil; accessed at http://www.biocharinternational.org/sites/default/files/IBI Biochar Standards V2%200 final 2014.pdf
- 2. Gajalakshmi, S.; Abbasi, S. A. (2008). Solid Waste Management by Composting: State of the Art. Critical Reviews in Environmental Science and Technology. 38:311-400.
- 3. Jindo, K., Suto, K., Matsumoto, K., Garcia, C., Sonoki, T. and Sanchez-Monedero, M.A. (2012). Chemical and biochemical characterization of biochar-blended composts prepared from poultry manure. Bioresource Technology. 110:396-404.
- 4. Dias, B.O., Silva, C.A., Higashikawa, F.S., Roig, A. and Sánchez-Monedero, M.A. (2010). Use of biochar as bulking agent for the composting of poultry manure: Effect on organic matter degradation and humification. Bioresource Technology. 47:1239-1246.
- 5. Fischer, D. and Glaser, B. (2012). Synergism between compost and biochar for sustainable soil amelioration, management and organic waste, in S. Kumer (ed.), Management of Organic Wastes, In Tech, pp 167 – 198.
- 6. Khan, N., Clark, I., Sánchez-Monedero, M.A., Shea, S., Meier, S. and Bolan, N. (2013). Maturity indices in co-composting with biochar. 2nd International Conference on Solid Waste 2013: Innovation in Technology and Management, Hong Kong.
- 7. Zhang, Lu, and Sun Xiangyang (2014). Changes in physical, chemical, and microbiological properties during the two-stage co-composting of green waste with spent mushroom compost and biochar. Bioresource Technology. 171:274 - 284.
- 8. Wang, C., Lu, H., Dong, D., Deng, H., Strong, P.J., Wang, H. and Wu, W. (2013). Insight into the Effects of Biochar on Manure Composting: Evidence Supporting the Relationship between N2O Emissions and Denitrifying Community. Environmental Science & Technology. 47:7341-7349.
- 9. Sonoki, T., Furukawa, T., Jindo, K., Suto, K., Aoyama, M. and Sánchez-Monedero, M.A. (2012). Influence of biochar addition on methane metabolism during thermophilic phase in composting. Journal of Basic Microbiology. 52:1-5.
- 10. Lopez-Cano, I., Roig, A., Cayuela, M.L., Alburquerque, J.A., Sanchez-Monedero, M.A. (2015). Biochar impact on olive mill waste composting. Proceedings of the III International Symposium on Organic Matter Management and Compost Use in Horticulture. Murcia, Spain.
- 11. Steiner, C., Das, K.C., Melear, N. and Lakely, D. (2010) Reducing Nitrogen Loss During Poultry Litter Composting Using Biochar. Journal of Environmental Quality. 39:1236-1242.
- 12. Steiner, C., Melear, N., Harris, K. and Das, K.C. (2011). Biochar as bulking agent for poultry litter composting. Carbon Management. 2:227-230.
- 13. Sánchez-García, M., Alburquerque, J.A., Sánchez-Monedero, M.A., Roig, A., Cayuela, M.L. (2015). Biochar accelerates organic matter degradation and enhances N mineralisation during composting of poultry manure without a relevant impact on gas emissions. Bioresource Technology 192, 272-279.
- 14. International Biochar Initiative (IBI) (2014b). 2013 State of the Biochar Industry; accessed at http://www.biocharinternational.org/sites/default/files/State of the Biochar Industry 2013.pdf

5