Norwegian University of Life Sciences
Faculty of Environmental Sciences
and Natural Resource Management

Philosophiae Doctor (PhD)
Thesis 2022:15

Biochar for N_2O mitigation and improved delivery and retention of mineral nitrogen in compost and soil

Bruk av biokull for reduksjon av N_2O utslipp og effektivisering av nitrogenutnyttelse i jord og kompost

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PhD Supervisors

Professor Peter Dörsch
Faculty of Environmental Sciences and Natural Resource Management (MINA)
Norwegian University of Life Sciences
P.O. Box 5003
NO-1432 Ås, Norway

Dr. Daniel Rasse
Division of Environment and Natural Resources, Soil and Land Use
Norwegian Institute of Bioeconomy Research
P.O. Box 115
NO-1431 Ås, Norway

PhD evaluation committee

Professor Samuel Abiven
Laboratoire de Géologie, Département de Géosciences,
Ecole Normale Supérieure, Institut Pierre Simon Laplace,
PSL University
24, rue Lhomond, 75005 Paris
France

Dr. Alessandra Lagomarsino
Consiglio per la Ricerca in Agricoltura e l'analisi dell'economia agraria (CREA),
Centro di Ricerca Agricoltura e Ambiente (AA)
Via di Lanciola, 12/A, 50023 Impruneta FI
Italy

Coordinator of the committee

Dr. Åsgeir Almås
Faculty of Environmental Sciences and Natural Resource Management (MINA)
Norwegian University of Life Sciences
P.O. Box 5003
NO-1432 Ås, Norway

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Summary

Biochar is a promising technology for simultaneously storing carbon in soils, improving crop yields and reducing greenhouse gases. In the last 20 years, research efforts into biochar and its application to soils have been growing exponentially. Biochar has been shown to influence multiple processes in soils and commonly reported biochar effects related to soil nitrogen (N) dynamics are increased crop yields, reduced N leaching and reduced N_2O emissions. However, the diversity and complexity of the proposed mechanisms, as well as the reported variability in biochar effects for different combinations of biochar, soil and environmental conditions still make it difficult to choose biochars for a given purpose.

In this thesis, through experimentation and review, I investigated how biochar can be applied to reduce N_2O emissions and retain mineral N in soil and compost. Across two different laboratory studies and in two soils and a compost, I observed that high temperature biochar (>500 ^oC Highest Treatment Temperature HTT) consistently reduced N_2O emission. In the soil experiment, the observed N_2O mitigation effect depended on the degree of carbonisation of the biochar which appeared to be important for the consistency of the N_2O supressing effect. Depending on the soil, low temperature biochar stimulated or inhibited denitrification and, more specifically, N_2O reduction to N_2. We found that the biochar effect on denitrification was best explained by pH increase after biochar addition and the surface area of the biochar.

Addition of biochar to compost also reduced N_2O emissions. Here, high pH of the compost material ruled out pH effects on denitrification and the evidence pointed to a structural effect of biochar on the compost material. Biochar addition increased the heterogeneity of the compost which may have influenced oxygen availability locally. We therefore believe that biochar addition influenced both production and consumption of N_2O through effects on both nitrification and denitrification.

Biochar addition to compost did not result in greater nitrogen retention in the compost or the soil to which the compost was applied. This may be because the quantity of ammonium in the digestate N, used as a feedstock for composting, exceeded the sorption capacity of the biochar or because additionally added garden waste functioned similar to biochar, masking the effect of biochar on nutrient retention.

To create a scientifically sound basis for the development of effective biochar fertilisers, I conducted an in-depth literature review and re-analysed published data of ammonium and nitrate retention by biochar. Re-analysis of absolute N retention per gram biochar revealed that the nutrient retention capacity of fresh or modified biochar for ionic nutrients is small. Methodological artefacts related to insufficient pH control were identified and are the likely reason for the often reported high retention capacity of biochar. It is concluded that more stringent determination of biochars' retention capacity is needed before designing fertilisers with biochar as a nutrient carrier.

The meta-analysis suggested that ion exchange is the primary mechanism by which biochars retain NH_4^+. Values of NH_4^+ retention exceeding measured cation exchange capacity (CEC) reported in the literature suggest that additional mechanisms may play a role. Again, methodological issues in determining both NH_4^+ retention and CEC may be responsible for this discrepancy. Moreover, potentially relevant variables, such as biochar porosity and surface area, are infrequently and inconsistently quantified in the literature, and could therefore not be evaluated in the present study.

In this thesis, I confirm that biochar can substantially reduce N_2O emissions from both compost and soil. Moreover, our review concluded that biochar may have promise for inclusion in a compound fertiliser, but our re-analysis of literature values showed that sorption of NH_4^+ on biochar surfaces is not sufficient to be used as a key principle onto which this development should be based. I conclude that biochar soil research would benefit from more standardised methodologies. I also argue for quantitative approaches when synthesising literature data, to better assess the absolute effect size of different biochar properties on soil processes.

Sammendrag

Biokull er en lovende teknologi for å kunne lagre karbon i jord, forbedre avlinger og redusere drivhusgasser. Forskning på biokull og ulike måter å utnytte biokull på innen jordbruket har økt kraftig de siste 20 årene. Biokull påvirker mange prosesser i jorda. Vanlige rapporterte effekter av biokull er økte avlinger, minskede nitrogen-tap og reduserte N_2O-utslipp. Men fordi biokull kan påvirke mange mekanismer, og fordi resultatene kan påvirkes av ulike biokull-kombinasjoner, jord og miljømessige forhold, er det en utfordring å finne den optimale type biokull til et spesifikt bruk.

I denne doktorgraden, undersøker jeg, gjennom eksperimenter og litteratur undersøkelser, hvordan biokull kan bli brukt for å redusere N_2O-utslipp samt bevare nitrogen i jord og kompost. I to ulike lab-eksperimenter samt to jord- og en kompost-studie, observerte jeg at biokull ved høy temperatur (>500°C høyeste registrerte temperatur under pyrolyse (HTT)) reduserte N_2O-utslipp. I lab-eksperimentet, var den reduserende effekten av N_2O avhengig av graden av biokull-karbonisering. Biokull-karboniseringen viste seg å være en viktig faktor for i hvilken grad og hvor mye N_2O som ble redusert. Biokull produsert på lav temperatur kunne både stimulere og hindre denitrifisering og samtidig gjør N_2O om til N_2, men dette var avhengig av hvilken jordtype som ble brukt. Effekten av biokull på denitrifisering kunne best forklares ut i fra en økning i pH etter tilsetting av biokull, i tillegg til overflate størrelsen av biokullet.

Tilsetting av biokull til kompost reduserer også N_2O -utslipp. I dette studiet, viste en høy pH ikke å på denitrifiseringen. Isteden viste biokull å ha en strukturell effekt på kompostmateriale. Ved å tilsette biokull økte man heterogeniteten av komposten, som igjen kan påvirke tilgjengeligheten av oksygen lokalt. Vi menter at tilsettingen av biokull påvirket både produksjonen og reduksjon av N_2O, gjennom nitrifisering og denitrifisering.

Tilsetting av biokull til kompost førte ikke til økt nitrogen-bevaring i komposten eller i jorden som ble tilsatt kompost. Dette kan ha ulike årsaker. Det kan skyldes at mengden av ammoniakk i biorest i kompost blandingen overskred absorpsjonsevnen til biokull. Eller så kan hageavfallet ha fungert på en tilsvarende måte som biokull, og dermed maskert effektene av biokull for oppbevaring av næringsstoffer.

For å vitenskapelig demonstrere behovet for å utvikle effektiv biokull-gjødsel, har jeg foretatt en grundig gjennomgang av publiserte artikler, og re-analysert publiserte data om biokulls

ammonium- og nitrat-retensjon. Mine resultater viste at absolutt N retensjon per gram biokull er relativt liten, både for ferskt og modifisert biokull. En utfordring ved biokull tilførsel er at pHen i substratet vil først øke, men etter noen timer vil pHen synke igjen, dette gjør det vanskelig å isolere hvorvidt retensjonen er styrt av pH eller biokull tilførsel. Vi tror at denne variasjonen er en sannsynlige årsak til at det ofte ble rapportert en høy retensjon av NH_4^+ av biokull i litteraturen. Mer nøyaktig fastsetting av retensjonskapasiteten til biokull er nødvendig før man produserer gjødsel som bruker biokull for å levere næringsstoffer til jord.

Metaanalysen indikerer at ionbytte er den viktigste mekanismen biokull beholder NH_4^+ på. Verdier av NH_4^+-retensjon som overgår de målte kation bytte kapasitet (CEC) rapportert i litteraturen, tyder på at det andre mekanismer som også spiller en viktig rolle. Igjen kan metodiske avvik i NH_4^+ retensjon og CEC være mulige bakenforliggende årsaker til dette. Andre mulige variabler som biokull porøsitet og overflateareal har ikke blitt konsekvent vurdert som variabler, og er derfor ikke inkludert i studien.

I denne avhandlingen, bekrefter jeg at biokull signifikant kan redusere N_2O-utslipp fra både kompost og jord. Studien vår konkluderer med at biokull kan være et positivt/lovende tilskudd i en sammensatt gjødsel. Reanalysene av tilgjengelig litteratur viser at NH_4^+ sorpsjon på biokull-overflaten ikke er tilstrekkelig for forsvare en fremtidig satsning på biokull gjødsel. Jeg konkluderer med det er behov for mer standardisert metodikk når det gjelder forskning innen biokull. Det bør også benyttes kvantitative teknikker/metodikker for syntetisering av data i litteraturen, for å bedre kunne vurdere de ulike effektene biokull har på jorda.

List of papers

Paper I: Weldon, S., Rasse, DP., Budai, A., Tomic, O., Dörsch, P. 2019. The effect of a biochar temperature series on denitrification: which biochar properties matter? Soil Biology and Biochemistry, 135, 173-183.

Paper II: Weldon, S., Rivier, PA., Coutris, C., Joner, E., Budai, A. Co-composting of biogas digestate and garden waste with biochar: Effect on greenhouse gas production and fertilizer value of the matured compost. Submitted to Journal of Environmental Management

Paper III: Rasse, D., Weldon, S., Joner, E., Joseph, S., Kammann, CI., Liu, X., O'Toole, A., Pan, G., Kocatürk-Schumacher, P. Enhancing plant N uptake with biochar-based fertilizers: beyond sorption. Submitted to Plant and Soil

Paper IV: Weldon, S., Van Der Ween, B., Farkas, E., Kocaturk-Schumacher, NP., Budai, A., Dieguez-Alonso, A., Rasse, D., A re-analysis of NH_4^+ sorption on biochar: have expectations been too high? Submitted to Chemosphere

Abbreviations

SOM	Soil Organic Matter
SOC	Soil Organic Carbon
GHG	Green House Gas
N	Nitrogen
CEC	Cation Exchange Capacity
AEC	Anion Exchange Capacity
VM	Volatile matter
IPR	Integrated Product Ratio of denitrification
PLSR	Partial Least Squares Regression
ANOVA	Analysis of variance
Sd	Standard deviation
SE	Standard error
GLM	Generalised Linear Model
WHC_{max}	maximum Water Holding Capacity
HTT	Highest Treatment Temperature during pyrolysis
GC	Gas Chromatography
TCD	Thermal Conductivity Detector (GC)
FID	Flame Ionising Detector (GC)
ECD	Electron Capture Detector (GC)
GMW	Green Municipal Waste
NPK	mineral fertiliser (Nitrogen, Phosphorus, Potassium)

Contents

Synopsis

1 Introduction

1.1 Global context

Policy makers and industry have recognised that agri-food systems need to be transformed fundamentally to produce food that does not come at the cost of the environment or the sustainability of food production systems (European Union., 2021). Current agri-food systems are built on the technological advances of the last century, in particular mechanisation and cheap production of mineral fertilisers. Mineral fertilisers, in particular, are considered to be responsible for the exponential increase in global human population (Smil, 1991, 2001).

Excessive use of synthetic and organic nitrogen (N) in crop production poses a wide range of challenges for sustainable agriculture. Global overuse of mineral N results in N pollution of non-target ecosystems through leaching and emission of N from cultivated soils. For example, agriculture is responsible for 78% of the global emissions of nitrous oxide (N_2O), a GHG with a global warming potential 290 times that of CO_2 over a 100-year time period (IPCC, 2013; Yue et al., 2018). The production of mineral N fertilisers consumes approximately 1.2% of the world's energy production which accounts for 1.2% of the total GHG production (Kongshaug, 1998). Yet, global food production needs to increase to provide food security that meets the demand of an ever-growing global human population. This is a technological and social challenge that necessitates new sustainable strategies for agricultural soil management.

There are two key challenges for agriculture in the future. Firstly, we must produce more food on less land and secondly, food production should have a reduced impact on both the climate and adjacent ecosystems. Reducing N use while increasing N demand for crop production requires technologies that improve N use efficiency and reduce N losses. For example, it is estimated that on average only 50% of the N fertiliser added to land is taken up by crops (Lassaletta et al., 2014; Martinez-Feria et al., 2018). Strategies to reduce N losses include, precision agriculture, which synchronizes N fertilization with the N need of crops and environmental conditions at the time of application (Cisternas et al., 2020), controlled release fertilisers (Rahman et al., 2021); and improved soil N retention by amending soils with minerals or by adopting soil management practices that increase soil organic matter (SOM) content through reduced tillage (Shakoor et al., 2021) or intercropping of catch or cover crops (Rasse et al., 2000; Young et al., 2021).

Another promising strategy is reuse and recycling of N from organic wastes emerging from both traditional and new bio-economies. Traditional waste streams consisting of animal manures and organic crop residues are increasingly supplemented by and transformed into digestates by anaerobic digestion. The challenge here is that these wastes often require processing before they can be applied to soil to avoid inhibition of plant growth, contamination of food products with pathogens or excessive N loss. The solution to this is the development of new technologies that exploit and valorise waste products before returning them to soils. With respect to nitrogen, new technologies are needed that reduce the need for industrially fixed N through effective exploitation of existing waste N resources. New technologies should also reduce the carbon footprint of agriculture through reducing GHG emissions, protecting soil organic carbon and minimizing the energy used for agricultural production. In Norway, green technologies are meant to replace the oil and gas economy that has dominated Norway in the last 100 years (Norwegian Government, 2016). Based on the need for new technologies and green economies, biochar has arisen as a promising technology addressing many of these issues.

1.2 Biochar

Biochar is essentially charcoal, produced by pyrolysis of waste biomass. Biochar is a functional definition, differentiating itself from charcoal through its intended application to soils and other organic media. Current interest in the topic has been triggered by the pioneering research carried out on the *Terra Preta* of Brazil. The *Terra Preta* are anthropogenic agricultural soils that were created as early as 400BC and supported an extensive civilisation until the Spanish colonisation in the 1500s. The *Terra Preta* was formed through repeated application of charcoal and organic matter to the typically nutrient poor soils of the Amazonas. The result is a nutrient rich, organic soil with a high water and nutrient holding capacity and a largely stable soil organic matter pool (Glaser et al., 2001). The recognition that it may be possible to achieve all these benefits through application of biochar to agricultural soils led to a surge in interest in biochar technology.

First and foremost, biochar is seen as a mitigation tool to tackle climate change through carbon sequestration and storage in soils (Lehmann, 2007a). Pyrolysis of plant biomass results in a product composed of refractory organic molecules that are resistant to decomposition over millennial timescales (Preston and Schmidt, 2006). Unlike other proposed methods for increasing carbon storage in soils, there is no theoretical limit to how much biochar can be added to soils (Lehmann, 2007b). However, wide-scale adoption of biochar amendment to soils for carbon storage is hampered by the cost of biochar production and the lack of financial incentives for land managers to apply biochar. Much of the biochar research has therefore focused on co-benefits of biochar addition to land with the aim of improving its value proposition (Sohi et al., 2010; Sohi, 2012). The *Terra Preta* example suggests that biochar could improve a wide range of soil functions including soil water holding capacity, nutrient retention and fertility (Glaser et al., 2001). However, the promise of the *Terra Preta* has proven elusive for soils outside the Tropics, as effects of biochar addition have been found to vary both in magnitude, duration and direction. These apparently contradictory results reflect the complexity of interactions between biochar, soil and climate (Jeffery et al., 2011; Mukherjee and Lal, 2014; Borchard et al., 2019) and highlight the need for improving our mechanistic understanding of biochar-soil-plant interactions, if commercially successful biochar products are to be developed.

1.3 Soil N interactions

Various mechanisms have been proposed by which biochar improves N efficiency in agriculture: increased retention of soluble N in soils, improved mineral N uptake by plants and reduced gaseous N losses (Jeffery et al., 2011; He et al., 2017; Borchard et al., 2019; Dai et al., 2020; Zhang et al., 2021). Documented effects of biochar on soil N dynamics are mainly based on averaged positive outcomes of field, pot and laboratory experiments (Schmidt et al., 2021). Meta analyses have reported 13-26% reduction in NO_3^- leaching, 38% reduction in N_2O emissions (Borchard et al., 2019) and a 13-16% increase in crop yield (Jeffery et al., 2011; Jeffery et al., 2017; Dai et al., 2020; Ye et al., 2020) following biochar addition to soil. Meta-studies summarise a range of findings, often with high uncertainty due to results showing positive, neutral and negative effects of biochar addition on key N parameters. In a meta-analysis by Sha et al. (2019), ammonium (NH_3) volatilisation was found to both increase and decrease with biochar addition. Jeffery et al. (2017) found that biochar addition had no effect on crop yield in temperate climates, while a meta-analysis by Ye et al. (2020) found that biochar added as part of fertilisation resulted in improved yields under the same conditions. Despite the different methods used in these meta-analyses, these results illustrate the wide range of possible agronomic outcomes when using different biochar types in different agricultural systems.

1.4 Biochar properties

Biochar itself is not a homogenous product. Biochar properties are highly variable depending on feedstock type, pyrolysis temperature, pyrolysis method and pre- or post-pyrolysis modifications (Budai et al., 2014). Biochar consists of different phases including aromatic and amorphous structural carbon, volatile organic matter (VOM) and ash (Keiluweit et al., 2010). The different phases interact with soil processes, each in a specific way. For example, both VOM and ash can be leached from biochar to soil where they can cause short-term effects such as soil pH increase (Singh et al., 2017) and positive priming of organic matter degradation (Rasul et al., 2022). With increasing pyrolysis temperature, the thermal reduction of the organic carbon results in more aromatic carbon which condenses into structured sheets forming a crystalline lattice (Keiluweit et al., 2010). These structures are highly recalcitrant (Lehmann, 2007a) and have electro-chemical properties (Klüpfel et al., 2014). Delineating the effects of different biochar properties in soil is complicated by the collinearity of many of these effects.

1.5 Biochar and N_2O

Across a range of meta-analyses, biochar has been shown to reduce N_2O emission by 12 – 38%, encompassing a wide range of biochar types, experimental systems and soil types (He et al., 2017; Verhoeven et al., 2017; Liu et al., 2018; Borchard et al., 2019). While it appears that biochar consistently supresses N_2O emission in soils (Schmidt et al., 2021), there still are studies reporting that biochar had no effect (Zheng et al., 2012; Wang et al., 2013a; Wang et al., 2013b; Case et al., 2014; Van Zwieten et al., 2014) or stimulated N_2O emissions (Yanai et al., 2007; Clough et al., 2010; Shen et al., 2014).

Sign and size of the biochar effect on N_2O emission appear to depend on experimental system, study duration, soil type and climate, as well as biochar feedstock, production temperature and method. In soil, N_2O is produced through a number of abiotic and biotic reactions, with the biological processes nitrification and denitrification being the most significant ones globally (Firestone and Davidson, 1989). Each process involved in N_2O turnover in the soil will respond differently to soil conditions and climate and will therefore interact with biochar in a distinct way. Meta-analyses of biochar effects on N_2O (Cayuela et al., 2014; He et al., 2017) indicate that there are a range of probable mechanisms that could be responsible for the recurrently observed suppression of N_2O in soil. For instance, biochar is a highly pH active compound with both structural and chemical alkalinity (Fidel et al., 2017) and liming acidic soils with biochar has been shown to reduce N_2O production by decreasing the inherent $N_2O/(N_2O+N_2)$ product ratio of denitrification (Clough et al., 2010; Obia et al., 2015). Biochar also mediates redox processes in soil both through improving soil aeration (Yanai et al., 2007) and through mediating redox reactions (Cayuela et al., 2013; Klüpfel et al., 2014; Chen et al., 2018). Biochar may act as a sorbent and has been shown to sorb N_2O under anhydrous conditions (Cornelissen et al., 2013). Additionally, biochar could alter the availability of NO_3^- (Yao et al., 2012) and DOC (Lu et al., 2014), which are key substrates for denitrification. Studies have also identified an effect of biochar on the genetic diversity of soil denitrifier communities (Harter et al., 2014), as well as on the expression of multiple genes involved in soil N cycling (He et al., 2021), which could affect the balance of microbial N_2O turnover.

1.6 Biochar and crop yield

A recent review of meta-analyses of agronomic effects of biochar (Schmidt et al., 2021) confirmed that biochar has a generally positive effect on plant productivity with a mean stimulation between 10 and 16% (Liu et al., 2013; Jeffery et al., 2017; Dai et al., 2020; Ye et al., 2020). Similar to the N_2O effect, reported yield effects are variable with one meta-analysis reporting yield effects ranging from -32% to +974% (Dai et al., 2020). Jeffery et al. (2017) reported that biochar has no significant yield effect in temperate soils, while Ye et al. (2020) argued that biochar could have a more universal effect on yield when applied together with a fertiliser. The proposed mechanisms of biochar effects on crop yields vary and range from increased root growth (Xiang et al., 2017) and N uptake (Huang et al., 2018b; Zhou et al., 2021) to increased mycorrhizal colonization (Blackwell et al., 2015). Biochar also impacts soil pH (Nielsen et al., 2014), nutrient retention (El Sharkawi et al., 2018; Shi et al., 2020) and nutrient availability (Farrar et al., 2019) and reduces the inhibitory effects of toxic elements and plant compounds (Shetty et al., 2021). Biochar addition has also been shown to affect soil nutrient cycling through interactions with microbial populations (Nielsen et al., 2014; Chew et al., 2020; Liao et al., 2020). The properties of biochar believed to be responsible for these effects include pH change by biochar liming, increased availability of plant nutrients (Devau et al., 2009; Farrar et al., 2018) and decreased aluminium toxicicty (Shetty et al., 2021). Biochar porosity and structure also reduce soil bulk density (Omondi et al., 2016) and increase moisture retention (Razzaghi et al., 2020), benefiting root growth and development. Biochar effects on nutrient retention are thought to be a function of biochar sorption capacity which in turn is a function of surface area, surface functionality and porosity (Ahmad et al., 2014). Recent studies suggest that biochars also affect plant nutrient uptake by changing the soil's electrical conductivity (Chew et al., 2020).

1.7 Biochar and N retention

The capacity of certain biochars to retain plant nutrients has led to the idea to use biochars for recovering nitrogen from wastes, which could reduce the contamination of non-target ecosystems by mineral N (Ahmad et al., 2014). N retention in the *Terra Preta* is mediated by cation exchange capacity (CEC) which apparently has increased due to long-term addition of pyrogenic organic matter to these soils (Cheng et al., 2006). Fresh biochar has a net negative charge at agriculturally relevant soil pH. This means that biochar has the potential to retain cations which include important plant nutrients such as NH_4^+. The CEC of biochar largely depends on the amount of oxygenated functional groups within the biochar structure (Mia et al., 2017), the abundance of which can be manipulated through feedstock choice and most importantly, pyrolysis temperature (Tag et al., 2016), but also through post pyrolysis oxidation of biochar, chemical activation (Wang et al., 2016) or ageing (Suliman et al., 2016). Alternatively, biochar CEC can be increased through coating biochar with high-CEC materials such as clay (Gao and Goldfarb, 2021).

Although there is much focus on biochars' CEC as a key property for cation retention, biochar has also been reported to retain anions such as NO_3^- (Kammann et al., 2015; Haider et al., 2020) and organic nutrients such as urea (Shi et al., 2020), but the underlying mechanisms are less clear. In particular, porosity and surface area appear to be important for the retention of non-cationic nutrients (Mukherjee et al., 2011). Biochar porosity is believed to benefit nutrient retention through protection from microbial consumption (Brewer and Brown, 2012) or entrapment by pore blocking through organo-mineral coatings (Hagemann et al., 2017a; Joseph et al., 2018). Anion sorption is also thought to be a consequence of biochar interactions with organic acids (Heaney et al., 2020).

1.8 Applied biochar science

The indication that biochar increases retention and plant utilisation of N and reduces N loss from soils and organic media has fostered the idea to use biochars as slow-release fertilisers. For this, biochar must be 'loaded' with nutrients, be it from conventional fertilizers or from waste streams. It has been argued that the addition of N-loaded biochar to soil may increase the likelihood of achieving positive yield effects (Schmidt et al., 2021). The reasoning behind this is that the N source is intimately associated with the biochar as opposed to separate applications where the interaction between biochar and nutrients depends on the distribution of biochar and fertilizer in the soil matrix (O'Toole et al., 2018). The earliest published research into biochar-based fertilisers involved the combination nutrients together with clay and biochar (Joseph et al., 2010). Industrialisation of biochar based fertiliser production was pioneered in China and reached commercial scale in 2017 (Pan et al., 2017; Sun et al., 2018). The primary role of biochar in industrially produced biochar compound fertilisers (BCF) is to act as a carrier for the N source. Here the functional properties of biochar are emphasised to suggest that biochar will hold substantial amounts of N and release it slowly (Manikandan and Subramanian, 2013; El Sharkawi et al., 2018; Liao et al., 2020). Biochar addition together with an N source has also been suggested to increase N use efficiency of crops through physical and chemical interactions between the plant and the BCF (Xiang et al., 2017; Liu et al., 2020b; Shi et al., 2020). While these mechanisms rely on the biochar as a carrier of N, other studies have suggested that it is the water soluble extract of the biochar which promotes plant growth through hormone-like effects (Liu et al., 2020a).

Aside from the industrial development of biochar-based fertilisers, biochar application to organic wastes has been studied for the purpose of utilizing and recycling waste N resources. Studies have shown that application of biochar to compost can result in an intimate association between biochar and nutrients (Joseph et al., 2013; Kammann et al., 2015; Hagemann et al., 2017a; Hagemann et al., 2017b). In addition to retaining nutrients during composting, biochar application to compost has been shown to improve the composting process itself and reduce GHG emissions (Agyarko-Mintah et al., 2017) as well as improving maturation rates (Waqas et al., 2018). Biochar has also been shown to improve the fertiliser value of the mature compost (Kammann et al., 2015). Biochar effects on the composting process may be explained by structural effects of biochar on compost aeration (Awasthi et al., 2017a; Liu et al., 2017a), sorption of nutrients (Chen et al., 2010; Agyarko-Mintah et al., 2017; Awasthi et al., 2017b) and pH buffering (Chen et al., 2010; Sanchez-Garcia et al., 2015). Biochar has been shown to support microbial growth during composting, as evidenced by compost temperature development, changes in mineralisation rates and altering the balance of CO_2, CH_4 and N_2O production (Sanchez-Garcia et al., 2015; He et al., 2021).

1.9 Thesis goals

Biochar research often emphasises the complexity of biochar interactions in soils and organic matrices (Joseph et al., 2021). The primary goal of this thesis was to contribute to unravelling parts of this complexity through experimental approaches and by reviewing and re-analysing literature data.

Reduction of N_2O emission is one of the most commonly quoted co-benefits of biochar in agricultural soils (Schmidt et al., 2021). This effect appears relatively consistent despite a wide range of biochar types and soil/environmental conditions. However, there is still no consensus regarding the mechanisms responsible for the observed emission reductions. Recognising the complexity of N_2O forming processes in soil, we undertook a laboratory study on denitrification, the quantitatively most important source process for N_2O emissions from soil. Experiments were conducted to explore which biochar properties are responsible for the N_2O supressing effect and asked whether the mechanisms are consistent across different soil types.

The role of biochar as an additive to compost is well established, however few studies have examined the implications of biochar addition to compost both from the perspective of the composting process itself and the performance of the final product as a fertiliser. For this, we set up a replicated composting experiment in which we quantified the effect of biochar addition on CO_2, CH_4 and N_2O emissions during composting; and studied fertilizer value and N leaching in a subsequent pot trial. In this way we hoped to see how improvements to the composting process translate to the quality of the final product as a fertiliser.

Positive biochar effects on crop yields are commonly related to improved nutrient retention in soil and the assertion that biochar can retain and slowly release significant quantities of nutrients has led to the idea of biochar-based fertilisers. We challenged this assertion by systematically exploring capacity and apparent mechanisms of nutrient retention by biochar from literature data. To this end, we combined a classical review of the literature with a reanalysis of published data aiming to understand how biochar properties might be leveraged to store and release nutrients in future biochar compound fertilizers.

1.10 Objectives

The objectives of my thesis were to:

1) elucidate mechanisms responsible for the N_2O suppressing effect of biochar in soil denitrification

2) explore the practical application of biochar to compost for reducing GHG emissions during composting and compare the final biochar compost with mineral fertilizer to evaluate fertilizer value and N retention

3) review the state of the art pertaining to biochar compound fertilizers and improved N use efficiency, focussing on an in-depth evaluation of cationic sorption as the central mechanism for N retention and identifying the most promising approaches to achieve this goal

4) provide a reliable range of estimates for the NH_4^+ sorption capacity of biochars and explore which biochar properties and modifications sustain high sorption

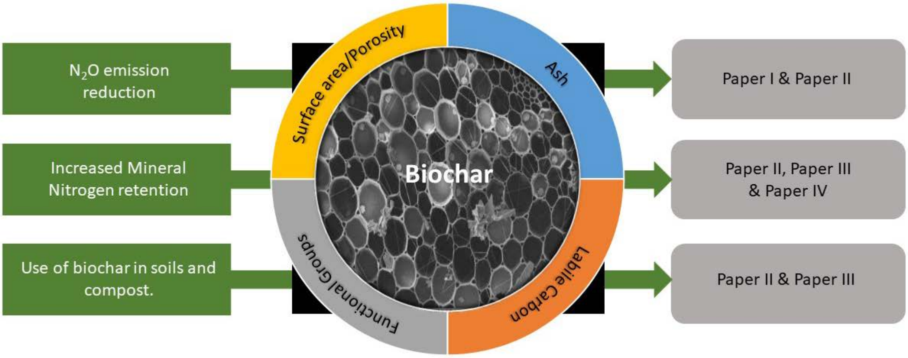

Figure 1: Flow chart relating the Phd thesis’ research goals to the four studies conducted.

2 Materials and Methods

2.1 Paper I: Effect of biochar on N_2O production and reduction in denitrification

The effect of biochar on N_2O emissions is one of the best documented co-benefits of biochar in agricultural soils (Schmidt et al., 2021). However, as we have discussed, there is still uncertainty regarding the mechanisms by which biochar affects N_2O emission and, at the time this study was conceived, there were relatively few mechanistic studies attempting to elucidate these mechanisms. Recognising that the biochar effect on N_2O must be mediated by specific properties of the biochar, and that this effect may not be consistent between soil types or environmental conditions, we designed a controlled experiment with a well-defined temperature series of a corn cob biochar (Budai et al., 2014). We chose to focus on heterotrophic denitrification because it is an important N_2O source and the only biological sink for N_2O. Our goal was to test whether biochar would reduce N_2O emission by affecting the overall process rate of denitrification or by altering the stoichiometry of gaseous intermediates relative to the final product N_2, thus promoting a more complete denitrification of added N. We used two contrasting soils and biochars from a single feedstock, spanning a range of pyrolysis temperatures. Multivariate regression analysis was used to elucidate which biochar properties explained best the observed changes in denitrification kinetics in each of the two soils.

2.1.1 Choice of biochar

The term 'biochar' covers a broad range of products which vary in chemical and physical properties. Variations comes from both the nature of feedstock and the mode of pyrolysis. In the present study, we worked with biochar from one feed stock (*Zea mays* corncob), pyrolyzed at different temperatures, thus spanning over a range of reproducible biochar properties. Corn cob is an abundant agricultural waste which is often used as feedstock in biochar studies. The corn cob biochar used in the present study had been extensively characterised by Budai et al. (2014), which had the advantage that differences in biochar properties along the temperature series were well known. We used corn cob biochar produced at highest temperature treatments (HTT) of 372, 416, 562 and 796 ^{o}C (hereafter named FS105, BC372, BC416, BC562 and BC796) in addition to the feedstock dried at 105 ^{o}C. Key biochar variables were pH, CEC (Cation Exchange Capacity), Surface area, Volatile Matter (VM), Aromaticity and ash content (Table 1).

Table 1. Key properties of corn cob biochars used. HTT - highest temperature treatment; BPCA:C - benzene polycarboxylic acid to carbon ratio, an indicator of aromaticity; B6CA:C – benzenehexacarboxylic acid to C ratio, an indicator of condensation; aliCH:aroCH – ratio of aliphatic to aromatic CHs measured by MIR; H:C, O:C – Elemental ratios; VM – Volatile matter; fC – Fraction of fixed carbon; Ash – Ash fraction; CEC – Cation exchange capacity; SA – Surface area. All data from Budai et al. (2014).

HTT	BPCA:C	B6CA:C	aliCH: aroCH	H:C	O:C	N:C	VM	fC	Ash	pH	CEC	SA
°C	Ratio			Molar ratio			%	%	%		cmol_c/kg	m^2/g
105	18.3	0.00	4.5	1.6	0.9	0.01	81.1	17.5	1.5	5.3	14.9	1.8
372	122.2	32.8	1.6	0.8	0.3	0.01	40.5	57.4	2.1	8.8	14.9	1.3
416	164.2	45	0.8	0.6	0.2	0.01	26.4	70.5	3.2	10.1	16.2	3.68
562	167.5	61.4	0.2	0.4	0.1	0.01	12.7	83.9	3.4	9.4	13.5	44.9
796	192.6	136	0.2	0.1	0.04	0.01	6.9	88.7	4.5	9.4	5.1	27.4

2.1.2 Choice of soil

To test our hypothesis that biochar effects on denitrification and net N_2O production are soil specific, we chose two well characterised Norwegian soils – an arable mineral soil (Umbric Epistagnic Albeluvisol) and a drained organic soil (Hemic Histosol) used for forage production. Organic soils drained for crop production have been identified as a hotspot for N_2O production (Kasimir-Klemedtsson et al., 1997). The soils differed in C:N ratio, total carbon content, mineral content and CEC, but were both acidic (Table 2).

Table 2. Key soil properties. (Mean and Standard deviation; n=3)

	Peat		Mineral soil	
$pH_{(H2O)}$	5.08	(±0.00)	5.86	(±0.04)
C %	53.00	(±0.10)	2.83	(±0.01)
N %	1.79	(±0.04)	0.29	(±0.00)
C:N	29.53	(±0.70)	9.87	(±0.21)
H^+ (mmol/kg)	689.73	(±9.43)	93.27	(±0.90)
Ca (mmol/kg)	314.40	(±5.06)	44.69	(±0.68)
K (mmol/kg)	7.91	(±0.17)	2.80	(±0.03)
Mg (mmol/kg)	68.35	(±0.98)	2.34	(±0.03)
Mn (mmol/kg)	0.09	(±0.00)	0.11	(±0.00)
Na (mmol/kg)	16.75	(±0.14)	0.75	(±0.01)
CEC (cmol/kg)	1480.10	(±21.04)	191.08	(±2.35)
Base saturation (%)	53.38	(±0.20)	51.07	(±0.16)

2.1.3 Experimental system

Since the effect of a biochar property on soil processes may depend on the amount of biochar added, we set up soil incubations with increasing doses of biochar (0% (control), 1%, 5%, 10%, 20% w/w). After adding the biochars, the soils were dispersed in distilled water and incubated in closed bottles while continuously steering the slurries with magnetic stirrers. This approach was chosen to bring the biochar in intimate contact with soil particles and microbes, as we were most interested in direct chemical and biological effects. At the same time, stirred batch incubations allowed us to control for temperature and oxygen availability, while eliminating soil-specific diffusional constraints. After amending the bottles with nitrate and making them anoxic by helium washing, we observed the kinetics of N gas production and consumption using an automated incubation system (Fig. 1). The system consists of a GC (Model 7890A, Agilent, Santa Clara, CA, USA) and an autosampler (CTC PAL) attached to a temperature-controlled water bath (Fig 2). The system is described in detail by Molstad et al. (2007) with modifications in Molstad et al. (2016) and allows for high-resolution analysis of headspace gas concentrations in 30 continuously stirred, airtight 120 ml serum bottles.

Figure 2. Photograph showing the robotized incubation system at the time of experimentation. Shown are (from left to right) the temperature-adjustable water bath with submersed magnetic stirring boards allowing simultaneous incubation of 30 120ml serum bottles and 10 non-stirred standard bottles, the peristaltic pump, and the gas chromatograph (GC). The robotic arm samples the bottles periodically (here 4 hourly) by piercing the crimp-sealed butyl septa of the bottles with a hypodermic needle. Ca. 1 ml of headspace gas is transferred with a peristaltic pump to a multi-column, multi-detector GC with loop injection for analysis of N_2, O_2, CH_4, CO_2 and N_2O and a chemiluminescence analyser for analysis of NO (not shown). Upon injection, the pump is reversed, and unused sample is pumped back into the bottles together with helium, keeping flask pressure at ~1 atm. The resulting dilution is corrected for as outlined by Molstad at al. (2007). For a detailed description of the setup, see Molstad et al. (2016).

Assessing denitrification kinetics necessitates measurement of N_2, the final product of denitrification. This is a challenge as atmospheric N_2 is abundant and even small amounts leaking into the bottles or the measurement system confound the measurement of biogenic N_2 production. To correct observed N_2 production for contamination, the routines devised by Molstad et al. (2007) were followed, which are based on subtracting the N_2 accumulation observed in He-filled blank bottles from that in biologically active bottles. Another, unexpected source of confounding was the gradual release of N_2 still adsorbed to soil and biochar after helium washing. While atmospheric N_2 contamination through the measurement system can be expected to be equal for all bottles, the amount of N_2 adsorbed differs with soil and biochar. This was verified for biochar in an abiotic incubation experiment with different biochars and doses (see SI of paper I). We used these data to model the N_2 desorption and found that it followed an exponential rise to maximum. We retained the exponent to model the maximum N_2 accumulation from desorption for each of the experimental bottles, which was then used to correct observed N_2 accumulation for desorption. N_2 release from desorption clearly overrode biogenic N_2 production during the first hours of incubation, which we deemed acceptable as induction of denitrification upon making the bottles anaerobic takes several hours during which biological N_2 production is small. For more details, see SI of paper I.

The automated incubation produced time series (kinetics) of headspace gas concentrations of CO_2, NO, N_2O and N_2 (Fig. 3). The corrected N gas kinetics were subsequently used to extract denitrification parameters as indicated in figure 3:

- DR_{max} and T_{DRmax}: maximum denitrification rate; maximum rate of total N gas (NO + N_2O + N_2) accumulation, corrected for N_2 influx and desorption, and time elapsed before reaching this rate
- IPR: integrated $N_2O/(N_2O+N_2)$ product ratio of denitrification, calculated as the ratio of the sums of accumulated N_2O to accumulated $N_2O + N_2$, for the first 20 μmol N denitrified (shaded area in Fig. 3). The sums were derived by trapezoidal integration (Liu et al., 2010)
- NO_{max}, N_2O_{max} and N_{2max}: maximum observed accumulation of N_2O, NO and N_2, respectively

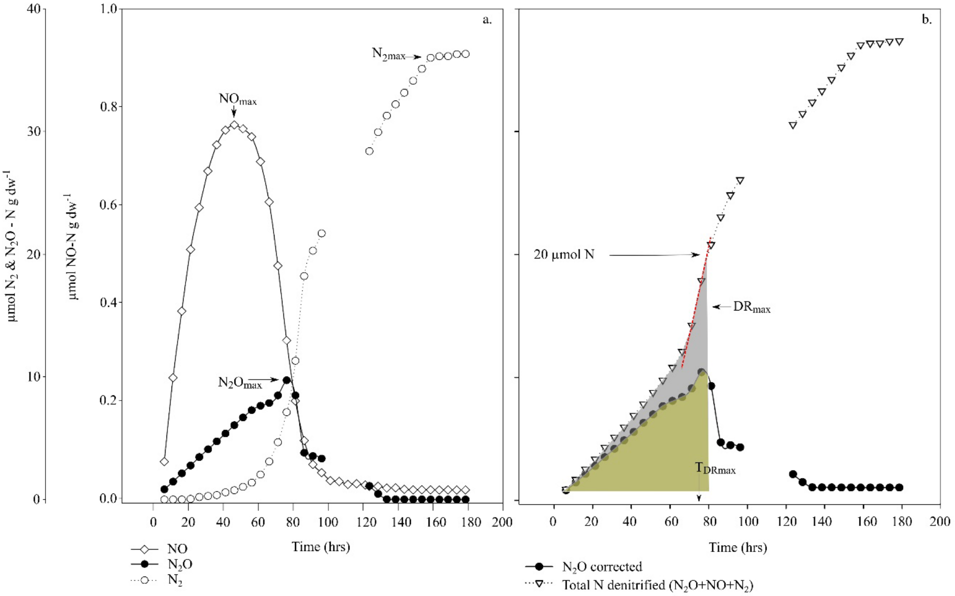

Figure 3. Gas kinetics (a: NO, N_2O, N_2; b: N_2O, $NO+N_2O+N_2$) and denitrification parameters derived. Shown are the kinetics measured for peat soil amended with 10% w/w of BC372 (single flask values). N_2 values in Fig. 1a are corrected for sampling loss, leakage and desorption whereas the transient accumulation of the intermediates NO and N_2O are shown uncorrected. In figure 1b, both N_2O and $NO+N_2O+N_2$ are corrected for sampling loss to derive the integrated product ratio (IPR) from the integrals with a cut off at 20 µmol N g dw soil^{-1} total denitrification. Denitrification parameters shown in figure 1a are NO_{max}, N_2O_{max} and N_{2max} and in figure 1b, DR_{max}, TDR_{max} and IPR. The shading signifies the area under the curves which were used to calculate IPR

2.1.4 Statistical analysis

The incubations were set up as dose-response experiments without replicates (except for the controls). This was done because in this process study we were interested in dose responses and thresholds rather than in differences between single biochar doses. We considered this a valid approach for a regression analysis, where the estimate error can be derived from the fit of the model.

Table 3. Data structure for the PLSR model including descriptions of abbreviations and analysis methods

Data Block*	Variable	Units	Description	Analysis method
X01	NO_{max}	µmol N g dw^{-1}	Maximum measured N_2O or NO-N accumulation	GC incubation
X02	N_2O_{max}	µmol N g dw^{-1}		
X03	N_{2max}	µmol N g dw^{-1}		
X04	IPR	Ratio	Integrated Product Ratio. This is the N_2O product ratio $[N_2O/(N_2O+N_2)]$ calculated using the integral of each curve.	
X05	$NO:N_2O$		This is the ratio of NO to N_2O calculated using the integral of each curve.	
X06	DR_{max}	µmol N g dw^{-1} hr^{-1}	This is the maximum rate measured for the total N curve.	
X07	T_{DRmax}	hr	This is the time at which the maximum rate was achieved	
Y01	VM[1]	g $flask^{-1}$	Volatile matter - ASTM method D 1762-84	ASTM method D 1762-84
Y02	Ash[1]	g $flask^{-1}$	Ash content - ASTM method D 1102	ASTM method D 1102
Y03	fC[1]	%	Fixed carbon calculated by difference between 100% and the sum of measured VM and ash contents: $\%fC_{ash-free} = 100 \times \frac{\%fC}{\%fC + \%VM}$	derived from VM and Ash content
Y04	SA[1]	m^2 $flask^{-1}$	Surface area - measured using	Brunauer–Emmett–Teller method
Y05	CEC[1]	cmol $flask^{-1}$	Cation Exchange Capacity	modified ammonium acetate compulsory displacement method
Y06	FastCpool[2]	g $flask^{-1}$	Biochar fast mineralised labile C pool	derived from a 2 pool model fitted to an oxic incubation
Y07	H:C[1]		Elemental ratios derived from Elemental analysis	Leco CHN1000 analyzer and coal reference material TruSpec Makro analyzer and O add-on module (Leco Corp.)
Y08	N:C[1]			
Y09	O:C[1]			
Y10	BPCA:C[3]	Ratio: No scaling	Ratio of total aromatic bound C to total elemental C. BPCA:C is an indicator of condensation.	Benzene polycarboxylic acid method.
Y11	B6CA:C[3]		Ratio of full 6 carbon bound to elemental C. B6CA:C is an indicator of aromaticity.	
Y12	Ali-CH:Aro-CH[3]		The ratio of aliphatic CH to Aromatic CH	derived from Mid Infrared (MIR) analysis.

* X block measurements were made using the incubation system and were recorded per flask. Y block measurements are biochar properties calculated on a dose per flask basis where possible. All the values and methods for the Y block variables were taken: [1]. Budai et al. (2014) [2]. Budai et al. (2016) [3]. Budai et al. (2017). Ratios were not scaled to dose.

The statistical analysis had to take account for the highly co-linear nature of the data. A correlation matrix was set up with many X and Y variables but few objects (Table 3). We therefore chose to apply Partial Least Squares regression (PLSR) (Wold et al., 1984), which is a multivariate method that finds components that describe common variation between two data matrices. This method was chosen for several reasons: (1) its ability to handle high dimensional, autocorrelated data, which avoids arbitrary variable selection and (2) PLSR does not require a large number of measurements for building statistical models.

Counter-intuitively, we chose to model biochar properties as response of denitrification kinetics. This approach was chosen because the data were highly structured, and the model imposed this deterministic structure on the fit of the data. Since we were not parametrising a predictive model, we chose to swap the X/Y matrix so that we could see how the more stochastic data derived from the gas kinetics was structured relative to the biochar properties. The denitrification matrix derived from the control soils was projected onto the model after parametrising the model with only the biochar treatments. This was done to avoid that the lack of biochar in the control soils would influence the fit of the model.

2.2 Paper II: Composting experiment

The goal of this study was to examine how biochar addition to compost impacts both the composting process and the value of the final product as a fertiliser. Our main goals were to understand how biochar influences the production of GHG and retains N both during the composting process and when applied to soil. We chose to study biogas digestate because it is a N rich waste that requires processing before it can be utilised as a crop fertiliser (Alburquerque et al., 2012). Composting has been recommended as a method of processing digestate prior to use, however, as a high-N product with a low organic carbon content and a poor structure, it is difficult to compost (Walker et al., 2009) and prone to N losses through volatilisation and leaching (Martins and Dewes, 1992). Biochar has been shown to improve compost structure in general and reduces leaching and GHG emissions (Awasthi et al., 2017a; Liu et al., 2017b). Additionally, biochar can improve the fertiliser properties of the final product by acting as a slow release compound fertilizer (Kammann et al., 2015).

We tested two doses of biochar at application rates of 5 and 17% (w/w) to understand whether the effect was dose dependent. Various studies have identified thresholds of >10% to >12% (w/v) biochar addition above which biochar inhibits the composting process (Awasthi et al., 2017b; Liu et al., 2017a; Liu et al., 2017b). We hypothesized that biochar addition would i) improve the composting process, as measured by maximum compost temperature while reducing GHG production, ii) result in a product with a higher nutrient content and iii) improve N retention after addition to soil. We further hypothesized that iv) nutrients stabilized by biochar would be plant available and that the presence of biochar would not reduce plant yield and v) that effects hypothesized under i-iv would depend on biochar application rate.

2.2.1 Input materials for composting

The base compost material consisted of biogas digestate (dry matter content 29 %) collected from a biogas plant at Vormsund, Norway, using food waste as substrate for biogas production. We also added fresh garden waste which was collected at a municipal waste facility at Bølstad, Southern Norway, where it had been coarsely ground and sieved to remove large twigs and branches. Biochar used in this experiment was made from mixed wood and pyrolyzed by Novo Carbo using Pyreg slow pyrolysis technology at 550 $^{\circ}$C HTT. A detailed characterization of the biochar is given in the SI of Paper II).

2.2.2 Composting experiment

We chose to work at a mesoscale using commercially available compost tumblers (Joraform 270, Sweden), which were small enough to allow for replication and could be made relatively gas tight for periodically monitoring gas production. We retrofitted the tumblers with removable covers for the integrated air vents and a sampling port for extracting gas. Gaps in the internal tumbler insulation were sealed with a multi-purpose mastic adhesive. Although seals were not fully gas tight, closing the tumblers allowed gas accumulation above ambient that could be used to estimate GHG emission rates. All treatments were set up in triplicate and equipped with combined temperature and moisture sensors (Decagon GS3) attached to data loggers. Daily GHG measurements were taken over the first 10 days of composting, before leaving the compost to mature for four months in the tumblers.

We monitored temperature development and GHG emissions during the first 10 days of composting. The rationale behind this was that the initial thermophilic phase is most critical for GHG production, while the subsequent maturation phase is most critical for N_2O emissions (Sánchez-Monedero et al., 2010). Time and resources did not allow to extend the measurements beyond the first two weeks, but since we did not quantify mass balances and treatment effects were analysed as relative differences in compost temperature and GHG emissions, we assumed that this limitation would not affect our conclusions on principal biochar effects.

We estimated GHG fluxes by measuring the increase in GHG concentration over time in the closed tumblers. In a microbially active compost, gas concentration may not increase linearly with time due to feedback effects of high gas concentrations on GHG production (Kutzbach et al., 2007). Visual assessment of the CO_2 accumulation confirmed that there was a non-linear increase in all treatments. We therefore estimated the time-zero flux using a second order polynomial. Before each flux measurement, compost tumblers were turned several times and aerated with a fan for several minutes before fully closing the ventilation and starting gas sampling.

2.2.3 Plant growth experiment and leaching

A pot experiment was set up to test the hypotheses that iii) that biochar addition to compost would reduce the leaching of mineral N and iv) biochar addition would improve the fertiliser properties of the compost. We used a loamy sand soil and planted spring onion (*Allium fistulosum*) as a crop. Spring onions are a useful crop for this experimental design since it is relatively easy to ensure equivalent numbers of plants in each pot and to estimate the yield on a dry-weight basis. Spring onions are also known to be sensitive to nitrogen availability. The soil used in this experiment was high in phosphorous (P) due to long term fertilization, so that P limitation played no role. A NPK treatment was used as control. Due to different N contents of the compost with and without biochar, we calculated all compost additions based on the total N content of the dry weight material.

Nutrient availability and leaching

Three out of six replicates per treatment were submitted to a leaching event corresponding to 400 mL water above the WHC_{max} (equivalent to 10 mm of precipitation). WHC_{max} was determined following the methods proposed by Margesin and Schinner (2005). Pots that were not subjected to leaching were watered the same day to 95 % of the WHC_{max} so that the plants experienced comparable soil oxygen levels. The leaching experiment was carried out two weeks prior to harvest, at the beginning of a sunny day to minimize potential stress due to excess watering. Leachates were collected from each pot and a subsample of 50 mL was filtered through a 0.45 µm filter and stored at -22 °C until analysis. Nitrate (NO_3^-N) and nitrite (NO_2^--N) concentrations were measured by spectrophotometric methods using a SEAL analyser, with a limit of detection of 0.01 mg N L^{-1}.

2.2.4 Compost analysis

Compost feedstocks, mature compost and soils were analysed for physical and chemical parameters by a commercial analytical laboratory (ALS Global) using ISO methods. Plant available P, K Ca, Mg and Na were extracted using ammonium lactate (Egner et al., 1960) and are reported as -AL.

2.2.5 Statistical analysis

To test hypothesis i) we fitted separate Generalized Linear Models for each of the gases CO_2, CH_4 and N_2O at each measurement point. We chose GLM because it allowed us to specify the distribution family and in each instance the values were skewed. For this reason, we chose a gamma distribution with a Log link function. Our explanatory variables were treatment and compost temperature. We used ANOVAs to test hypotheses ii-v using a TUKEYS test to compare significance between levels of each treatment.

2.3 Paper III: Reviewing the development of biochar-based fertilisers

The goal of this review was to assess the state of the art in enhancing plant N uptake with biochar-compound fertilizers (BCF). How such products are created, which properties are leveraged in their functions and what is their future? We structured the review to first examine questions related to functions of biochar in a compound fertiliser. We first identified the reported effects from combining biochar with nutrients. This included the reported effects of biochar addition on crop growth and included a detailed examination of N use efficiency. We then considered the properties of biochar that support these functions in BCF. We found several literature reviews with published values for CEC and mineral N sorption. To quantify the range of values reported for mineral N sorption, we chose to limit ourselves to studies with fresh, unmodified biochars and studies reporting sorption in batch systems. The reason for this is that we were interested in the inherent potential of biochar to act as a sorbent for mineral N independent of the interferences from different soil types and environmental conditions.

We then reviewed the literature to assess which pre or post pyrolysis modifications have been shown to significantly improve the N retention and delivery of BCF. We ended by examining how our current knowledge regarding BCF might be used to inform the development of effective BCF products. Following topics were reviewed:

- The rationale for making biochar fertilizers. Why is biochar suitable as a component in a compound fertiliser? What effect can we expect biochar to have on plant yield? What are the requirements to accept biochar as a fertiliser?
- What are the proposed mechanisms by which biochar mediates its effects on crop growth? Which properties of biochar are theorised to support its function as part of a component fertiliser?
- How much N can be stored in biochar? How important is the CEC of the biochar? How does this compare to the measured sorption capacity for mineral N and what is the theoretical maximum?
- How can the properties of biochar for N retention and release be enhanced through pre or post pyrolysis treatments?
- What are the implications for biochar-based fertilizer design?

2.4 Paper IV: Quantitative review of biochar properties relevant to NH_4^+ sorption

Our literature review of biochar compound fertilisers (Paper III) identified a challenge with interpreting the absolute estimates for NH_4^+ and NO_3^-sorption by biochar. We discovered that the estimates for mineral N sorption were highly skewed, and the magnitude of the estimates appeared to vary with study rather than biochar HTT or feedstock. Some studies reported sorption capacities for NH_4^+ orders of magnitude higher than the median or even upper quartiles of the available data (Gao et al., 2015; Liu et al., 2016; Takaya et al., 2016). These high estimates for biochar sorption capacity have led some to conclude that biochar is a highly competitive sorbent for NH_4^+ and can be used for NH_4^+ retention in environmental applications (Huang et al., 2018a). It is unclear, however, whether these high values represent an upper limit for biochar sorption capacities or whether they represent artefacts in the quantification of biochar sorption.

Our original literature review identified that measurements for maximum sorption capacity were estimated via the batch method either from single high concentrations of NH_4^+ or by fitting Langmuir isotherms to a range of NH_4^+ concentrations. The challenge with comparing estimates derived by the different methods is that measurements based on single high concentrations are relative to the concentration at which they were estimated and do not take account for the concentration dependency of sorption. By contrast, the coefficient Q_{max}, which represents the maximum sorption capacity estimated by the Langmuir isotherm, integrates measurement at multiple equilibrium concentrations and therefore provides a more reliable estimate for the theoretical maximum sorption capacity of a material. To meet our aim to standardise and quality check estimates for maximum sorption capacity, we chose to only use measurements that were suitable for fitting Langmuir isotherms. This posed a challenge with respect to standardisation, since there are multiple methodologies for model fitting as well as different units of measurement. We therefore chose to digitise the original data (Engauge Digitizer, Mitchell et al., 2020) and applied a single method, consisting of a non-linear fitting procedure, to estimate Q_{max}.

To determine sorption isotherms, increasing concentrations of a sorbate are introduced to a fixed amount of sorbent and the amount of adsorbed sorbate (q_e) is calculated according to Eq 3;

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad \text{Eq 3.}$$

Where C_0 is the initial concentration of the sorbate solution, C_e the equilibrium concentration, V the solution volume and M the mass of the sorbent. Isotherm models were plotted as a function of q_e against C_e. Therefore studies plotting q_e against C_0 were excluded.

We checked all studies for data and unit consistency, i.e. that all data presented in the paper were consistent among themselves (if presented in different forms) and were expressed in consistent units. We also checked if the data set resembled a Langmuir distribution. Following this consistency check, four studies were removed, resulting in a quality-checked collection of 125 isotherms reported in 31 papers.

2.4.1 Data remodelling

We applied a non-linear fitting procedure to estimate the Langmuir coefficients. Many studies linearize sorption isotherms to derive model parameters. However, linear methods introduce bias and result in poor estimates (Barrow, 2008; Foo and Hameed, 2010; Tran et al., 2017; Al-Ghouti and Da'ana, 2020; Cherkasov, 2020). Our own tests on this data set confirmed that estimates derived by linear versus non-linear methods vary significantly. Therefore, we used the non-linear method only.

We estimated the parameters using the nls function in the nlme package (Pinheiro et al., 2019) in R (R Core Team, 2019). We set a condition to accept only positive estimates for the coefficients on the basis that negative values for Q_{max} or K_L confound the theoretical assumptions of the Langmuir model. For the sake of clarity, we distinguish between the previously published and our remodelled estimates for Q_{max} using the terms Q_{pub} and Q_{new}, respectively.

We assessed the quality of the fitted isotherms using the standard error of the estimate. We removed all isotherm models with standard errors greater than the value of the estimate, for any of the coefficients. This resulted in a subset of 101 isotherms from 28 studies (see SI of paper IV), which resulted in a robust dataset.

2.4.2 Biochar properties.

To test the effect of biochar properties on values of Q_{new}, we fitted generalised linear models (glm). Due to variability in the reporting of specific biochar properties, we performed the GLM on multiple subsets of the data. The variables included in the model fitting are reported in table 4. In fitting the GLM, an analysis of the data distribution informed the choice of a gamma family with a log link function. We chose variables and model fit through minimisation of the AICc, which is an information criterium developed for use with small sample sizes, using the package MuMln (Barton, 2020). We accepted all models within a delta + 2 AICc of the best fitting model. We then used the R function glmmTMB (Brooks et al., 2017) to fit the parameters both with and without a random effect. We fitted multiple models with different subsets of data to test specific hypotheses regarding Q_{new} responses to biochar properties and data quality.

Table 4. Biochar properties included in the final models

			Model parametrisation	
Variable	Units	Levels of factor	Sub set 1	Sub set 2
Activation	Factor	Yes, No	+	+
Solution pH	pH		+	+
Biochar HTT	°C		+	+
Feedstock type	Factor	Agwaste, Biosolids, Combi, Herbaceous, Wood	+	+
(O+N):C	Molar ratio			+

3 Results and discussions

3.1 Biochar for reducing N_2O emissions

Biochar addition consistently reduced N_2O accumulation/emission in both studies quantifying N_2O (Paper I and II). In paper I we found that the consistency of the biochar effect on N_2O depended on pyrolysis temperature (Fig. 4). High temperature biochar (BC562 and BC796) consistently reduced N_2O accumulation across both soil types. A similar effect was observed in the composting study (Paper II), where the 550 HTT mixed wood biochar significantly reduced N_2O emissions compared with a control (Fig. 5).

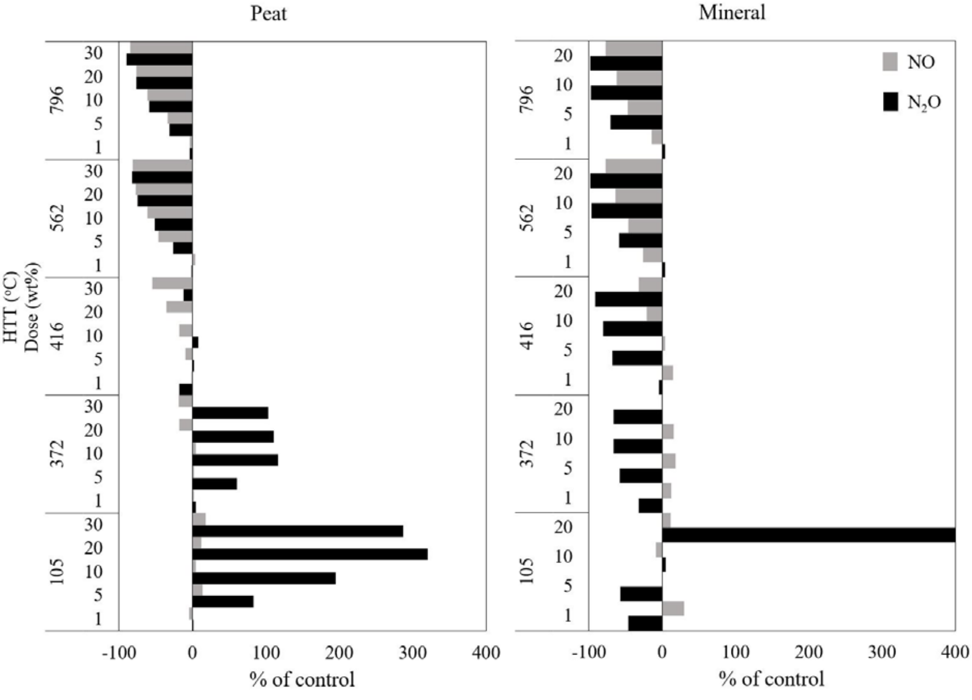

Figure 4. Effect of biochar addition on maximum N_2O and NO accumulation in anoxic batch incubations of peat and mineral soil. The values are calculated as relative difference from the un-amended control (in %).

Cayuela et al. (2015) found in a meta-analysis that high temperature biochars consistently reduced N_2O emission. By contrast, a later meta-analysis by Borchard et al. (2019) found no pronounced effect of pyrolysis temperature. However, this meta-study grouped biochars produced below HTT 500 °C, which may have reduced the sensitivity of the study for HTT. In the soil experiment (Paper I), we found that for BC416 and BC372, the effect on N_2O

accumulation was not consistent and appeared to be soil specific. Both low temperature biochars reduced N_2O accumulation in the mineral soil but in the peat, the BC372 stimulated N_2O accumulation, while the BC416 had no effect. We saw a non-linear effect of biochar dose on N_2O accumulation/emission in both studies (Paper I and II), with decreasing effect size with higher biochar doses suggesting a threshold of some biochar property for the N_2O effect. The meta-analysis by Borchard et al. (2019) also reported a significant dose effect on N_2O emission reduction.

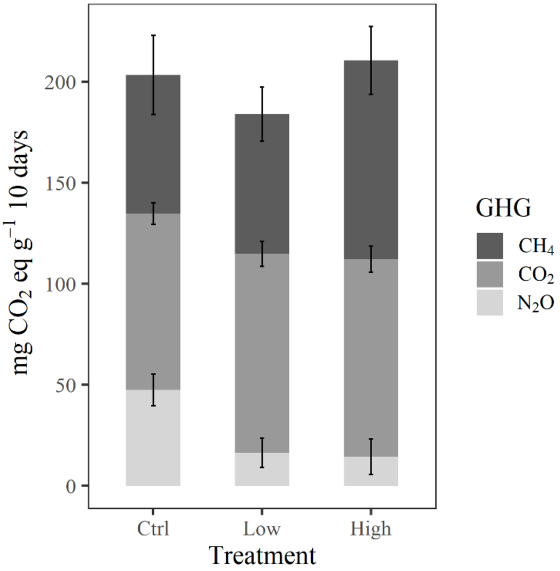

Figure 5. Stacked boxplot of the mean cumulative GHG emissions in CO_2 equivalents (eCO2). Error bars are standard error (Control compost, n=4; compost with 5 and 17 % biochar, n=3).

3.1.1 Contrasting effects of biochar in different soils and compost

We studied the N_2O effect of biochar in two different soils and as an additive to compost. Despite the consistent effect of high temperature biochars on N_2O emissions (Paper I; BC 562, BC796; Paper II; 550 HTT), there was evidence that the mechanisms supporting this effect differed between the systems. Additionally, we found that low temperature biochar (BC372, BC416) stimulated N_2O accumulation in the peat.

In the soil study (Paper I), we worked with anoxic slurries amended with ample amounts of NO_3^-. There are several pathways that reduce NO_3^- under anoxic conditions; canonical denitrification, DNRA, anammox, chemodenitrification and co-denitrification. We found that our experimental system (stirred anoxic slurries with a low DOC/NO_3^- ratio) strongly favoured canonical denitrification as the dominant pathway of NO_3^- dissipation. This finding was based on i) the mass balance of gaseous N returns relative to added N, ii) the transient accumulation of denitrification intermediates (NO_2^-, NO, N_2O) and iii) the observed alkalization of the slurries during anoxic incubation. There were clear differences between the two soils in denitrification rate and accumulation kinetics of intermediates which became apparent within the first five days of incubation (Fig. 6). Most notably, the slightly more acidic peat soil accumulated 10 times more NO and N_2O than the mineral soil. The main discriminant variable between the two soils was the abundance of soil organic matter, which was larger in the peat (53% w/w) than the mineral soil (2 % w/w). The difference in pH (peat pH 5.0; mineral soil pH 5.8) was relatively small, but the larger pool of organic matter in the peat conveyed a large buffering capacity, so that biochar addition resulted in less pH rise in peat than in mineral soil (Fig. 7). The peat also had a larger denitrification capacity than the mineral soil. Both pH and SOM are master variables for soil microbial community composition (Kaminsky et al., 2017; Neal et al., 2020), which has been shown to impact denitrification capacity and inherent product stoichiometry (Highton et al., 2020). This might explain the differences in denitrification phenotypes in peat and mineral soil found in the present study.

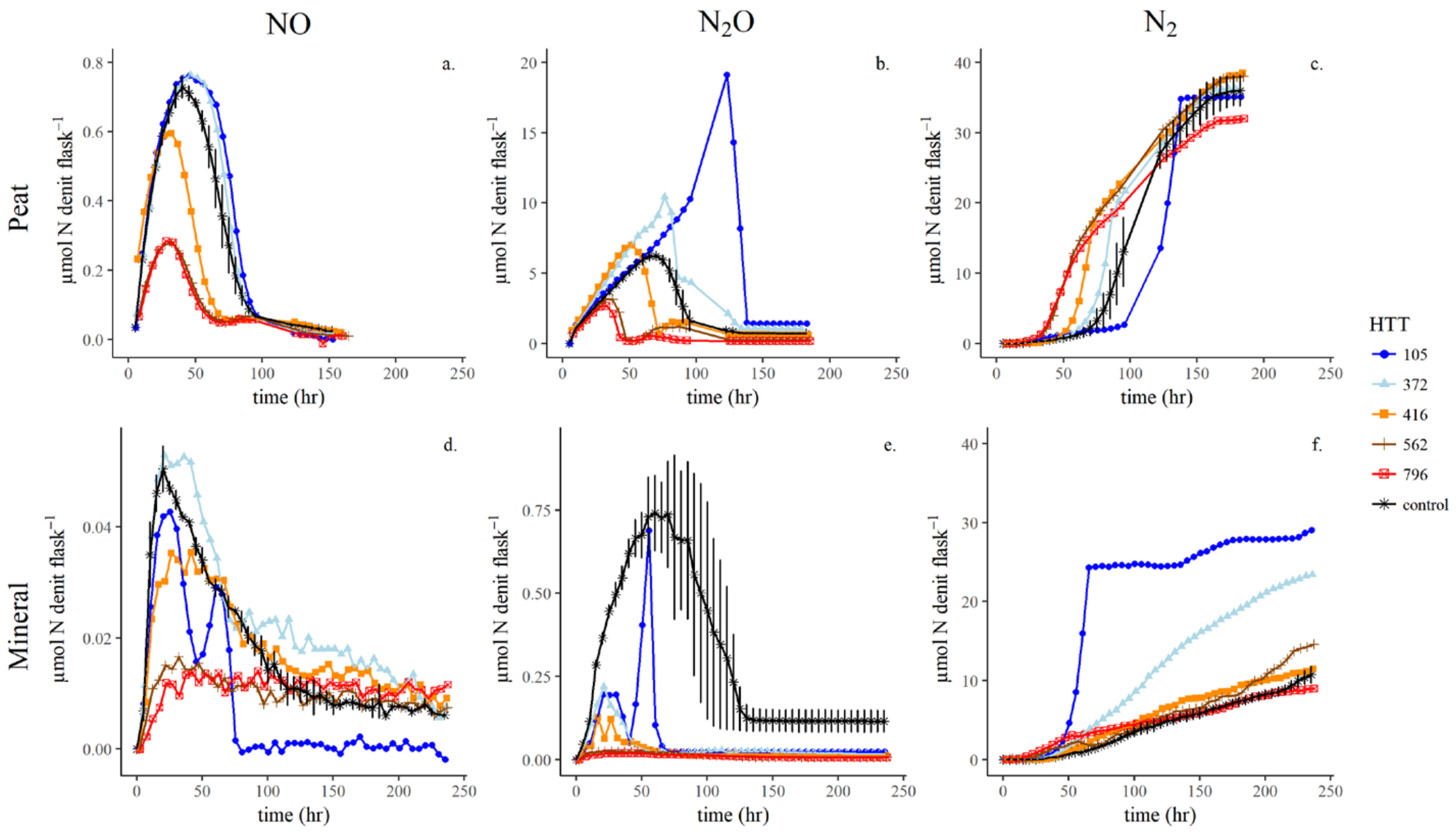

Figure 6. Kinetics of NO, N_2O and N_2 production in anoxic batch incubations of peat (upper panel) and mineral soil (lower panel) amended with 10%w/w biochars of different HTT. Including control with standard error (n=3) peat soil and (n=2) mineral soil.

When comparing denitrification kinetics between both soils, we found that biochar was more effective in reducing N_2O accumulation in the mineral soil and that this effect was more sensitive to dose than in the peat (Fig. 4). However, the peat accumulated more intermediates relative to the final product N_2 than the mineral soil (Fig. 6) so that biochar addition had a larger effect in reducing N_2O accumulation in absolute terms. In the peat, measured accumulation of the final denitrification product N_2 at the end of the incubation (Fig. 6c) suggested that the addition of high temperature biochars (BC562, BC796) stimulated denitrification activity, resulting in a larger rate of total denitrification (DR_{max}) and a reduction in the product ratio ($N_2O/(N_2O+N_2)$). In the mineral soil, while the high temperature biochar (BC 562 796) also reduced the accumulation of N_2O, N_2 accumulation showed no evidence that biochar was stimulating N_2O reduction to N_2 (Fig. 8).

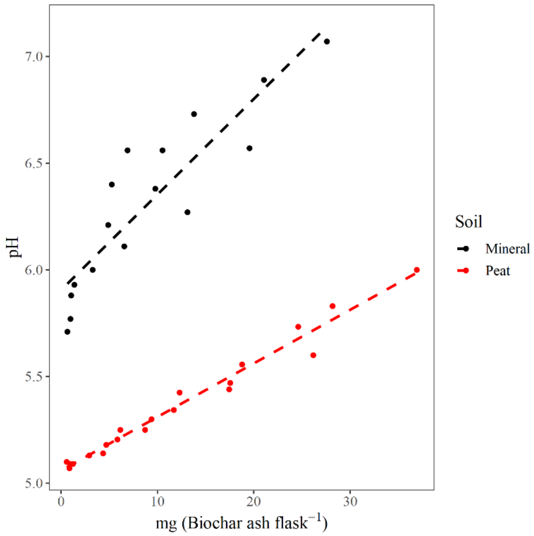

Figure 7. Scatter plot and linear regression of pH values measured in biochar amended soil slurries before incubation and ash content of the biochar. Shown are the complete range of biochar and biochar doses for mineral and peat soil excluding control and feedstock treatments (Linear fit: Peat R^2 0.98; Mineral soil $R^2 = 0.81$).

Denitrification and N_2O accumulation in mineral soil and peat also differed in response to low temperature biochar (BC372, BC416). BC372 appeared to stimulate denitrification in the mineral soil (Fig. 6f) resulting in less N_2O accumulation, while in the peat it increased N_2O accumulation by more than 100% relative to the control (Fig. 4). In the mineral soil, which had less organic carbon than the peat, the BC372 and the FS102 both stimulated denitrification, as judged by the more complete removal of NO_3^- and the larger return of N_2 in these treatments (Fig. 8). The addition of labile C contained in low temperature biochars to a system with a large recalcitrant pool of organic C like the peat may have resulted in positive priming, supporting the growth of denitrifier communities with a initially high $N_2O/(N_2O+N_2)$

product ratio. Changes in product stoichiometry of growing denitrifier communities have been demonstrated previously (e.g. Brenzinger et al., 2015) and are tightly linked to the progressing alkalization of the slurries. Stimulation of N_2O emissions by biochar has also been shown by other studies (Kammann et al., 2012; Li et al., 2013), however these studies are not specific for denitrification. The H:C ratio of biochar, used as a proxy for carbonisation degree, has been used as an indicator of the N_2O emission reduction potential of biochar (Cayuela et al., 2015). While our data confirm that low H:C biochar consistently reduces N_2O accumulation, our reanalysis of the data synthesized in Cayuela et al. (2015) also showed that high H:C biochar tends to stimulate N_2O emissions (supplementary information paper I; $p < 0.01$), which is consistent with our findings for the peat.

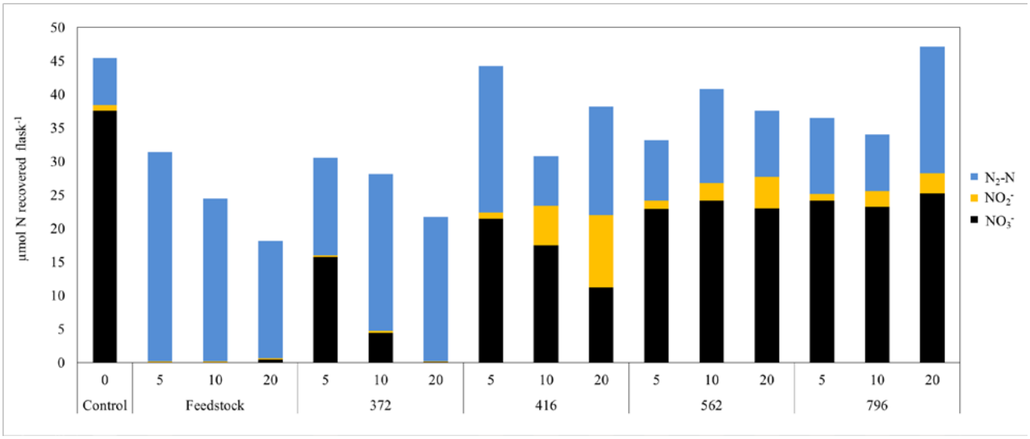

Figure 8. Recovery of mineral and gaseous N for the bottles with mineral soil. The 1% treatment was not measured.

In paper II we saw a clear reduction in N_2O emission during composting when treated with a 550 HTT wood biochar. Biochar addition to compost has been shown to have either negligible effects on N_2O emission (Sanchez-Garcia et al., 2015) or to reduce N_2O emissions by as much as 98 % (Awasthi et al., 2017a). In our study, we saw an average reduction in cumulative emissions of 65 and 70 % relative to the control for low and high biochar doses respectively. By comparison with the soil study (Paper I), the compost experiment was less controlled and the substrate was highly heterogeneous both in terms of material composition and matrix effects. Heterogeneity of compost material can result in coexistence of both aerobic and anaerobic sites with steep O_2 gradients (Beck-Friis et al., 2000; Hao et al., 2001), which promote N_2O production by nitrifier denitrification or coupled nitrification-denitrification (Béline et al., 1999; Nadeem et al., 2020). Originally, we hypothesised that biochar would improve oxygen diffusion, which may have supported a lower N_2O yield of nitrification and reduced denitrification (Paper II). However, some studies have argued that biochar promotes local anoxia through stimulation of microbial activity (Van Zwieten et al., 2012; Harter et al., 2014). In our study, higher microbial activity in the presence of biochar was indicated by higher compost temperatures (Fig. 9) and larger CO_2 and CH_4 emissions, though not statistically significant (Fig. 5). This may indicate larger O_2 consumption rates, which would increase the anaerobic volume in the compost and support local denitrification. Studies have shown that biochar can stimulate the development of active denitrifier populations in biochar treated soils and compost, as inferred from *nos*Z abundance, the gene that encodes the N_2O reductase enzyme (Harter et al., 2016; He et al., 2021). A larger stable anaerobic volume may also reduce N_2O production by nitrifier-denitrification which occurs at low O_2 concentrations (Béline et al., 1999; Zhu et al., 2013). This suggests that biochar may influence both production and reduction of N_2O via controls on oxygen availability and microbial gene abundance.

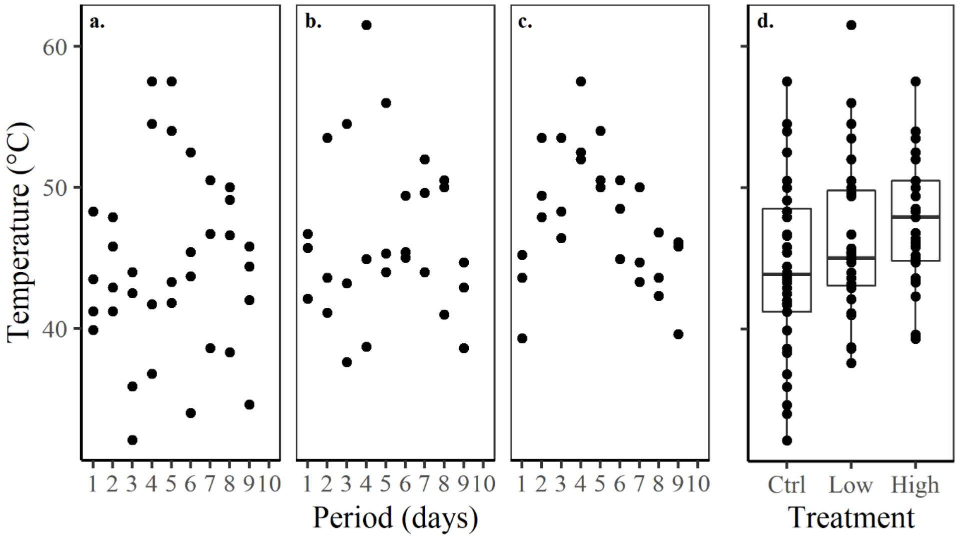

Figure 9. Daily maximum temperature prior to GHG measurement in each tumbler in (a) Compost control (Ctrl, n=4); (b) Compost with 5 % biochar (Low, n=3); (c) Compost with 17 % biochar (High, n=3). Plot (d) is a boxplot of max temperatures summarising differences between treatments.

3.2 Biochar for retaining nutrients

The nutrient retention capacity of biochar is a central theme in biochar research and a key variable in three of the four articles presented in this thesis. In paper II we hypothesised that biochar could increase the retention of nutrients in composted digestate, both during composting and when applied to the soil. In paper III and IV we examined the literature to assess biochar's quantitative potential for N retention and how we might leverage this property to create effective biochar-based fertilisers.

The compost study (Paper II) showed that retention of mineral nutrients in biochar treated compost was not significantly different from that in untreated compost (Table 5). Instead, high biochar additions significantly diluted nutrients, as shown by lower concentrations of total N, total P, plant available P, Mg, Ca and Na (P-AL, Mg-AL, Ca-AL, Na-AL), and ash (Table 5). Compared to concentrations in untreated compost, these elements showed 8-14 % dilution in the compost with 5 % w/w biochar addition, and 19-29 % dilution in the compost with 17 % w/w biochar. Banegas et al. (2007) showed that bulking agents such as sawdust added to compost at high mixing ratios significantly dilutes nutrients, as seen with the high biochar treatment.

Table 5. Physical and chemical properties of the matured composts (Ctrl: without biochar, Low: 5 % biochar, High: 17 % biochar). P-AL, K-AL, Mg-AL, Ca-AL and Na-AL correspond to plant available P, K, Mg, Ca and Na extracted using ammonium lactate. Results are provided as mean and standard error in parentheses (n=4 for Ctrl, n=3 for Low and High). Means with different letters are statistically different (Tukey, $p < 0.05$).

	Ctrl	**Low**	**High**
pH (H_2O)	8.1 (0.2)^a	8.0 (0.3)^a	8.5 (0.3)^a
C/N	7.8 (0.3)^a	8.3 (0.48)^a	13.4 (0.43)^b
Total N (g 100g^{-1} dw)	3.4 (0.1)^b	3.4 (0.14)^b	2.6 (0.14)^a
NH_4-N (mg kg^{-1} dw)	9.9 (2.2)^a	12.7 (3.1)^a	7.9 (3.1)^a
NO_x-N (mg kg^{-1} dw)	2233 (366)^a	1733 (517)^a	983 (517)^a
Total Organic C (% dw)	26 (1.0)a	27 (1.4)a	35 (1.4)b
P-AL (mg 100g^{-1} dw)	550 (19)^b	503 (27)^{ab}	443 (27)^a
Total P (g 100g^{-1} dw)	1.2 (0.04)^b	1.1 (0.06)^b	0.8 (0.06)^a
K-AL (mg 100g^{-1} dw)	393 (17)^a	387 (24)^a	403 (24)^a
Mg-AL (mg 100g^{-1} dw)	193 (6)^b	173 (8)^b	147 (8)^a
Ca-AL (mg 100g^{-1} dw)	4600 (193)^b	3933 (274)^{ab}	3667 (274)^a
Na-AL (mg 100g^{-1} dw)	160 (4)^c	140 (5)^b	113 (5)^a
Dry matter content (g L^{-1})	171 (4)^a	173 (6)^a	163 (6)^a
Dry matter content (%)	37.4 (1.8)^a	38.6 (2.6)^a	33.6 (2.6)^a
Ash content (% dw)	39.5 (0.9)^b	37.1 (1.2)^{ab}	34.5 (1.2)^a
Loss on ignition (% dw)	60.5 (0.9)^a	62.9 (1.2)^{ab}	65.5(1.2)^b

The addition of biochar to compost in our study did not result in a product that increased mineral N retention when added to soil and leached (Fig. 10). Other studies have reported increased retention of mineral N by composted biochar, which they attributed to sorption, pore blocking and the development of organic coatings (Kammann et al., 2015; Haider et al., 2016; Hagemann et al., 2017a; Haider et al., 2017). We did not see any significant biochar effect on either mineral N retention in the original compost (Table 5) or when applied to soil at equal N rates and leached two weeks before harvest (Fig. 10). A possible explanation for this is that the addition of green municipal waste (GMW) to the compost as a co-substrate may have performed a similar function as biochar in retaining N. Additionally, the use of a high-N waste such as composted digestate may have prevented detection of subtle changes in N retention by BC addition.

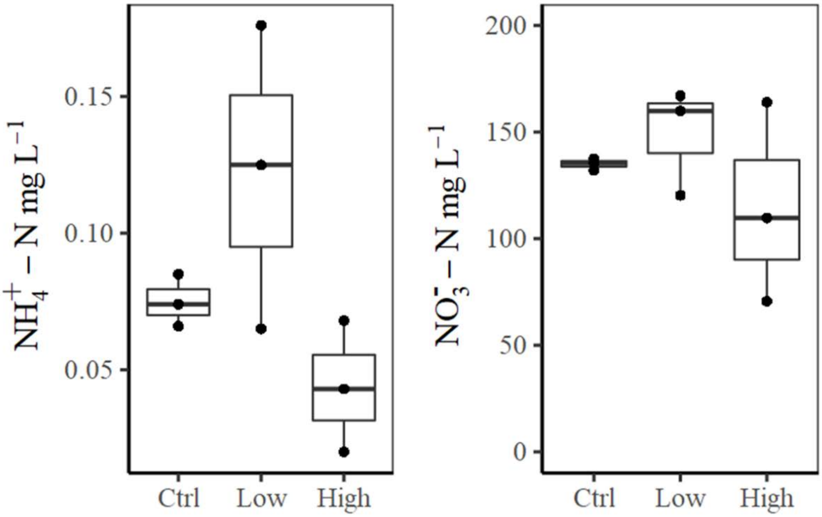

Figure 10. Total leached NH_4-N (a) and NO_3-N (b) following a leaching event. Shown are results from leached pots fertilized with compost without biochar (Ctrl), compost with 5 % biochar (Low), and compost with 17 % biochar (High). Differences tested by application of an ANOVA were not significant at $p = 0.05$.

A major finding of our review paper (Paper III) and our re-analysis of literature values for NH_4^+ sorption (Paper IV) was that biochar has a lower than previously believed capacity for sorbing mineral N. The sorption capacity of biochar is often reported as a key property explaining the observable increase in nutrient retention capacity in soils upon biochar application and in the reclamation of nutrients from waste resources. The function of biochar as a sorbent for N is also a major argument for the development of slow-release biochar compound fertilisers. Our review (Paper III) challenges the notion that biochar has a large native sorption capacity for mineral nutrients and that classical sorption mechanisms would result in a slow release of NH_4^+.

We also confirmed that the retention capacity of biochar was much lower for NO_3^- than for NH_4^+ (Fig. 11). This can be explained by the fact that biochar often has a high net CEC at typical soil pH (5-7), thereby favouring the retention of NH_4^+. The low NO_3^- sorption capacity we found in the literature review (Paper III) contrasts single studies that report high NO_3^- retention by biochar (Kammann et al., 2015; Haider et al., 2016; Hagemann et al., 2017a; Haider et al., 2017). This may be because we focused exclusively on studies reporting the sorption capacity for ammonium and nitrate of fresh, unmodified biochars in single solute systems. All studies reporting high retention capacities for nitrate used biochars that had been recovered after incubation in compost or soils. This has been taken to suggest that high nutrient retention capacities of biochar can be achieved when loading the biochar with nutrients present in natural environments. In this sense, our compost experiment should have functioned as a slow-release compound fertilizer, but the effect on spring onion yields was insignificant as compared with compost alone.

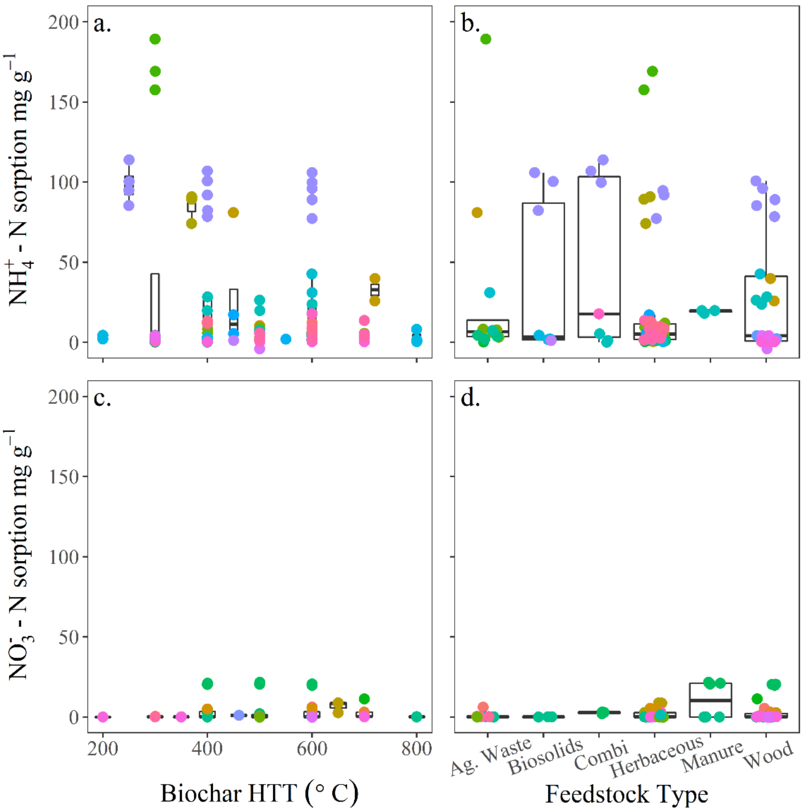

Figure 11 a, b: NH_4^+ maximum sorption. c, d: NO_3^- maximum sorption. a, c: Feedstock type. b, d: BC HTT. Point colours grouped by study. Feed type defined after Cayuela et al. (2014).

Our review of studies reporting biochar NH_4^+ sorption capacities (Paper III) revealed a large variability, ranging from negative estimates of -4 mg NH_4^+ g^{-1} biochar, as a result of a poorly fitted model (Wang et al., 2015), to exceptionally high estimates of 243 mg NH_4^+ g^{-1} biochar (Gao et al., 2015). These high estimates have been used to recommend biochar as a competitive and economically viable sorbent in industrial waste water treatment (Huang et al., 2018a). However, our initial analysis (Paper III) showed that the majority of values reported for NH_4^+ sorption on biochars are low, with a median of 7 mg NH_4^+ g^{-1} biochar. We did not find a relationship between sorption capacity and either HTT or feedstock type, instead the magnitude of the estimated maximum sorption capacity appeared to relate to source article, suggesting that there may be methodological issues with the quantification of NH_4^+ sorption capacities of biochars (Fig. 11).

We therefore examined the available data in more detail (Paper IV) and found that the majority of values >30 mg NH_4^+ g^{-1} biochar were from studies displaying inconsistencies and uncertainties that justified their exclusion from our analysis. Re-analysis of maximum NH4+ sorption capacities for non-activated biochar in the remaining studies confirmed that untreated biochar has a moderate sorption capacity with a median value of 4.2 mg NH_4^+ g^{-1} biochar and a maximum of 22.82 mg NH_4^+ g^{-1} biochar. We also found that activation only modestly increases the median to 7 and the maximum to 27.6 mg NH_4^+ g^{-1} biochar. To contextualise the significance of these values for using NH_4^+ loaded biochar as a fertiliser, relying on sorption alone, it would require 5 tons ha^{-1} biochar loaded with the maximum reported 22.82 mg NH_4^+ g^{-1} biochar for unmodified biochar, to achieve a fertilisation equivalent to 120 kg N ha^{-1}. The biochar application requirement would be disproportionally higher the lower the sorption capacity (Fig. 12).

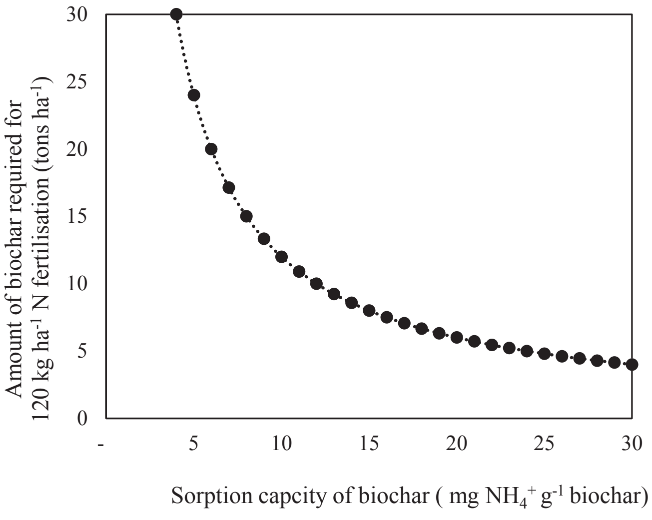

Figure 12. Dependency of biochar required for reaching a fertilisation of 120 kg N ha^{-1} on maximum sorption capacity of the biochar. The relation assumes that sorption is the only mechanism of nutrient loading.

3.3 Biochar properties relevant to N dynamics in soils

3.3.1 Biochar pH

Biochar liming and N_2O emissions

In the soil incubation study (Paper I) we found a biochar pH effect on denitrification kinetics and product stoichiometry, as evidenced by the position of maximum NO and N_2O accumulation opposite to sample pH in the PLSR loading plots (Fig. 13). Biochar HTT and dose had a clear effect on pH in the slurries when starting the incubations, which ranged from 5.2 to 7 for mineral soil and 5.08 to 6 for peat (Fig. 7). The obvious liming effect of high-temperature biochars clearly reduced the accumulation of NO, likely because less nitrate was protonated to HNO_2 which undergoes chemical dismutation to NO_2^- and NO (Chalk and Smith, 1983). This can indirectly impact the $N_2O/(N_2O+N_2)$ product ratio because, due to potentially cytotoxic effects of NO and NO_2^-, accumulation of these intermediates may trigger NO and NO_2^- reduction as a detoxification reaction, without a comparable increase in N_2O reduction (Zhu et al., 2013). More directly, low pH is known to impair N_2O reductase (N_2OR), the enzyme responsible for N_2O reduction to N_2, with increasing inhibition below pH 6.1 (Liu et al., 2014; Brenzinger et al., 2015). This suggests that the liming effect of biochar on NO chemistry and N_2OR functioning may be a significant factor responsible for the recurrently observed N_2O suppression of biochar in acid soils.

Biochar also reduced N_2O emissions during the maturation phase of composting (Paper II). Since the compost pH was high, owing to the high pH of the digestate, there was no alkalization associated with biochar addition (Table 5). The observed N_2O suppression in compost is in line with the meta study by Borchard et al. (2019), who found that biochar reduced N_2O emissions over a wide range of pH values even in relatively high pH soils (pH > 7). However, unlike the soil slurries, which were deliberately kept anoxic to study denitrification (Paper I), the compost study was conducted in rotating tumblers with aeration holes. This likely restricted denitrification to anoxic microsites, while nitrification was the dominant source process for N_2O emission (Béline et al., 1999). Since pH was not affected by biochar addition (Table 5), other biochar properties must have been involved in the observed N_2O suppression, which is discussed later in this section.

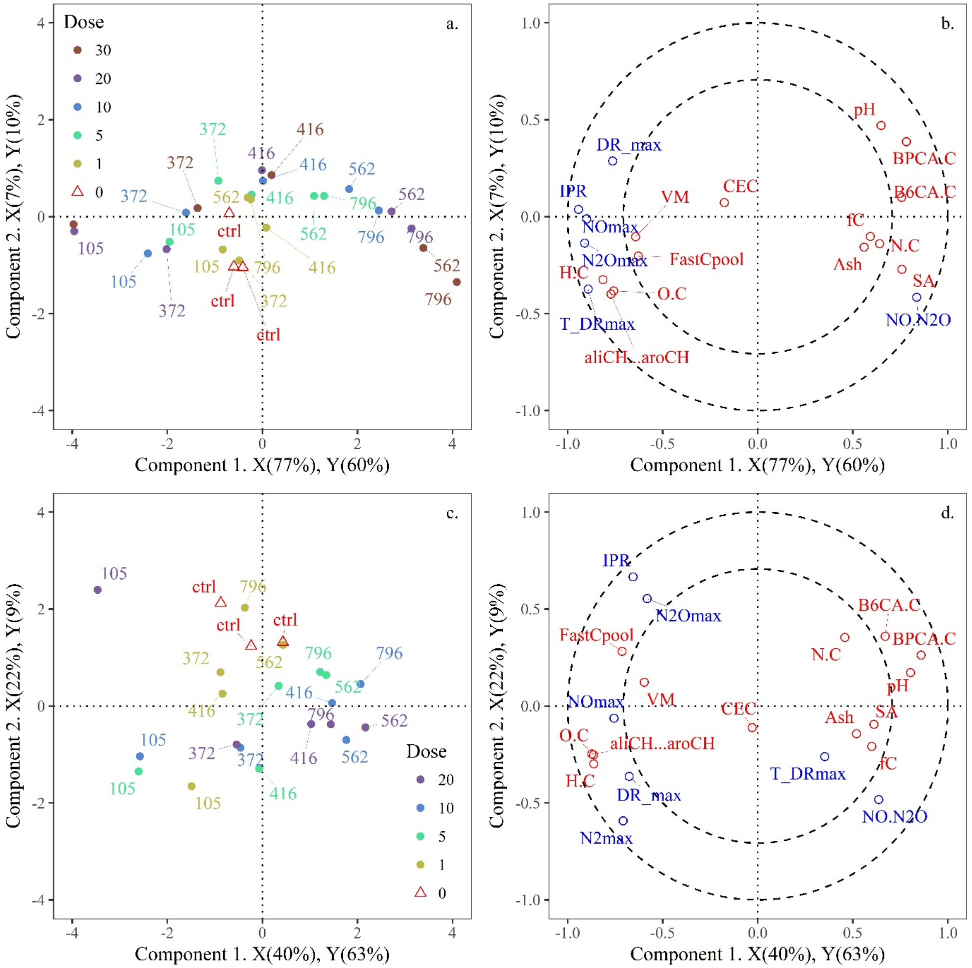

Figure 13. PLSR models for peat (top: a & b.) and mineral soil (bottom: c & d). X scores plots (left a & c.) represent the objects/rows in matrix X and Y and show how the objects relate to one another in the multivariate space spanned by the model. X & Y correlation loading plots (right b & d) show the X (explanatory, blue) and Y (response, red) correlation loadings. The X & Y loading plot represents percent explained variance of each variable, variables within the inner circle have less than 50% of variance explained by the components, variables within the outer ring have greater than 50% variance explained by the 2 plotted components. Variables close to one another on this plot are highly positively correlated for the part of the data explained by the 2 components.

Biochar pH effects on NH_4^+ sorption

Re-calculating maximum sorption capacities of biochar for NH_4^+ by Langmuir modelling of published values (Paper IV) revealed that pH control during batch equilibration tests is crucial as changes in pH strongly affect NH_4^+ sorption. Studies without pH control or removal of ash resulted in persistently higher estimates of biochar NH_4^+ sorption capacity (Fig. 14). Changes in pH during equilibration also affect the NH_4^+:NH_3 equilibrium and may therefore lead to NH_3 volatilisation. Volatilisation of NH_3 can result in substantial N losses at high pH, which are generally not quantified in sorption studies (Kizito et al., 2015; Wang et al., 2015; Esfandbod et al., 2017). NH_3 can also chemisorb to biochar surfaces at standard temperatures and pressures forming amine groups (Hestrin et al., 2019). Both mechanisms may confound the interpretation of Langmuir isotherms which are based on the assumption that a change in concentration of the sorbate i) directly reflects the amount being sorbed, and ii) that this sorption is reversible.

In soils and other organic matrices, the liming effect of biochar not only influences the chemical equilibrium between NH_4^+ and NH_3, but also the charge of functional groups. Likewise, the charge of biochar is pH dependent. A study by Fidel et al. (2018) confirmed the effect of pH, showing greater NO_3^- sorption at lower pH and greater NH_4^+ sorption at higher pH. This means that biochar liming can increase or decrease N retention.

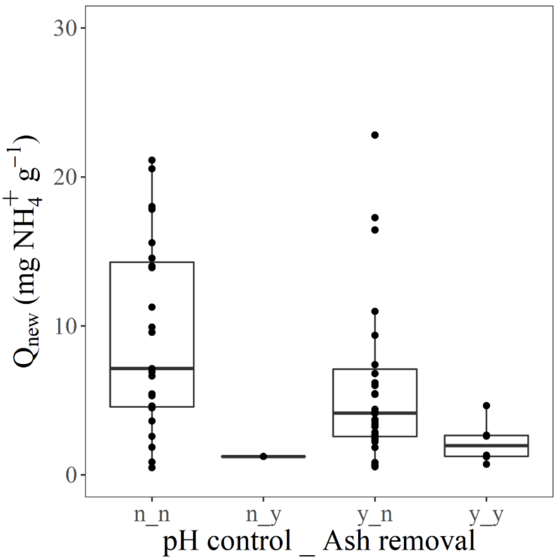

Figure 14 Q_{new} as a function of pH control and ash removal excluding activated biochar. X axis represents a grouping based on whether the batch solutions were subject to any form for pH adjustment (yes/no) and whether the biochar was previously subject to ash removal (yes/no). Points show individual measurements. Activated biochars were removed from this data set because activation often involves a washing step.

Biochar properties related to the liming effect

Besides buffering capacity of the recipient, the pH response of a soil or solution to biochar depends on multiple properties of the biochar including both structural alkalinity, i.e. the alkalinity governed by the composition and abundance of functional groups, and soluble alkalinity in the form of mineral ash (Fidel et al., 2017). Despite a linear increasing pH measured in the soil slurry solutions in paper I (Fig 7) the biochar pH_{H2O} plateaued at pH 9.4 - 10.07 (Table 1) for biochars produced above a HTT of 416 °C. Biochar pH is often determined in water (Singh et al., 2017), however biochar ash can contain secondary carbonates (Yuan et al., 2011), which are a source of alkaline buffering, therefore the total alkalising potential of biochar is often not represented by pH_{H2O} (Fidel et al., 2017). Together, this suggests that, for the corn cob biochar used in paper I, ash contributed significantly to the observed alkalisation.

In the meta-analysis (Paper IV) we found that removing ash from the biochar influenced the magnitude of the estimates for NH_4^+ sorption capacity (Fig. 14). We argued that the dominant effect of biochar ash was on the pH control of the sorption solution. In an unpublished pilot study, we found that it is challenging to control the pH of unwashed biochar and that the resulting pH depends on both feedstock and pyrolysis temperature. We applied acid to a biochar suspension in water to adjust the pH to 7. Between each application the slurry was allowed to equilibrate for 24 hours. It took five days of repeated acid application to reach a stable pH. Additionally, after drying and rewetting of the pH controlled biochar, we found that the alkalinity once again increased. It is possible that drying and wetting caused fracturing of the biochar, increasing porosity and exposing fresh sources of alkalinity. This highlights the difficulty to control pH in biochar experiments. This is especially problematic for experiments where pH control of the system is a pre requisite for correct determination of the response, as it is in the batch sorption experiments.

3.3.2 *Biochar surface functionality*

The functional nature of biochar surfaces is commonly characterized by total surface area, surface charge (point of net zero charge PNZC), physical porosity (total porosity and pore size distribution) and the abundance of surface functional groups (elemental ratios, CEC, AEC). Identifying which of these properties will have the greatest impact on target parameters, such as mineral N retention or N_2O suppression, is important because optimising these variables often involves trade-offs. For instance, maximising biochar surface area, may result in a reduction in the abundance of surface functional groups (Budai et al., 2014).

Total surface area is often quoted as a key property of biochar since it is often used as a proxy for multiple properties of biochar surfaces, including the density of functional groups and porosity. In the soil incubation study (Paper I) the total surface area was positively correlated with reduction in N_2O accumulation (Fig. 13). Cornelissen et al. (2013) showed that biochar has a considerable potential to irreversibly sorb N_2O under anhydrous conditions, which was positively correlated with surface area measured by the BET method. However, mass balance of the returned gaseous N via denitrification in our experiment did not support permanent sorption as a reason for lower N_2O accumulation (Fig. 6). In theory, biochar could promote enzymatic N_2O reduction to N_2 by transiently increasing N_2O concentrations through reversible sorption on biochar particles as proposed by Harter et al. (2016), but this is difficult to prove without micro sensors measuring N_2O concentrations around biochar particles. N_2O is a polar molecule and therefore has an affinity to both negatively charged functional groups and to weak negative Van der Waals forces produced by condensed aromatic structures in high temperature biochars. We did not find evidence that high CEC correlated with reductions in N_2O accumulation in the soil study (Paper I). However, the strongly negative correlation with N_2O accumulation and B6CA:C and BPCA:C, which we used as indices for aromaticity and condensation (Fig. 13), may support the idea that biochar retains N_2O through the function of weak electrostatic forces and thereby supports its enzymatic reduction to N_2. A weakness of this hypothesis is that it considers N_2O retention without considering N_2, which competes with N_2O for surface area. We saw evidence of greater N_2 desorption from high temperature char, which we had to control for in the soil study (Paper I). However, we saw no overall reduction in the mass balance of returned N_2-N in our bottles (Fig. 6).

When analysing the dependency of NH_4^+ sorption capacity on biochar properties (Paper IV), we observed a correlation between maximum NH_4^+ sorption and the elemental ratio ((O+N):C) and CEC of the biochar, which are commonly used as metrics for functional group abundance (Fig. 15). A meta-analysis by Hassan et al. (2020) confirmed that sorption of ionic nutrients is favoured by the abundance of functional groups, which are more abundant in biochars pyrolysed at low temperatures. Budai et al. (2014) reported a peak in CEC at intermediate pyrolysis temperatures of 400 to 500 ^{o}C HTT, which is consistent with the finding that peak sorption of NH_4^+ correlates with peak CEC at intermediate pyrolysis temperatures (Gai et al., 2014; Yang et al., 2018; Zhang et al., 2020).

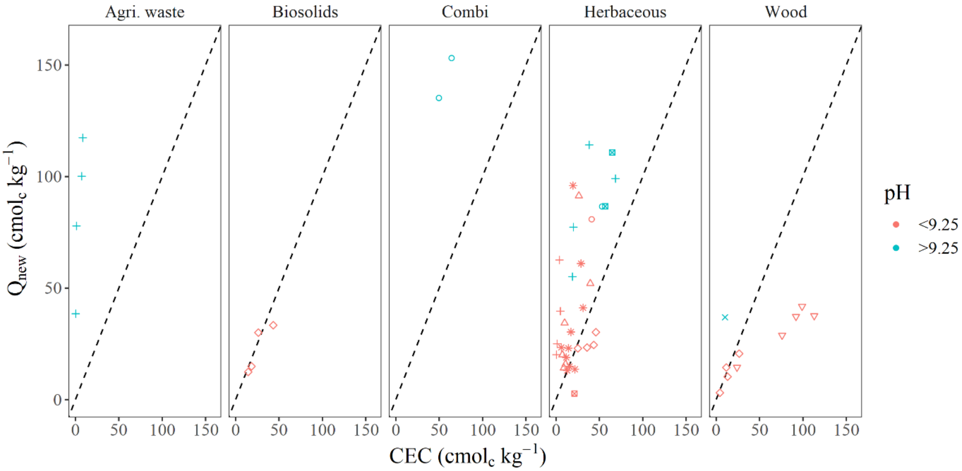

Figure 15. CEC vs. Q_{new} in cmol$_c$ kg^{-1}. Symbols refer to study and colour refers to pH. Activated biochars are included and account for 8 of the 53 measurements presented.

Not only the abundance, but also the type of functional group determines the charge of the biochar surface at specific pH values. Fidel et al. (2017) highlighted that the structural alkalinity responsible for biochar's CEC at agriculturally relevant pH is dominated by low pKa functional groups (e.g. carboxylic acid groups). These groups are more abundant in biochars with low pyrolysis temperature (Bezerra et al., 2007) and they may be lost at higher pyrolysis temperatures in favour of high pKa functional groups (e.g. hydroxyl groups). High pKa functional groups remain protonated even at high pH and therefore have a positive charge which can function for anion exchange at agriculturally relevant pH (pH 6-7). This is supported by observations that net anion exchange capacity is higher for biochars produced at higher pyrolysis temperatures, which may therefore be more suited for NO_3^- retention (Lawrinenko and Laird, 2015; Lawrinenko et al., 2017).

Another source for variability in surface functionality is feedstock type. Hassan et al. (2020) reported greater abundance of functional groups for grass and manure biochar by comparison with wood biochar. This is supported by Fidel et al. (2017) who found that Red Oak biochar contained fewer functional groups than a corn stover biochar. This may explain the significantly lower NH_4^+ sorption capacities we found for wood biochars in paper IV (Fig. 16).

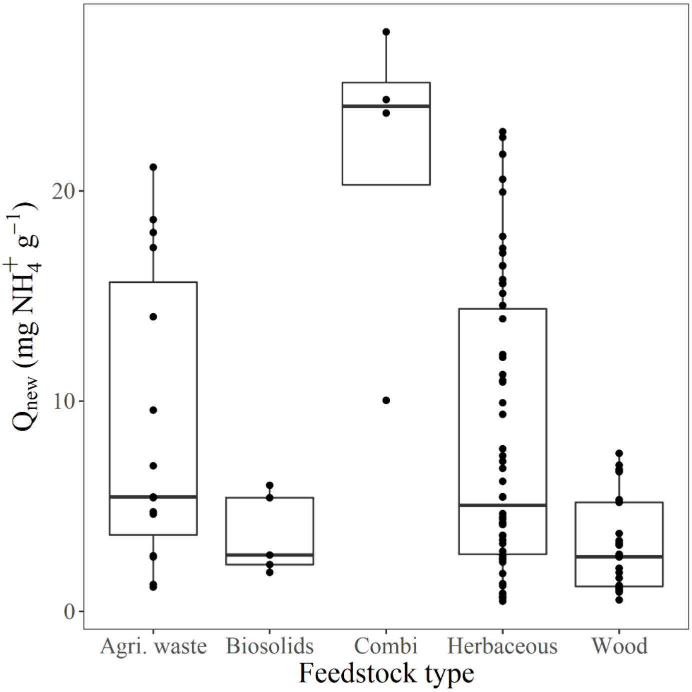

Figure 16. Distribution of Q_{new} values by feedstock. Data are for non-activated biochar only. Based on data subset 4 (Table S4, Supplementary Information)

Although we argue that ion exchange mechanisms explain much of the observed capacity for retaining NH_4^+, we found that the maximum CEC reported in the literature (Paper III) of 14 mg NH_4^+ g^{-1} biochar (80 $cmol_c$ kg^{-1} biochar) was lower than the maximum sorption potential of 23 and 28 mg NH_4^+ g^{-1} biochar for non-activated and activated biochar, respectively. If NH_4^+ sorption was entirely driven by ion exchange, the range of reported CEC values should closely overlap with the range of biochar NH_4^+ sorption capacities. Several studies have argued that a discrepancy between CEC and NH_4^+ sorption provides evidence for the contribution of biochar properties other than ion exchange capacity to the total sorption capacity for NH_4^+ (Jassal et al., 2015; Fidel et al., 2018). In our review of the literature (Paper IV) we found that pH and study methodology may at least partially explain this discrepancy. However, Fidel et al. (2018) provided compelling evidence that ion exchange may explain most but not all of the total sorption potential of a Red Oak and a corn stover biochar.

Biochar porosity and physical structure

The physical structure of biochar, including macro and microporosity, is commonly invoked for explaining positive biochar effects on composting (Barthod et al., 2018; Waqas et al., 2018). In the compost study (Paper II) we argued that biochar reduced the formation of large anaerobic clumps, which may have resulted in greater oxygen infiltration and increased the microbial activity (Awasthi et al., 2017a; Liu et al., 2017a). This was supported by a significant increase in maximum temperature of the compost in the 17% wt/wt biochar treatment (Fig. 9). We also saw a moderate increase in CO_2 and CH_4 production in this treatment (Fig. 5), that appeared to be correlated with temperature increase, which is indicative of greater microbial activity.

Several studies have argued that biochar porosity could benefit nutrient retention through protection of nutrients from microbial attack and pore blocking (Gul et al., 2015; Hagemann et al., 2017a). As mentioned before, our composting study (Paper II) did not confirm increased nutrient retention in biochar treated compost. This may have two explanations; first, because the control treatment included MGW as a porous co-substrate and second, because the high N content of the digestate prevented detection of subtle retention effects of the biochar exceeding that of MGW. In our review of NH_4^+ sorption we did not find enough studies consistently reporting pore structure to explore the effect of biochar structure on NH_4^+ sorption. Notwithstanding, the mismatch between maximum NH_4^+ sorption capacities (23 – 28 mg NH_4^+ g^{-1} biochar; Paper IV) and reported maximum value of biochar CEC (14 mg NH_4^+ g^{-1} biochar; Paper III) suggests that mechanisms other than cation exchange are relevant.

Taken together, this illustrates the need for understanding mechanisms of nutrient retention by biochar in more detail. Biochar porosity may be important in this context, as nano porosity interacts with the abundance of surface functional groups to increase biochars' sorption potential. For example, Gong et al. (2019) argue that micropores with a diameter of 0.6 – 2 nm are important for the sorption of nutrients. Conte et al. (2013) hypothesise that the nano-confinement of water in the nano pores of biochar also facilitates nutrient retention. In biological systems, nutrient retention could also be related to occlusion either through entrapment in nano-pores too small for microbial access or through blockage of pores by organic and mineral coatings. It is also possible that surface functionality, porosity and the gross physical structure of the biochar particle interact to govern nutrient retention. Liu et al. (2017c) found that particle size, shape and porosity act together to influence soil hydraulic properties. Others have shown a negative correlation between biochar particle size and NH_4^+ sorption, with higher sorption capacities reported for biochar that had been ball milled (Fan et al., 2019; Qin et al., 2019). This suggests that there may be a trade-off between maintaining the biochar physical structure and increasing the available surface area when optimising biochar for moisture or nutrient retention, respectively. .

The relative importance of biochar porosity remains uncertain both because it is infrequently quantified and because quantification methods may introduce artefacts (Maziarka et al., 2021). It is also unclear how biochar porosity changes following application to soils and organic media, and how this might influence biochar function. Hagemann et al. (2017a) for example, found that biochar pores became blocked following incubation in compost. Ismadji et al. (2016), combining biochar and bentonite, found that sorption capacity of the mix exceeded that of either pure bentonite or biochar, despite a significant reduction in the measured porosity of the biochar. This suggests that there is still much that is unknown regarding the importance of biochar porosity for biochar effects in soil.

3.4 Biochar as a fertiliser

As the topic of biochar application to agricultural soils has developed, there has been increasing interest in biochar-based fertilisers as a method for optimising N application and facilitating N recycling in agriculture. The development of biochar-based fertilisers represents an attempt to exploit biochar properties and interactions with N and to produce commercially viable products that can compete with mineral fertiliser, notably through improved N use efficiency and slow-release effects.

Our review (Paper III) found that while biochar properties governing the retention of mineral N could be enhanced via biochar choice and/or modifications, the native sorption capacity of biochar (Fig. 12) may be too small to result in an economical or practical product as compared with conventional compound fertilizers. We also found that despite the often cited assertion that nutrient loaded biochars can act as a slow-release fertiliser (Manikandan and Subramanian, 2013; Cai et al., 2016; Dong et al., 2019; Ibrahim et al., 2020), desorption of N from biochar occurs relatively rapidly, often over timescales of less than a day (Kizito et al., 2015; Wang et al., 2020). Other studies have found that N retained on biochar is strongly bound (Hestrin et al., 2019), which would reduce biochars' effectiveness as a fertiliser. This also challenges the assumption that biochar can be used to retain and subsequently release fertilizer N.

Our own investigations into the development of a biochar fertiliser through co-composting with biogas digestate (Paper II) found that biochar addition to compost did not improve nutrient retention (Fig. 10) and that the application of biochar amended compost as a fertiliser did not result in larger crop yields than the application of compost alone (Fig. 17). We argue that this may be because the compost was produced with a high N feedstock and already contained porous organic media in the form of Green Municipal Waste (GMW). This is in accordance with Jeffery et al. (2017) who found that the application of biochar to temperate soils with high fertility and circum-neutral pH did not support higher crop yields. In a meta-analysis, Wang et al. (2019) found that co-composting of biochar with green waste (GW) did not result in a significant increase in yield when applied as a fertiliser. It has been argued that the effect of biochar on yield is a function of basic biochar properties such as its liming effect or its ability to retain soil moisture (Jeffery et al., 2017). Our results suggests that key biochar properties are too similar to those of composted GMW to bring substantial improvement to the final product. This finding is supported by the significantly lower crop yield in the NPK treatment, where the lower pH and organic matter content of the sandy soil without compost experienced high leaching and nutrient loss and hence supported less crop growth (Paper II).

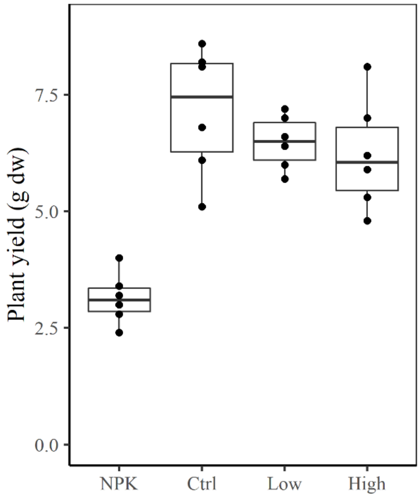

Figure 17. Plant yield at maturity (g dw), showing the following treatments; Mineral fertiliser treatment (NPK), compost without biochar (Ctrl), compost with 5 % biochar (Low), and compost with 17 % biochar (High). Differences between treatments, tested by an ANOVA followed by a TUKEYS test revealed a significant difference between NPK and all other treatments ($p < 0.001$) but no significant difference between compost treatments.

Overall, our results lend more support to the use of biochar as a liming agent and analogue for native SOM, with respect to its function for soil structure and moisture retention, than as an agent for nutrient retention. However, a limitation of our study and many other studies reported in the literature is that we studied biochar of only one biochar feedstock over a short timescale. This means that we are unable to see how biochar contributes to long term fertility in soils and how accumulation of pyrogenic organic matter will affect the properties of the soils with time.

4 Conclusions and outlook

Better utilization of N resources in crop production is needed to increase food security, while decreasing nitrogen pollution. We also need solutions to mitigate climate change through carbon storage and reductions in the carbon footprints of industries and land use. Biochar has been proposed as a technology that has the potential to simultaneously address these challenges by acting as an effective carbon store and through its interactions with the soil N cycle. In this PhD I have explored interactions of biochar with N cycling processes to better understand whether and how biochar can be used to achieve the specific goals of reducing N_2O emissions and increasing N retention in soils.

I set out by exploring the mechanisms behind the well documented N_2O supressing effect of biochar in soil and found that this effect was consistent for high temperature biochars (HTT 550 – 796 ^{o}C) of corn cob and wood, reducing N_2O emissions in two different soil types and a compost reactor by up to 65 – 98%. By contrast, the effect of low temperature biochar was variable and soil dependent, resulting in significant stimulation of net N_2O production in a peat but not in a mineral soil. These results substantiate the finding of Cayuela et al (2014) that high temperature biochars with a low H:C elemental ratio mitigate N_2O emissions across different soil systems.

Biochar has been recommended for inclusion in fertiliser products largely because of its perceived high nutrient retention properties and expected slow-release effect. However, upon closer inspection of published data we discovered that the N retention properties of biochar often are overstated, especially with respect to sorption and slow release of NH_4^+. This overstatement appears to have two main roots: 1) the assessment of biochar functions is often based on qualitative rather than quantitative evaluations and 2) maximum estimates of NH_4^+ retention are often quoted as target values, even though their determination may be compromised by inconsistent methodologies and experimental artefacts. To arrive at more realistic estimates of possible NH_4^+ retention by biochar, we undertook a quantitative review and re-analysis of literature values. Our approach resulted in the removal of many high estimates for NH_4^+ sorption to biochar based on methodological uncertainties. In particular, choices related to pH control of the batch solution and ash removal were identified as confounding factors. This quantitative approach differed from traditional meta–analyses and allowed us to contextualise the absolute rather than relative effect size of a specific biochar property for NH_4^+ retention. The question of absolute *versus* relative effect has direct significance for the development of biochar products as a measurable and reproducible effect is the basis upon which a product is marketed.

‘Biochar’ as a term encompasses a wide range of products that differ not only by the choice of feedstock, pyrolysis method and temperature, but also by the application of pre and post pyrolysis technologies. We found that this variability was so great that across a total data pool of 125 measurements and 31 source articles, there was almost no replication in feedstock type within or across studies. This has significant implications for the interpretation of biochar N effects in different systems and has resulted in a highly uncertain picture of biochar effects in soils and other organic matrices. The inability to contextualise absolute effect sizes may have resulted in an inclination to emphasize complexity as a reason for the observed variability of biochar effects in different systems. Notwithstanding that some of this complexity may be real, this thesis shows that basic mechanisms often can explain variable findings. For example, we confirmed that pH had a key effect on N_2O emissions from denitrification in our laboratory experiment. In the compost experiment, we concluded that biochar may be functionally redundant with structured organic matter. Likewise, NH_4^+ sorption appeared to be largely well explained by ion exchange mechanisms, even though we could not rule out other mechanisms. We also found evidence that a failure to consider the contribution of methodological artefacts in the determination of NH_4^+ sorption capacity likely resulted in an overestimation of biochar effects which perhaps leads to the overemphasis of marginal properties of biochar to explain these effects.

This thesis advocates quantification of biochar properties and responses with respect to N cycling in absolute terms using standardised methodologies. This would greatly facilitate the comparison of biochar effects across different biochar types but also with analogous compounds such as clay or SOM, or agricultural amendments, such as lime. This approach might lead to the conclusion that biochar is functionally redundant with naturally occurring compounds such as minerals or unpyrolysed organic matter. However, biochar is not a product with a singular effect, but a green technology with the potential to deliver multiple benefits when holistically considering its contributions to challenges such as waste valorisation, GHG mitigation and carbon storage. Despite the *Terra Preta* standing as the inspiration for biochar application to soils, there is a lack of long-term studies showing the effect of continued biochar addition to soils. This is a question we need to resolve if we wish to fairly assess the value for biochar to promote long-term sustainability goals and its relative value compared with other technologies addressing similar challenges. Notwithstanding carbon sequestration as a key driver for biochar development, the economic justification for biochar addition to agricultural soils must be made based on consistent and predictable effects on key parameters and its competitive advantage when compared to existing products.

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The effect of a biochar temperature series on denitrification: which biochar properties matter?

Simon Weldon[a,c,*], Daniel P. Rasse[a], Alice Budai[a], Oliver Tomic[b], Peter Dörsch[c]

[a] *Department of Soil Quality and Climate Change, Norwegian Institute of Bioeconomy Research, NIBO, Ås, Norway*
[b] *Faculty of Science and Technology, Norwegian University of Life Sciences, NMBU, Ås, Norway*
[c] *Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, NMBU, Ås, Norway*

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ABSTRACT

Biochar has been shown to reduce nitrous oxide (N_2O) emissions from soils, but the effect is highly variable across studies and the mechanisms are under debate. To improve our mechanistic understanding of biochar effects on N_2O emission, we monitored kinetics of NO, N_2O and N_2 accumulation in anoxic slurries of a peat and a mineral soil, spiked with nitrate and amended with feedstock dried at 105 °C and biochar produced at 372, 416, 562 and 796 °C at five different doses. Both soils accumulated consistently less N_2O and NO in the presence of high-temperature chars (BC562 and BC796), which stimulated reduction of denitrification intermediates to N_2, particularly in the acid peat. This effect appeared to be strongly linked to the degree of biochar carbonisation as predicted by the H:C ratio of the char. In addition, biochar surface area and pH were identified as important factors, whereas ash content and CEC played a minor role. At low pyrolysis temperature, the biochar effect was soil dependent, suppressing N_2O accumulation in the mineral soil, but enhancing it in the peat soil. This contrast was likely due to the labile carbon content of low temperature chars, which contributed to immobilise N in the mineral soil, but stimulated denitrification and N_2O emission in the peat soil. We conclude that biochar with a high degree of carbonisation, high pH and high surface area is best suited to supress N_2O emission from denitrification, while low temperature chars risk supporting incomplete denitrification.

1. Introduction

Biochar has a significant potential to mitigate greenhouse gas emissions from agriculture, both by storing carbon in soils (Lehmann et al., 2006; Lorenz and Lal, 2014) and through mitigating N_2O emissions (Cayuela et al., 2014; He et al., 2017; Grutzmacher et al., 2018). In a recent meta-analysis, Borchard et al. (2019) reported an average reduction of N_2O emission by biochar of 38 percent. This is a notable reduction in the estimated effect strength of 54 percent from a previous meta-analysis (Cayuela et al., 2014) and highlights the variability in biochar effects on N_2O emissions from study to study. Some studies do not find any effect (Zheng et al., 2012; Wang et al., 2013; Case et al., 2014; Van Zwieten et al., 2014) while others report stimulation of N_2O emissions (Yanai et al., 2007; Clough et al., 2010; Shen et al., 2014). Despite a significant body of research on the N_2O suppressing effect of biochar, it is still not possible to predict whether the addition of a specific biochar will have a measurable effect on soil N_2O emissions for a given combination of soil type, biochar feedstock, production method and dose. Variable effects may be expected, given the fact that N_2O is produced by a number of abiotic and biotic reactions in soil, with microbial nitrification and denitrification considered to be the most significant ones (Firestone and Davidson, 1989). Both processes respond differently to changes in abiotic factors brought about by biochar in soil, and it is unlikely that the N_2O supressing effect is governed by any singular property of the biochar. Here, we focus on denitrification and study in detail how biochar influences the microbial turnover of NO and N_2O under anaerobic conditions.

Many studies examining the N_2O suppressing effect of biochar have focused on N_2O emissions (Jia et al., 2012; Fungo et al., 2014; Verhoeven and Six, 2014; Edwards et al., 2018), while relatively few have addressed underlying processes (Ameloot et al., 2013; Cornelissen et al., 2013; Nelissen et al., 2014; Obia et al., 2015; Harter et al., 2017; Chen et al., 2018). Among the latter, studies addressing the enzymatic reduction of N_2O to N_2 in denitrification are of particular interest. Biochar has been implicated to act directly as a redox mediator supporting the reduction of N_2O to N_2 in denitrification (Cayuela et al., 2013) or by changing the denitrifying community composition to be more efficient in reducing N_2O (Van Zwieten et al., 2014; Harter et al.,

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[*] Corresponding author. Department of Soil Quality and Climate Change, Norwegian Institute of Bioeconomy Research, NIBO, Ås, Norway.
E-mail address: simon.weldon@nibio.no (S. Weldon).

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2017). Others have highlighted the alkalizing effect of biochar in acid soils as a possible explanation for increased microbial N_2O reduction in acidic soils (Obia et al., 2015; Harter et al., 2016).

Providing evidence for complete denitrification in soil is not trivial, because quantification of N_2 production requires sophisticated incubation setups or stable isotope approaches. Recent studies have inferred the functioning of denitrification from copy numbers of key denitrification gene transcripts (Xu et al., 2012; Harter et al., 2017), documenting increased ratios of *nosZ* (coding for N_2O reductase) over *nirK* and/or *nirS* transcripts (coding for NO_2^- reductase), which was taken as evidence for biochar promoting N_2O reducing microorganisms. However, primer-based studies into the composition of actively denitrifying communities may be biased (Roco et al., 2017) and biochar mediated changes in the taxonomic composition of denitrifier communities require time to manifest (Brenzinger et al., 2015). By contrast, monitoring of the gaseous denitrification products can quantify direct effects of biochar on N_2O turnover by denitrification and provide valuable information about the stoichiometry of denitrification products (Cayuela et al., 2013; Obia et al., 2015; Chen et al., 2018).

Nitric oxide (NO), the precursor of N_2O in denitrification, is rarely studied in the context of biochar research (Nelissen et al., 2014; Obia et al., 2015). NO is a significant atmospheric pollutant (Molina-Herrera et al., 2017; Pourhashem et al., 2017), but also an important signalling molecule during the early induction of denitrification (Nadeem et al., 2013). Therefore, studying denitrification kinetics, i.e. the sequential production and consumption of NO and N_2O and the accumulation of the final product N_2 in the presence and absence of biochar may shed light on the underlying biochar-driven mechanisms suppressing denitrification-induced N_2O production.

Biochars comprise a wide array of structural and chemical properties, all of which may affect the redox reactions involved in denitrification. The physico-chemical properties of biochar are a function of feedstock type, pyrolysis method and pyrolysis temperature (Antal and Gronli, 2003; Kloss et al., 2012). Increasing pyrolysis temperature decreases volatile matter and increases the relative content of C to O and H in biochar. Indices such as a H:C ratio of < 0.3 of biochar have been suggested as proxies for N_2O suppressing properties (Cayuela et al., 2015), but little is known about the actual properties responsible or their modes of action. Increasing pyrolysis temperature also increases ash content and aromaticity, while surface area and surface functionality, i.e. the capacity to donate and receive electrons, increase nonlinearly with pyrolysis temperature (Budai et al., 2014; Klüpfel et al., 2014a). This suggests that thresholds in pyrolysis temperature with respect to N_2O suppression may exist.

Biochar properties may affect denitrification in various ways; through sorption or desorption of NO_2^- or NO_3^- (Yao et al., 2012; Hagemann et al., 2017), DOC (Lu et al., 2014) and gaseous intermediates (Cornelissen et al., 2013), through increasing the activity and/or completeness of denitrification by pH increase (Wijler and Delwiche, 1954; Bakken et al., 2012) or by redox mediation (Cayuela et al., 2013; Klüpfel et al., 2014a; Chen et al., 2018). However, the effects may be antagonistic, as more complete denitrification may go along with increased denitrification, thus potentially nulling out N_2O suppression.

The present study focuses on the effect of biochar on NO and N_2O turnover in denitrification under controlled conditions, with biochar treatment temperature, dose and soil type being the main variables. We used batch incubations of constantly stirred soil slurries in a helium atmosphere to minimize matrix effects and monitored the accumulation of gaseous denitrification products (N_2, N_2O, NO, CO_2) at high temporal resolution. Our objective was to elucidate how the N_2O suppressive effect of a corncob biochar, in two contrasting soils (a mineral soil and a peat), depends on its physico-chemical properties as affected by highest treatment temperature during pyrolysis.

Table 1
Key soil properties. (Mean and Standard deviation n = 3).

	Peat		Mineral soil	
$pH_{(H2O)}$	5.08	(± 0.00)	5.86	(± 0.04)
C %	53.00	(± 0.10)	2.83	(± 0.01)
N %	1.79	(± 0.04)	0.29	(± 0.00)
C:N	29.53	(± 0.70)	9.87	(± 0.21)
H^+ (mmol/kg)	689.73	(± 9.43)	93.27	(± 0.90)
Ca (mmol/kg)	314.40	(± 5.06)	44.69	(± 0.68)
K (mmol/kg)	7.91	(± 0.17)	2.80	(± 0.03)
Mg (mmol/kg)	68.35	(± 0.98)	2.34	(± 0.03)
Mn (mmol/kg)	0.09	(± 0.00)	0.11	(± 0.00)
Na (mmol/kg)	16.75	(± 0.14)	0.75	(± 0.01)
CEC (cmol/kg)	1480.10	(± 21.04)	191.08	(± 2.35)
Base saturation (%)	53.38	(± 0.20)	51.07	(± 0.16)

2. Materials and methods

2.1. Biochars and soils

Samples of top-soils (0–10 cm) were collected from a cultivated peatland and an acid mineral soil, classified as Hemic Histosol and Umbric Epistagnic Albeluvisol (WRB), respectively. Soils were stored at 4 °C until experimentation and sieved to 2 mm before incubation. Table 1 gives key properties of the soils.

A series of biochars was prepared from *Zea mays* corncobs using slow pyrolysis in N_2 atmosphere. Methods of preparation and storage are given in Budai et al. (2014). In brief, a heating rate of 2.5 °C min^{-1} was used, and highest treatment temperatures (HTT) were measured within the 1 L retort. HTTs of samples selected for this study were 105, 372, 416, 562 and 769 °C, hereafter referred to as FS105, BC372, BC416, BC562 and BC796. The sequence was chosen to span a wide range of biochar key properties such as pH, CEC, volatile matter (VM) and ash content. The biochars were crushed through a 2 mm sieve and stored dry.

Table 2 lists the biochar properties. $pH_{(H2O)}$ ranged from 8.8 to 10.1 and ash content from 2.1 to 4.5% w/w. Volatile matter content ranged from 6.9 to 40.5% and the C content from 71.9 to 91.5% w/w. Less than 0.1% w/w was readily biodegradable in soil regardless of pyrolysis temperature, as determined in a one-year incubation study (Budai et al., 2016). The yearly mineralization rate of the remaining C pool of the biochars was approximately 0.005 y^{-1}. Where possible, variables were scaled to the biochar dose added. Where this was not possible, e.g. for elemental ratios, properties are given as single value.

2.2. Experimental design

Denitrification kinetics were studied in two separate incubation experiments, one with each soil type. Each soil was incubated with multiple combinations of HTT and dose, each unique combination being represented by one incubation flask on which time-repeated measures were carried out to determine denitrification kinetics and derive denitrification parameters. Non-amended soils where incubated in triplicate to judge the extent of variability in N gas kinetics in our experimental set up. The statistical power of the experiment resides in the controlled nature of our incubations (see ch. 2.3) which typically guarantees high reproducibility between replicates (e.g. Obia et al., 2015). Soils were homogenised and incubated as constantly stirred, temperature controlled slurries to reduce matrix effects and ensure homogeneity. Oxygen was removed effectively (data not shown) by repeated evacuation and He-washing prior to each experiment, creating a highly controlled experimental system for testing the effect of incremental biochar HTTs and doses in two contrasting soils. This design was chosen to focus on relative changes in denitrification responses induced by linear changes in biochar properties. Our cross-validated partial least squares regression (PLSR) model confirmed that there was a high

Table 2

Key properties of corn cob biochars used in this study. HTT - highest temperature treatment; BPCA:C - benzene polycarboxylic acid to carbon ratio, an indicator of aromaticity; B6CA:C – benzenehexacarboxylic acid to C ratio, an indicator of condensation; aliCH:aroCH – ratio of aliphatic to aromatic CHs measured by MIR; H:C, O:C – Elemental ratios; VM – Volatile matter; fC – Fraction of fixed carbon; Ash – Ash fraction; CEC – Cation exchange capacity; SA – Surface area. All data from Budai et al. (2014). See Table 3 for methods of determination.

HTT	BPCA:C	B6CA:C	aliCH:aroCH	H:C	O:C	N:C	VM	fC	Ash	pH	CEC	SA
°C	ratio			Molar ratio			%	%	%		cmol/kg	m^2/g
105	18.34	0.00	4.52	1.62	0.89	0.0066	81.08	17.47	1.45	5.34	14.88	1.82
372	122.16	32.76	1.56	0.80	0.27	0.0061	40.46	57.42	2.12	8.84	14.86	1.26
416	164.16	45.01	0.75	0.59	0.17	0.0056	26.38	70.46	3.16	10.07	16.21	3.58
562	167.45	61.36	0.22	0.37	0.08	0.0083	12.66	83.94	3.40	9.36	13.46	44.93
796	192.58	136.02	0.23	0.13	0.04	0.0096	6.88	88.67	4.46	9.44	5.07	27.44

degree of predictability in denitrification response by both dose and biochar HTT.

2.3. Denitrification kinetics

Soil-biochar mixtures were incubated as continuously stirred anoxic slurries in 120 ml serum flasks. Slurries were chosen to ensure full mixing of biochars with the soil, to minimize diffusional constraints and to aid equilibration of gasses between the liquid and the gaseous phase (i.e. headspace of the flasks). After washing the slurries with helium, headspace concentrations of O_2, N_2, N_2O, NO and CO_2 were measured every 5 h for 182–235 h in the peat and mineral soil, respectively, using a fully automated, temperature controlled incubation system similar to that described by Molstad et al. (2007) with modifications documented in Molstad et al. (2016). We varied the length of the incubations with the aim of allowing time for treatments with lower denitrification rates to achieve complete denitrification of soil native and added NO_3^-, as indicated by a plateau in N_2 accumulation.

The flasks were incubated in a temperature controlled water bath holding 30 flasks, continuously stirred by submersible magnetic stirrers in a water bath. The flasks were sampled every 5 h by a hypodermic needle operated by an auto-sampler (CTC PAL). For each sampling, ~1 ml of headspace gas is pumped to dedicated sampling loops of a gas chromatograph (Model 7890A, Agilent, Santa Clara, CA, USA) using a programmable peristaltic pump (Gilson minipuls3) with Marpren tubing. The GC is equipped with a 30 m PoraPLOT-U column operated at 36 °C for separating N_2O, CH_4 and CO_2 from bulk gases and a 30 m 5 Å Molsieve column operated at 50 °C for separating N_2 and O_2. Low concentrations of N_2O were quantified by an electron capture detector operated at 340 °C using $ArCH_4$ (90/10 vol%) as make up gas. CO_2, O_2, N_2 and high mixing ratios of N_2O were quantified by a thermal conductivity detector. Nitric oxide (NO) concentrations were measured by a chemoluminescence NO_x-analyzer (Model 200A, Advanced Pollution Instrumentation, San Diego, CA) coupled inline to one of the sampling loops of the GC. Headspace pressure was kept constant at ~1 atm by automatically reversing the pump after sampling and backfilling with helium. Multiple internal standard gases were included. He-dilution and O_2/N_2 leakage were evaluated in blank flasks and used to correct the gas kinetics as described by Molstad et al. (2007). Based on the observation that there was a significant early accumulation in N_2 in our flasks, an additional abiotic experiment with stirred biochar suspensions was performed to assess desorption kinetics of residual N_2 into the He-atmosphere of the headspace as a function of biochar HTT and dose. This experiment is described in detail in the supplementary information (SI Section 1). Dissolution of gas and modelled desorption of N_2 after helium-washing were modelled and subtracted from the measured N_2 accumulation (for details see SI Section 1).

2.4. Treatments

Soil equivalent to 1.5 g dry weight of peat and 2 g dry weight of mineral soil was weighed into 120 ml serum flasks equipped with magnetic stirrers. Biochar was added at increasing rates of 1, 5, 10, and 20% w/w. For the peat soil an additional treatment 30% w/w was set up because we expected that the BC effect might be masked at low doses in the carbon rich peat. After adding 30 ml of MilliQ water, the flasks were sealed with butyl rubber septa and made anoxic by repeated evacuation and He-filling (six times), while continuously stirring the slurries. 10 ml of degassed 4 mM KNO_3^- solution was added, resulting in a final concentration of 1 mM KNO_3^- (40 μmol N $flask^{-1}$). All flasks were He-washed for an additional cycle before placing them in the water bath of the incubation system which was set to 15 °C. We chose this incubation temperature as it is closer to actual soil temperature in the temperate region than room temperature. After 10 min temperature equilibration, excess He was released. Headspace gases (CO_2, O_2, NO, N_2O and N_2) were monitored every 5 h until N_2 accumulation levelled off, indicating complete conversion of NO_3^- to N_2. After termination of the incubation, the flasks were opened and slurry pH and residual NO_3^- and NO_2^- (in the mineral soil only) were measured (SI section 2), before drying the slurries to determine dry weight soil in each bottle.

2.5. Data analysis

Measured denitrification kinetics (Fig. S4 a, b) were used to calculate a number of denitrification indices (Table 3, Fig. 1), including the N_2O product ratio, $N_2O/(N_2+N_2O)$, calculated as a ratio of the integrated area under the curves for N_2O and $N_2O + N_2$ (Liu et al., 2010). We refer to this index as the Integrated Product Ratio (IPR). Since the amount of total N denitrified throughout the incubation differed between treatments, a cutoff had to be defined for calculating IPR. To account for differences in denitrification activity between the soils, the cut off for the peat was chosen at 20 μmol denitrified N, whereas the cut off for the mineral soil, which was less active, was chosen at 5 μmol denitrified N. The cut offs were chosen based on the lowest return of total μmol N denitrified among all treatments of each soil type throughout the full length of the incubation. Setting our limit in terms of μmol N denitrified, and not time, allowed us to normalise the treatments and to provide a more accurate comparison between treatments within each soil type. Other indices used were maximum denitrification (DR_{max}) calculated as the maximum rate of NO + N_2O + N_2 accumulation and the time needed since onset of anoxic incubation to obtain this maximum rate (T_{DRmax}), as well as the maximum NO, N_2O and N_2 concentrations reached during incubation, referred to as NO_{max}, N_2O_{max} and N_{2max}, respectively.

2.6. Statistical analyses

In order to examine the relationship between the indices of denitrification and biochar properties, we used PLSR (Martens, 1987). This method is not sensitive to issues of collinearity or autocorrelation and avoids arbitrary variable selection. We chose to use the biochar

Table 3

Data structure for the PLSR model including descriptions of abbreviations and analysis methods.

Data Block[a]	Variable	Units	Description	Analysis method
X01	NO_{max}	µmol N g dw^{-1}	Maximum measured N2O or NO-N accumulation	GC incubation
X02	N_2O_{max}	µmol N g dw^{-1}		
X03	N_{2max}	µmol N g dw^{-1}		
X04	IPR	Ratio	Integrated Product Ratio. This is the N_2O product ratio $[N_2O/(N_2O + N_2)]$ calculated using the integral of each curve.	
X05	$NO:N_2O$		This is the ratio of NO to N_2O calculated using the integral of each curve.	
X06	DR_{max}	µmol N g dw^{-1} hr^{-1}	This is the maximum rate measured for the total N curve.	
X07	T_{DRmax}	hr	This is the time at which the maximum rate was achieved	
Y01	VM[1]	g $flask^{-1}$	Volatile matter - ASTM method D 1762-84	ASTM method D 1762-84
Y02	Ash[1]	g $flask^{-1}$	Ash content - ASTM method D 1102	ASTM method D 1102
Y03	fC[1]	%	Fixed carbon calculated by difference between 100% and the sum of measured VM and ash contents: $\%fc_{ash-free} = 100 \times \frac{\%fc}{\%fc + \%vm}$	derived from VM and Ash content
Y04	SA[1]	m^2 $flask^{-1}$	Surface area - measured using	Brunauer–Emmett–Teller method
Y05	CEC[1]	cmol $flask^{-1}$	Cation Exchange Capacity	modified ammonium acetate compulsory displacement method
Y06	FastCpool[2]	g $flask^{-1}$	Biochar fast mineralised labile C pool	derived from a 2 pool model fitted to an oxic incubation
Y07	H:C[1]	Ratio: No scaling	Elemental ratios derived from Elemental analysis	Leco CHN1000 analyzer and coal reference material TruSpec Makro analyzer and O add-on module (Leco Corp.)
Y08	N:C[1]			
Y09	O:C[1]			
Y10	BPCA:C[3]		Ratio of total aromatic bound C to total elemental C. BPCA:C is an indicator of condensation.	Benzene polycarboxylic acid method.
Y11	B6CA:C[3]		Ratio of full 6 carbon bound to elemental C. B6CA:C is an indicator of aromaticity.	
Y12	Ali-CH:Aro-CH[3]		The ratio of aliphatic CH to Aromatic CH	derived from Mid Infrared (MIR) analysis.

[a] X block measurements were made using the incubation system and were recorded per flask. Y block measurements are biochar properties calculated on a dose per flask basis where possible. All the values and methods for the Y block variables were taken:[1]. Budai et al. (2014)[2]. Budai et al. (2016)[3]. Budai et al. (2017). Ratios were not scaled to dose.

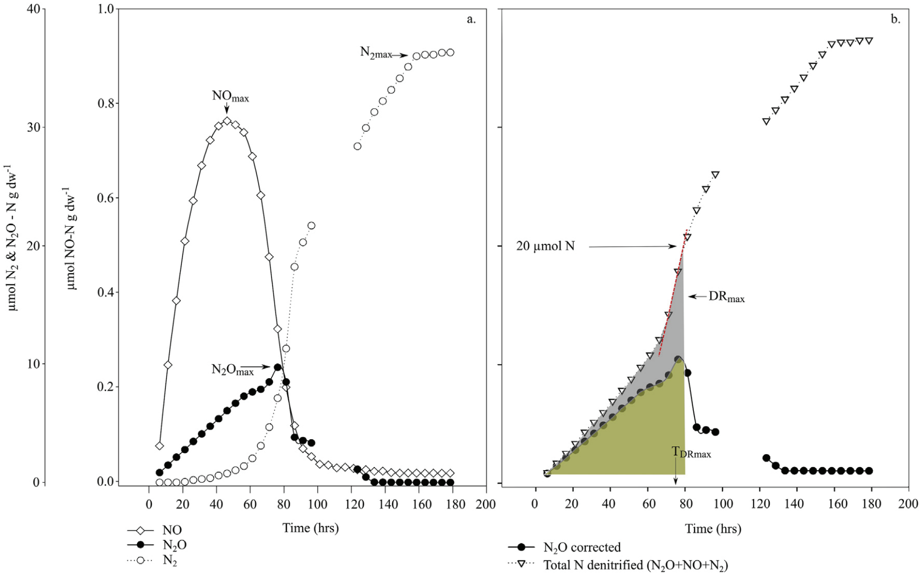

Fig. 1. Gas kinetics (a: NO, N_2O, N_2; b: N_2O, NO + N_2O + N_2) and derived denitrification parameters in peat soil BC372 10% wt/wt (single bottle values). N_2 values in Fig. 1a are corrected for sampling loss, leakage and desorption whereas the transient accumulation of the intermediates NO and N_2O are shown uncorrected. In Fig. 1b both N_2O and NO + N_2O + N_2 are corrected for sampling loss to derive the integrated product ratio (IPR) from the integrals with a cut off of 20 μmol N g dw soil^{-1} total denitrification. Denitrification parameters shown in Fig. 1a are NO_{max}, N_2O_{max} and N_{2max} and in Fig. 1b, DR_{max}, T_{DRmax} and IPR. The shading signifies the

properties as response variables and denitrification indices as independent variables, as this allowed us to examine the distribution of treatments based on denitrification indices in the X matrix without imposing the highly structured values describing the pyrolysis gradient. This was appropriate since we do not intend to use the PLSR for predicting denitrification responses, but rather for exploring correlations between denitrification indices and biochar properties. Models were first built without the control soils, before subsequently projecting the control soil samples into the model. In this way we show the relation of the control soils to the biochar treatments without the lack of biochar properties in the control soils defining the model. Model fit was judged by comparing the calibrated and validated explained variance in Y. All models were fit using the pls package in R (Mevik et al., 2015; R Core Team, 2017).

3. Results

3.1. Effect of biochar HTT

In peat, the response of the IPR to biochar varied with HTT (Fig. 2a); FS105 and BC372 strongly increased IPR at doses above 1%, BC416 had no effect, while BC562 and 796 strongly decreased IPR. Hence, the N_2O product ratio of peat displayed a marked threshold with respect to HTT in the range between 372 and 562 °C, where the effect shifted from increasing to repressing N_2O production relative to total denitrification. In the mineral soil, biochars strongly reduced IPR independent of their HTT. Only the high (20%) dose of feedstock (FS105) increased the IPR (Fig. 2d). In non-amended controls, peat had a large innate N_2O product ratio, while mineral soil produced little N_2O and had a small innate N_2O product ratio.

Biochars had little effect on the maximum denitrification rate (DR_{max}) in the carbon-rich peat soil except for the two highest doses of FS105 and BC416, which stimulated denitrification (Fig. 2b). Maximum denitrification was reached earlier with high-temperature biochars (Fig. 2c) in the acid peat soil. By contrast, denitrification in the mineral soil was stimulated by low HTT biochar, particularly by BC372, and the feedstock (Fig. 2e), without affecting the time needed to reach maximum denitrification activity (Fig. 2f).

Fig. 3 summarizes the effect of biochar addition on maximum N_2O and NO accumulation over all HTT treatments and doses. N_2O and NO accumulation was consistently reduced relative to the non-amended control when biochar produced at 562 °C and 796 °C was added to either soil, with a maximum reduction in N_2O accumulation of 89% observed in peat soil with 30% w/w BC796 and of 98% with 20% w/w BC796 in the mineral soil (Fig. 3). The mineral soil accumulated approximately ten times less N_2O than the peat soil (Fig. S4a, b). Interestingly, even the low-temperature biochar BC372 and low doses of FS105 reduced N_2O accumulation in the mineral soil, which was not the case for the peat (Fig. 3). Likewise, NO and N_2O accumulation in response to BC416 differed between soils. In peat, BC416 reduced NO accumulation but had little effect on N_2O, whereas the opposite was the case in mineral soil. BC372 and FS105 stimulated N_2O accumulation in the peat but reduced it in the mineral soil except for the 20% w/w dose of FS105. Thus, the N_2O and NO response appeared to be soil dependent for biochar produced at or below 416 °C.

3.2. Effect of biochar dose

In both soils, IPR responded strongly to biochar dose in the range of 1–5% w/w (Fig. 2a, d). Increasing the dose above 5% resulted in increasingly smaller response, irrespective of whether the effect was an increase or a decrease. Increasing the dose of biochar consistently decreased the accumulation of both NO and N_2O in the BC562 and BC796 treatments of both soils (Fig. 3 a, b). BC416 varied in its effect between the two soils, showing no dose effect on N_2O accumulation in the peat soil while showing a dose effect comparable to the high temperature chars in the mineral soil. Higher application rates of FS105 and BC372 increased NO and N_2O accumulation, particularly in the peat soil (Fig. 3

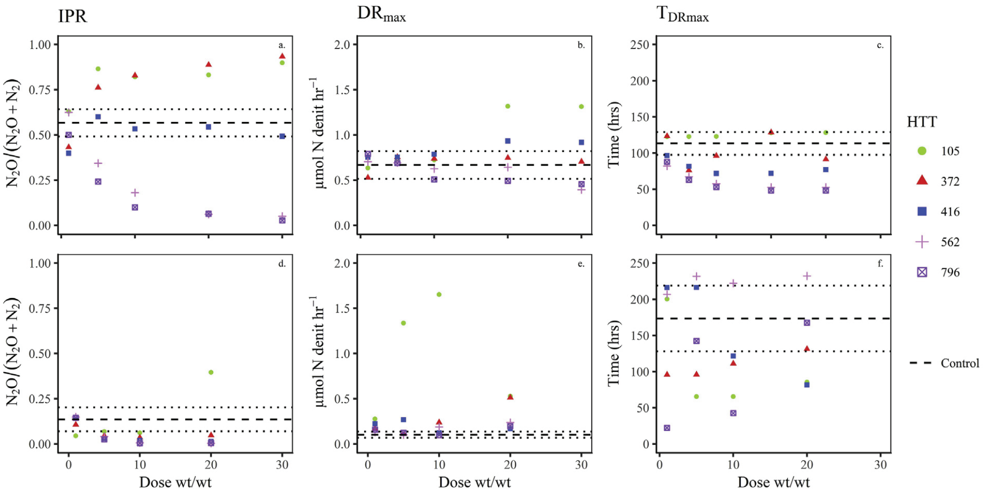

Fig. 2. Scatter plot showing selected denitrification variables (Integrated product ratio (IPR), Maximum denitrification rate (DR_{max}) and Time needed to reach maximum denitrification (T_{DRmax})) in slurries of peat (a, b, c) and mineral soil (d, e, f) amended with different corn cob HTT biochars plotted against dose. Mean values for control soils without biochar are represented along with the standard deviation (n = 3) as dotted lines.

a, b).

3.3. Relationship to BC properties

PLSR models for both soils (Fig 4a, c) confirmed the strong effect of pyrolysis temperature (HTT) on denitrification. HTT is represented by the first component in the model (Fig. 4a, component 1: X scores 77%, Y scores 60% explained variance, Fig. 3b, component 1: X scores 40%, Y scores 63% explained variance) with higher doses of BC372 and FS105 located at the left side of the plot and high temperature chars (BC416, 562 and 796) located to the right. For the peat, the second component (Fig. 4a, component 2: X scores 7%, Y scores 10% explained variance, Fig. 3b, component 2, X scores 22%, Y scores 9% explained variance) appears to represent biochar dose, with low doses located at the top and high doses located towards the bottom of the score plot. In the mineral soil, this trend was much less apparent, reflecting the variability between the two soils in the overall effect strength of dose. The higher overall explained variance in both Y and X in the first component shows that the effect of temperature treatment prevailed over the effect of dose in affecting denitrification kinetics. The central grouping of the control soils (which were subsequently projected onto the model) and the 1% dose treatments confirms that low-dose biochar treatment had little effect on denitrification kinetics since they contributed little to the variation explained by component 1 and 2. The loading plots (Fig. 4b) revealed that in the peat, all denitrification indices except for the NO:N_2O ratio were strongly positively correlated with H:C, O:C and the aliCH:aroCH ratio, and strongly negatively correlated with BPCA, B6CA, pH and SA (Fig. 4b). In the mineral soil, the correlation structure was similar, except for T_{DRmax} (Fig. 4d). FastCpool appeared to play a more significant role in the minerals soil, while the opposite was true for SA. In the peat, measurements of denitrification activity, DR_{max} and T_{DRmax}, were strongly negatively correlated to SA and pH along component 1, respectively, whereas in the less active mineral soil, DR_{max} was strongly negatively correlated to pH and less so to SA. T_{DRmax}

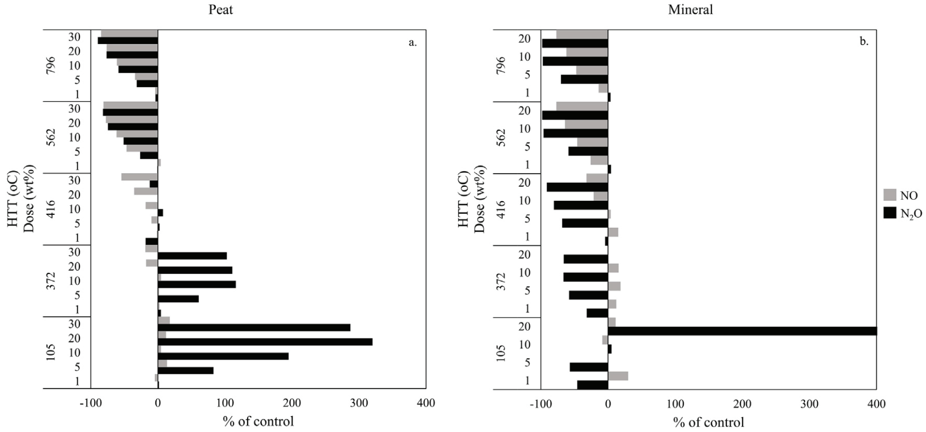

Fig. 3. Effect of biochar addition on maximum N_2O and NO accumulation in anoxic batch incubations of peat and mineral soil. The values are calculated as relative difference from the un-amended control (in %).

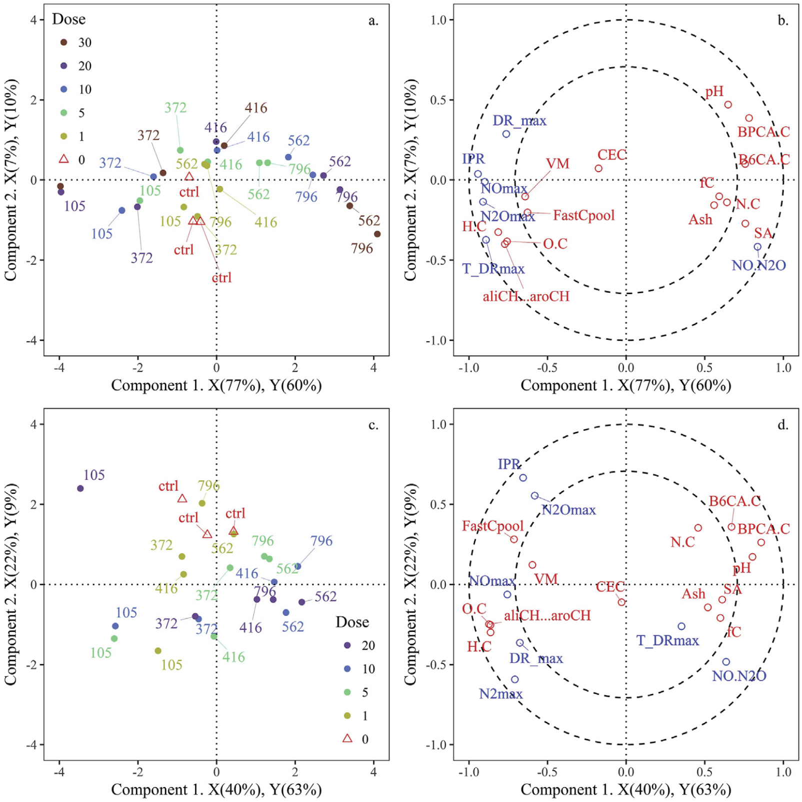

Fig. 4. PLSR models for peat (top: a & b.) and mineral soil (bottom: c & d). X scores plots (left a & c.) represent the objects/rows in matrix X and Y and show how the objects relate to one another in the multivariate space spanned by the model. X & Y correlation loading plots (right b & d) show the X (explanatory, blue) and Y (response, red) correlation loadings. The X & Y loading plot represents percent explained variance of each variable, variables within the inner circle have less than 50% of variance explained by the components, variables within the outer ring have greater than 50% variance explained by the 2 plotted components. Variables close to one another on this plot are highly positively correlated for the part of the data explained by the 2 components. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

played no role in the mineral soil owing to the lack of exponential product accumulation in this soil.

Biochar pH was highly negatively correlated with maximum NO and N_2O accumulation in both soils and positively correlated with the ratio of NO to N_2O along component 1, which increased with increasing pyrolysis temperature and dose in both soils (Fig. S7). SA, which was scaled to flask, showed a strong positive correlation with NO:N_2O in the peat, but a somewhat weaker correlation in the mineral soil. VM and CEC had little impact on the correlation structure in both soils. The FastCpool which mainly represents the large labile carbon pool in the feedstock, appeared to play a more significant role for NO and N_2O accumulation in the mineral than the peat soil.

N_{2max} was removed from the peat model since added N was completely transformed to N_2 in all treatments (Fig. S4a), i.e. reaching close to mass balance between added and recovered gaseous N. By contrast, in the mineral soil, analyses of residual NO_3^- and NO_2^- post-incubation (Fig. S3) revealed that denitrification was incomplete for treatments with high-temperature chars and low doses of BC372. Interestingly, less gaseous N was recovered with high doses of FS105 and BC372 despite complete conversion, indicating immobilization or sorption of added NO_3^--N. Therefore, N_{2max} was positively correlated with biochar properties representing C availability (FastCpool, aliCH:aroCH, O:C and H:C) and negatively with properties indicating the degree of carbonisation (B6CA:C, BPCA:C) in the mineral soil (Fig. 4d).

In the mineral soil only the 20% w/w dose of BC372 and all doses of FS105 induced exponential N_2 accumulation indicative of denitrifier growth (Fig S4b). In the peat, all biochar treatments showed exponential N_2 accumulation, which, however, differed strongly with biochar HTT (Fig. S4a). The onset of exponential production occurred earlier with high HTT chars, which was well captured by T_{DRmax}, i.e. the time needed to achieve the steepest slope of N_2 production. N_2 accumulation eventually changed to linear accumulation (Fig. S4a) suggesting that denitrifier growth became substrate limited. This change occurred earlier with high temperature chars (Fig S4a). No such linear phase in product accumulation was seen in peat soil amended with feedstock and the highest doses (20 and 30%) of BC372 (Fig. S4a).

4. Discussion

4.1. Which process dominated nitrate reduction?

We assert that the predominant NO_3^- reduction pathway in our flasks was denitrification, even though there exist a number of alternative pathways (DNRA, anammox, chemodenitrification, co-denitrification) dissipating NO_3^- under anoxic conditions. Both DNRA and anammox are favoured by high pH (Zhang et al., 2015) and are considered to be of limited significance in well drained upland soils (Schmidt et al., 2011; Ligi et al., 2015; Xi et al., 2016). Anammox, in particular, requires the accumulation of nitrite (Long et al., 2013), which only occurs in moderately acidic to alkaline soil. The mineral soil incubations accumulated considerable amounts of NO_2^- (Fig. S3) concomitant with rising pH in the slurries (Fig. S5b), however, the fact that NO_2^- accumulated at the end of the experiment suggests that NO_2^- consumption by anammox was not the dominating process. Co-denitrification (Spott et al., 2011) may have been an important process in our peat due to the abundance of organic N moieties. However, we assume that the utilisation of this additional N source would have altered the mass balance of recovered N_2-N relative to the added NO_3^--N. Since we did not see this in our incubations with the peat soil, we assume that co-denitrification was negligible. Chemodenitrification, i.e. the dismutation of protonized nitrite (HNO_2) to NO and N_2O and/or the reaction of HNO_2 with redox active compounds on mineral surfaces cannot be ruled out and is addressed later in the discussion. A study by Wankel et al. (2017), however, suggested that in the presence of high NO_3^- concentrations, bacterial and fungal denitrifiers are likely to dominate N_2O and N_2 production. For these reasons we are confident that the dominating process of NO_3^- consumption in our experiments was canonical denitrification, with minor interference from other NO_3^-/NO_2^- dissipating processes.

4.2. Biochar produced at high temperature reduces N_2O and NO emission

Accumulation of N_2O and NO was consistently reduced when corncob biochars produced at 562 °C and 796 °C were added to either soil. Our results do not allow us to define a precise HTT threshold responsible for this effect, however 416 °C appeared to be a pyrolysis temperature above which there was a neutral to supressing effect on NO and N_2O release in both soils (Fig. 2). The two biochars which reduced N_2O and NO the most were the ones with the highest degree of carbonisation as indicated by low H:C, O:C, aliCH:aroCH and high BPCA:C and B6CA:C ratios (Table 2). In a meta-analysis, Cayuela et al. (2015) found that a biochar H:C ratio < 0.3 is a good predictor for N_2O suppression. We found consistent N_2O suppression with BC562 and BC796, which had H:C values of 0.37 and 0.13, respectively, while BC416, which showed an inconsistent effect had a H:C ratio of 0.59. Therefore our results support the concept of H:C being a predictor for suppression of N_2O emissions from denitrification and extend this concept to NO emissions. Our results also suggest that there is a plateau in the mitigation potential beyond a specific HTT as evidenced by the quite similar responses to BC562 and BC796.

Pronounced NO and N_2O suppression in the presence of high temperature chars points towards several key properties involved in N_2O suppression. Carbonisation and aromaticity (BPCA:C, aliCH:aroCH) as well as condensation (B6CA:C) increase with increasing HTT and condensed polyaromatic structures of chars have been shown to carry electro-chemical properties (Klüpfel et al., 2014a), which may facilitate redox reactions taking place during denitrification (Chen et al., 2018). However, in our study, increasing degree of carbonisation also correlated positively with other properties such as ash content, pH and SA. The high correlation of SA with indicators of denitrification in the peat soil and pH in both soils suggests that pH and SA could be causally involved in N_2O suppression by biochar.

SA was negatively correlated with NO and N_2O accumulation and positively with the ratio of NO:N_2O. SA, which has been proposed as a proxy for the sorption capacity of biochar for organic compounds (Hale et al., 2016), may increase NO and N_2O reduction rates by concentrating these denitrification intermediates locally around chars thus increasing the effective concentration for the catalytic reaction (Harter et al., 2016). Interestingly, the effect of higher temperature chars in the peat soil was larger for N_2O than NO, suggesting a stronger relative effect of biochar on N_2O than NO accumulation (Fig S7). The shape of the SA response to pyrolysis temperature for our biochars differs substantially from that of H:C or pH (Budai et al., 2014), and is defined by a peak in SA at BC562 followed by a reduction at BC796. Although it has been shown that biochar can permanently sorb N_2O under anhydrous conditions (Cornelissen et al., 2013), this was probably not the case in our soil slurries as plateauing N_2-N accumulation in peat incubations indicated that N_2O-N was fully denitrified. Our results instead support the hypothesis of Harter et al. (2016), who argued that the ability of biochar to sorb N_2O transiently increases its residency time and local concentration, thereby facilitating microbial reduction.

Biochar pH appeared to be another key variable linked to NO and N_2O suppression, as indicated by the opposite position of these two variables in the PLSR loading plots (Fig. 4). Over the range of pyrolysis temperatures, the pH_{H2O} of our biochar, measured in water, plateaued at 416 °C with a value of 10.07 (Table 2). Despite highest pH in the BC416 treatment, measurements of slurry pH after 182–235 h of stirred anoxic incubation showed a strong linear correlation between pH and ash content of the biochar that increased with pyrolysis temperature through the entire range of BC pyrolysis temperatures (Fig. S6). This suggests that biochar ash contributed significantly to the observed alkalisation, likely owing its high proportion of secondary carbonates and base cations (Yuan et al., 2011). The liming effect of biochar in acidic soils can strongly reduce NO accumulation by repressing the chemical dismutation of nitrous acid (HNO_2), the protonated form of NO_2^-, to NO (Chalk and Smith, 1983). Low pH is also known to impair N_2O reductase (N_2OR), the enzyme responsible for N_2O reduction, with increasing inhibitory effects below pH 6.1 (Liu et al., 2014; Brenzinger et al., 2015). However, in our study, while the pH of the biochar strongly correlated with denitrification indices, the ash content did not (Fig. 4). This may be because the ash content can have confounding effects on other variables influencing denitrification. For instance, it has been suggested that ash can result in salting out of N_2O from solution, which would increase N_2O release (Yanai et al., 2007).

4.3. Biochar prepared at low temperature has contrasting effects on N_2O emission in mineral soil and peat

The low-temperature char (BC372) was characterized by a low degree of carbonisation and high O:C and H:C ratios, high VM and low ash content. Stimulation of N_2O emissions by low-temperature chars has been reported previously (Kammann et al., 2012; Li et al., 2013). A reanalysis of the data synthesized in Cayuela et al. (2015) shows that high H:C chars have a potential to stimulate N_2O emissions ($p < 0.01$, SI section 4). However, this effect appears to be less clear-cut than the < 0.3 threshold for N_2O suppression, suggesting that there are other, interacting factors modulating the relationship between H:C $>$ 0.3 and N_2O emission.

The contrasting effects of low temperature char (BC372) and feedstock (FS105) on N_2O accumulation in the two soils suggests that soil properties interacted with biochar in its effect on denitrification. The most obvious differences between peat and mineral soil were carbon content (53.0 vs 2.8%), C/N ratio (29.5 vs. 9.8), CEC (1480 vs. 51 cmol kg^{-1}) and pH_{H2O} (5.1 vs 5.9). Surprisingly, low-temperature char and feedstock increased N_2O accumulation in the carbon-rich peat, which supported high denitrification rates, indicating ample decomposable carbon. One would expect that adding low-temperature char and feedstock, with their relatively large pool of readily decomposable carbon, to this carbon rich peat would have little or no effect on denitrification and its product stoichiometry. Studies have suggested that adding labile C to a system with limited biologically available carbon would increase the reductant-to-oxidant ratio (DOC:NO_3^-), which should result in more complete denitrification (Senbayram et al., 2012). This mechanism could explain the observed kinetics in the mineral soil where low temperature char and feedstock caused an increase in total denitrification (Fig S4b, S3) accompanied by an overall reduction in N_2O accumulation (Fig. 3b). A closer inspection of the N_2 kinetics of peat revealed that the FS105 and BC372 treatments accumulated N_2 much slower than the treatments with high-temperature chars (Fig. S4b). Accordingly, T_{DRmax}, the time needed to express maximum denitrification activity, was larger and positively correlated with indices of low carbonisation degree (Fig. 4b). While the faster increase in denitrification activity with high-temperature chars may be explained by their stronger alkalizing effect (Fig. S5), it is unclear which properties of low-temperature biochar and feedstock caused this delay. Acid peat soils are known to harbour denitrifier communities with low taxonomic diversity and hence limited metabolic versatility (Palmer et al., 2010; Braker et al., 2012; Dörsch et al., 2012). Addition of allochthonous C-sources, in the form of dried corn cob or its low-temperature pyrolysis product, to anoxic incubations may have triggered growth of competing functional groups (e.g. fermenters). This may have initially repressed denitrifier activity, until denitrifier community composition changed (e.g. Brenzinger et al., 2015) and supported exponential N_2 accumulation with high DR_{max} values and rapid N_2O uptake. We therefore tentatively attribute the N_2O stimulating effect of low-temperature corncob biochar and its feedstock to some unidentified disruption of initial denitrification activity resulting in transiently incomplete denitrification.

4.4. Biochar and denitrification: which biochar properties matter?

The significant variables for explaining the N_2O mitigation effect of biochar in our study were carbonisation indices, pH and SA (Fig. 4 b, d). Carbonisation indices encapsulate concurrent changes in biochar properties: 1) disappearance of labile organic carbon with increasing temperature, and 2) formation and condensation of aromatic structures with increasing temperatures. This implies that one must consider the effects of both labile organic carbon structures at low pyrolysis temperature and condensed aromatic sheet formation at higher temperature when assessing potential biochar effects on denitrification.

Aromatic structures of chars formed at higher pyrolysis temperature have been shown to alter the electro-chemical properties of biochar (Klüpfel et al., 2014a) which can mediate redox reactions (Kappler et al., 2014; Chen et al., 2018). Our experiment does not provide direct evidence for this effect, but the more efficient denitrification, represented by smaller T_{DRmax} and lower accumulation of intermediates, could be due to redox reactions mediated directly by the biochar. In a peat soil, however, which contains abundant redox active components (Klüpfel et al., 2014b), it is unlikely that the addition of biochar would have a measurable impact on these processes.

The effect of pH on heterotrophic denitrification is well established (as reviewed in Blum et al., 2018). pH affects not only the accumulation of intermediates (Kappelmeyer et al., 2003) but low pH is also well documented to inhibit the reduction of N_2O to N_2 (Šimek and Cooper, 2002; Bakken et al., 2012). Low pH does not affect the transcription of *nosZ*, the gene encoding for N_2O reductase, but its functioning appears to be impaired post-transcriptionally (Bergaust et al., 2010). The pH of both of our soils was lower than the pH threshold of 6.1 for fully functional N_2O reductase proposed by Liu et al. (2010) and Brenzinger et al. (2015), i.e. pH 5.86 for the mineral soil and 5.08 for the peat (Table 1). However, the pH of the anoxic slurries increased as denitrification progressed, surpassing this threshold (Fig. S5). The peat was more buffered, with a higher CEC (Table 1), than the mineral soil (Fig. S6), which probably explains why the pH in biochar treatments of the peat soil was more highly correlated with IPR and T_{DRmax} and with the total accumulation of intermediates, i.e. NO_{max} and N_2O_{max}, (Fig. 4 b). The higher buffering capacity of the peat also resulted in a more progressive denitrification response to pH over the full range of dose (Fig. 3). The strong negative correlation between T_{DRmax} and pH (Fig. 4b) shows that biochar accelerated the induction of a measurable N_2O reduction.

Biochar SA is an indicator for the sorption capacity of biochar (Hale et al., 2015) and is a result of the concurrent loss of amorphous carbon and the development of graphitic structures and highly reduced surface functional groups. There are several potential mechanisms by which biochar SA could affect denitrification. Cornelissen et al. (2013) proposed permanent sorption of N_2O to biochar surfaces. Others have suggested that biochar can sorb DOC, reducing access to electron donors (Lu et al., 2014). Because we see no effect of high SA biochar on the recovery of added N, our results support neither permanent sorption of N_2O nor reduced access to DOC as mechanisms. By contrast, our results support the hypothesis of more complete denitrification due to increased residency time of N_2O on or near biochar surfaces through temporary sorption (Harter et al., 2016). Along with the other mechanisms we have discussed, such as pH and carbonisation degree, this could explain the positive correlation we observed between NO and N_2O suppression and SA of the biochars (Fig. 4b).

In summary, we used a well-characterized biochar temperature series with continuously scaled properties in standardized denitrification assays to examine which biochar properties are responsible for the observed effect of biochar on N_2O emissions from denitrification. Our results suggest that biochar effects on N_2O emissions from denitrification are variable, or even contrasting, depending on which soils are used. Biochar from a single feedstock type can shift from stimulating N_2O emissions to reducing them over a relatively small range of HTT, highlighting that the N_2O effect of biochar is likely not caused by a single property of the biochar. We further show that biochar is interacting not only with the final reduction step of denitrification but may also impact total denitrification.

Contrary to our highly standardized experimental design, environmental conditions in bulk soil vary substantially in time and space. *In situ* N_2O emissions are highly variable in time, driven by events such as fertilization, rewetting, tillage or freeze-thaw. In these conditions periods of high emissions can last over several days and are likely driven by denitrification (Flessa et al., 1995). While the effect of biochar on event-driven N_2O emissions is largely unknown (Edwards et al., 2018), our study focuses primarily on denitrifier response to longer lasting anoxia in the presence of biochar. Our study shows how biochar interacts with denitrification and potentially lowers the N_2O product ratio under those conditions. We demonstrate a link between biochar properties and denitrification functioning for one specific corncob feedstock. We are confident that our results with corncob biochar are relevant for a range of other biochars, as we have shown previously that corncob biochar is comparable in chemical and physical properties to those produced from other grass feedstocks over wide ranges of pyrolysis temperature (Budai et al., 2014, 2017). However, key response variables highlighted in our study, such as SA and pH, can be manipulated not only through feedstock selection but also through post-processing of biochar products (Chintala et al., 2013; Rajapaksha et al., 2016). Because substantial reduction of N_2O emission from agricultural soils is needed, future investigations should specifically target the effects of biochar-property enhancement, thereby supporting the transition from mechanistic understanding to pilot implementation.

Declaration of interests

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.soilbio.2019.04.018.

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Supplementary Information

Biochar and denitrification: Examining the effect of a biochar temperature series on the kinetics of gaseous N turnover. Which properties matter?

Simon Weldon [1,3*], Daniel P. Rasse [1], Alice Budai [1], Oliver Tomic [2], Peter Dörsch [3]

[1]Department of Soil Quality and Climate Change, Norwegian institute of Bioeconomy Research, NIBO, Ås, Norway

[2]Faculty of Science and Technology, Norwegian University of Life Sciences, NMBU, Ås, Norway

[3]Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, NMBU, Ås, Norway

Contents

1. Correcting for desorption and dissolution of N_2

Denitrification assays rely on the quantification of gaseous denitrification products. Traditionally, acetylene (C_2H_2) has been used to block N_2O reductase, which allows the quantification of N_2O as the final denitrification product, thereby circumventing problems with high N_2 backgrounds, contamination with atmospheric N_2 and poor sensitivity of detectors for N_2. However, the acetylene method cannot be used to study denitrification kinetics, i.e. the sequential production and consumption of denitrification products, since C_2H_2 catalyses the autoxidation of nitric oxide (NO) in the presence of small amounts of oxygen (Bollmann and Conrad, 1997; Nadeem et al., 2013) and blocks the reduction of N_2O to N_2 (Yoshinari and Knowles, 1976). Moreover, C_2H_2 may potentially interfere with the biochar effect on denitrification, as it resembles inhibitory compounds present in the biochar (Spokas et al., 2010; Spokas et al., 2011).

1.1 Abiotic experiment

In this study, we therefore chose to directly quantify NO, N_2O and N_2 in stirred anoxic batch incubations of soil slurries under He- atmosphere. To remove O_2 and N_2 efficiently, the incubation bottles were evacuated and purged five times with He 5.0, while stirring the slurries vigorously (450 rpm) in an automated manifold. Each cycle consisted of 280 s evacuation followed by 40 s He purging, leaving He overpressure in the bottles, which was released after equilibrating the bottles to the temperature of the water bath used for subsequent incubation. Contamination with atmospheric N during sampling and sample transfer was evaluated and corrected for based on He-filled dry bottles, which were included as samples in every experiment. Average contamination was 9 ± 6 ppm per injection (in 120 ml).

To explore desporption kinetics of residual N_2 from biochar after He-washing, we ran a controlled abiotic experiment. This experiment mimicked the experimental setup used for the soil incubation (4-hourly monitoring of N_2, N_2O, NO, CO_2 and O_2 after He washing at 15°C), but did not contain soil. Increasing doses of 276, 552 and 828 mg biochar from the temperature series were added to 30 ml of sterilised deionised MilliQ water in 120 ml serum bottle. The doses corresponded to the 10, 20 and 30% wt/wt treatments of the peat. The biochar was not sterilised because to avoid structural changes. Desoption curves are shown in figure S1.

1.2 Modelling abiotic N_2 accumulation

In order to capture abiotic N_2 desorption and distinguish it from biotic N_2 production in the soil experiments, we fitted a simple exponential rise to maximum model to the accumulation of desorbed and dissolved N_2 into the headspace (eq. S1 and fig. S1).

$$y = a(1 - e^{-bx}) \qquad \text{eq. S1}$$

Examining the fitted constants of the model, we found that the maximum amount of desorbed N_2 depended on biochar HTT (Tab. S1), whereas the effect of treatment temperature on the desorption rate was less clear. Recognising that the maximum N_2 desorbed (represented by the model coefficient 'a') would be both treatment and probably flask specific (depending on leaks from the atmosphere), we decided to set the rate coefficient 'b' while fitting the parameter 'a' for each bottle, when correcting for abiotic N_2 accumulation in our soil experiments. The rate coefficient 'b' was set to the average of the abiotic experiment, with the exception of BC796 which revealed a markedly higher desorption coefficient (Tab. S1).

Table S1: Regression coefficients for eq. S1 obtained in abiotic, stirred incubations with biochar dispersed in 30 ml MilliQ water. Each biochar was incubated with three doses, 1: 276 mg, 2: 552 mg, 3: 828 mg. All coefficients had a good fit to the data ($p < 0.0001$)

Biochar treatment	a	b
105_1	3.27	0.02
105_2	3.01	0.03
105_3	3.68	0.04
372_1	3.27	0.04
372_2	7.45	0.02
372_3	16.73	0.01
416_1	3.67	0.04
416_2	7.72	0.03
416_3	4.50	0.06
562_1	3.02	0.05
562_2	4.39	0.04
562_3	3.93	0.06
mean	**5.39**	**0.04**
standard deviation	**3.74**	**0.02**
796_1	12.76	0.02
796_2	12.04	0.09
796_3	13.99	0.09
mean	**12.93**	**0.07**
standard deviation	**0.81**	**0.03**

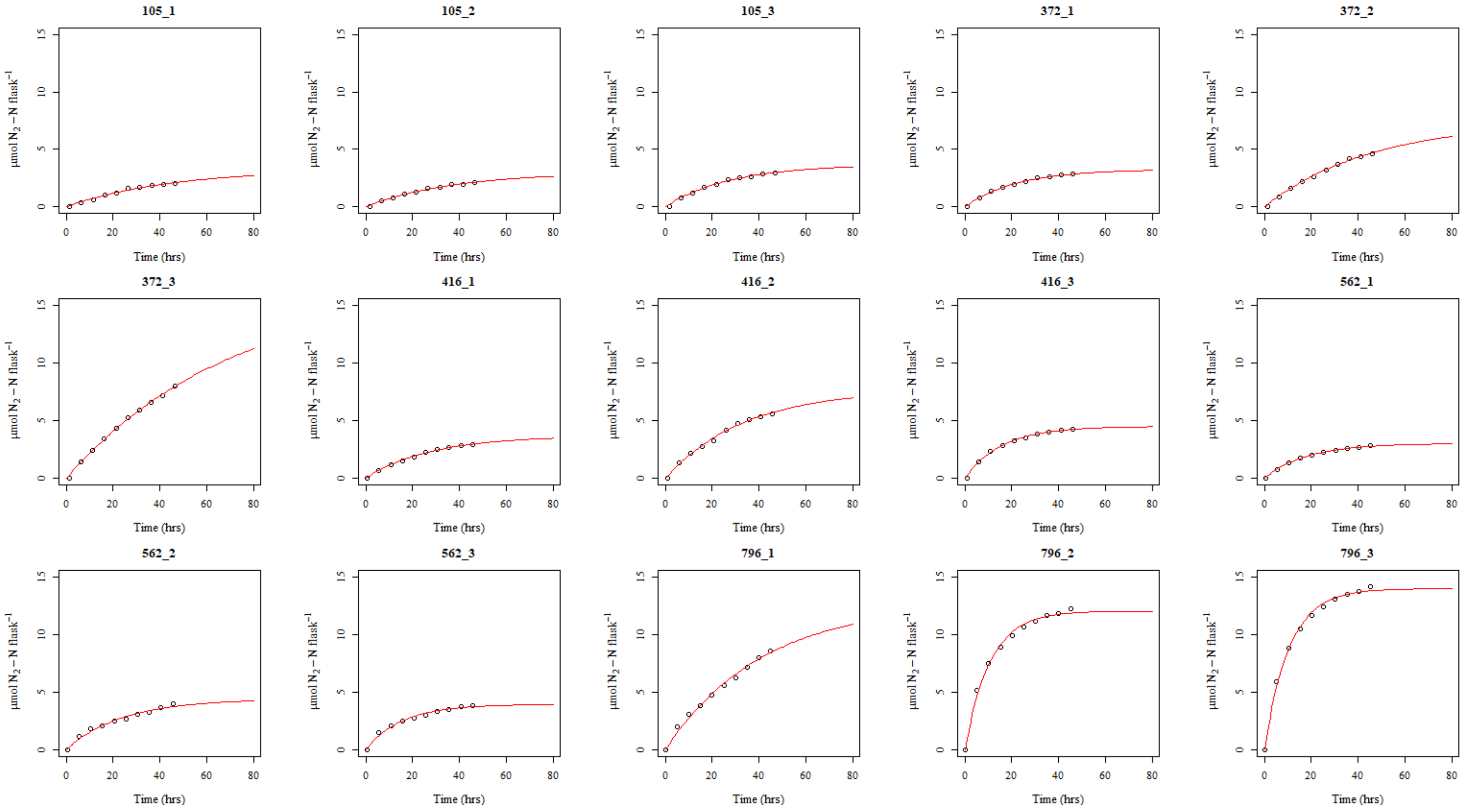

Fig S1. N_2 accumulation in the headspace after He-washing biochar slurries in sterile 120 ml serum bottles. Bottles were stirred continuously at 400 rpm to facilitate gaseous equilibration between slurry and headspace. Figure titles refer to the HTT treatment of the biochar and numbers 1-3 denote the increasing dose of biochar, 276, 552 and 828 mg per 30 ml MilliQ water, respectively. The red line represents the fitted model according to eq. R1.

1.3 Correcting for abiotic N_2 accumulation

To correct for abiotic N_2 accumulation in the soil experiments, the first five sampling points where used to fit the model (eq. S1), assuming that biotic N_2 production (i.e. denitrification) is negligible after the onset of anoxia (cf. Betlach and Tiedje, 1981). Modelled desorption curves for individual flasks are shown in figures S2 a, b. The modelled cumulative abiotic N_2 production was then subtracted from the total measured N_2 accumulation in the soil experiment, before calculating N_2-related denitrification parameters (N_{2max}, IPR, DR_{max})

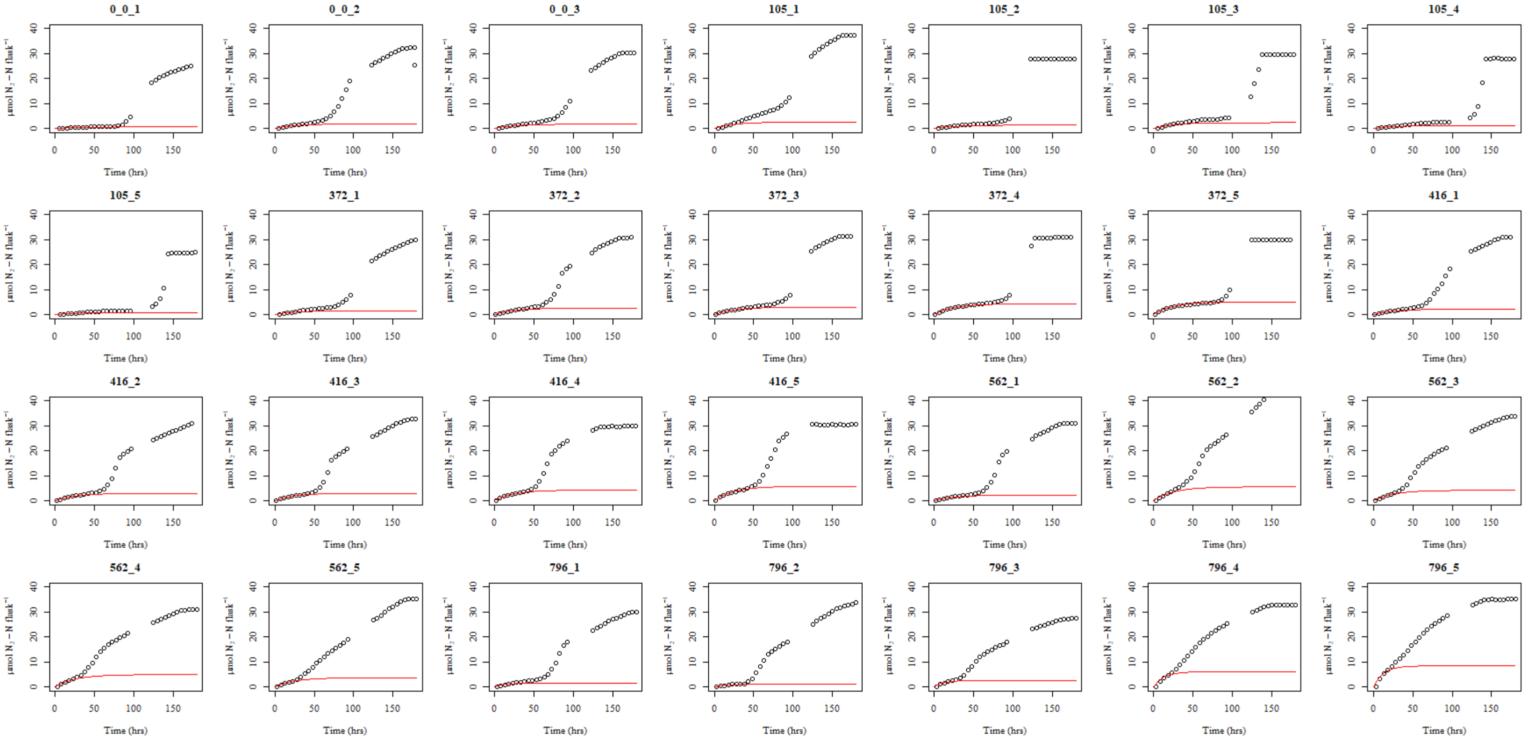

Fig S2a. Peat – Measured total N$_2$ accumulation (open dots) and modelled cumulative N$_2$ desorption (red line). Figure titles refer to HTT and dose (represented as a value between 1 and 5). The value 0 represents the control treatment without biochar amendment.

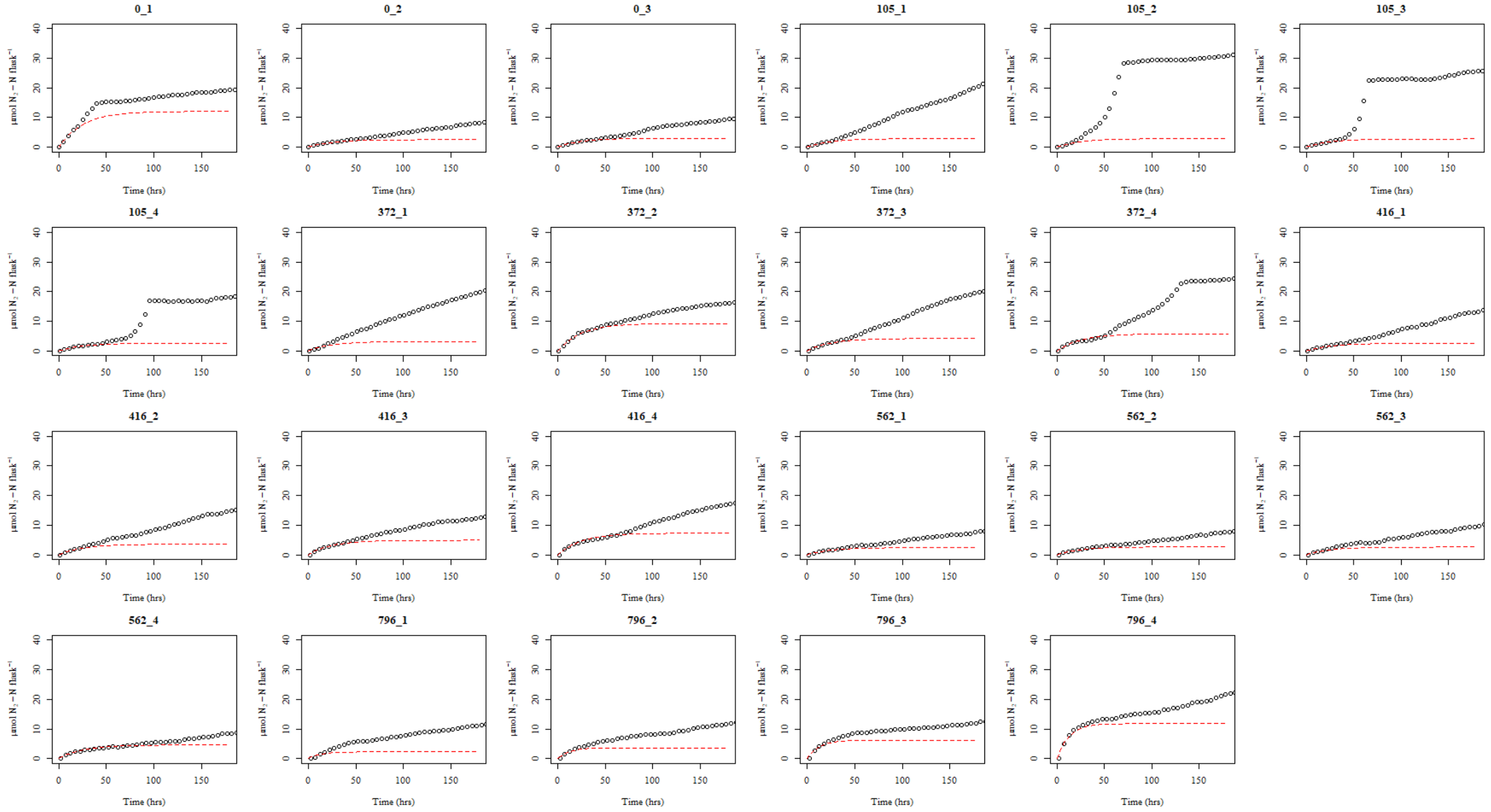

Fig S2b. Mineral soil - Measured total N_2 accumulation (open dots) and modelled cumulative N_2 desorption (red line). Figure titles refer to HTT and dose (represented as a value between 1 and 5). The value 0 represents the control treatment without biochar amendment

2. Measuring residual NO_3^- and NO_2^-

Recovery of gaseous N in the mineral soil incubations was small, indicating week denitrification activity in this soil. We therefore subsampled a selection of 3 flasks from each biochar HTT post-experimentally to quantify residual NO_3^- and NO_2^-. Supernatant (1 ml) was removed from each bottle and immediately centrifuged at 20 000 G and 4°C for 20 minutes in a micro-centrifuge. 500 µl of the clear supernatant was transferred to a clean Eppendorf cuvette and kept frozen prior to analysis within two days.

NO_3^- and NO_2^- were measured by chemiluminescence after conversion to nitric oxide (NO). For this, 10 µL of sample was injected into a purging device reducing NO_2^- or NO_3^-+NO_2^- (depending on reducing agent and temperature) instantaneously to NO, which is continuously transported by a stream of Ar to a Sievers NO Analyzer 280i (NOA, GE Analytical Instruments). The integrated NO peaks were used to estimate NO_2^- or NO_3^-+NO_2^- in the injected sample against known standards (0.1, 1 and 10mM KNO_3 for NO_3^- and NO_2^-). The reducing agents and temperatures were 50 mM vanadium chloride (III) in 1M hydrochloric acid at 90°C for NO_3^-+NO_2^- and 1% w/w NaI in 50% acetic acid at room temperature for NO_2^-. All samples were measured in duplicate. All samples were subsampled twice; where there were large deviations in reading from one sample to the next, a 3rd replicate was taken. A summary of recovered NO_3^- and NO_2^- is presented in figure S3 and compared to N_2 recovery.

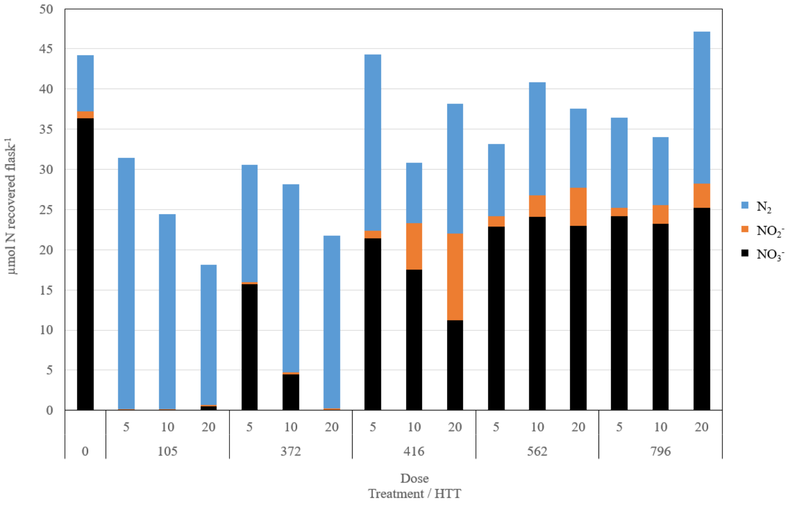

Fig S3. Recovery of mineral and gaseous N for the flasks with mineral soil. The 1% treatment was not measured.

3. Supplementary Figures

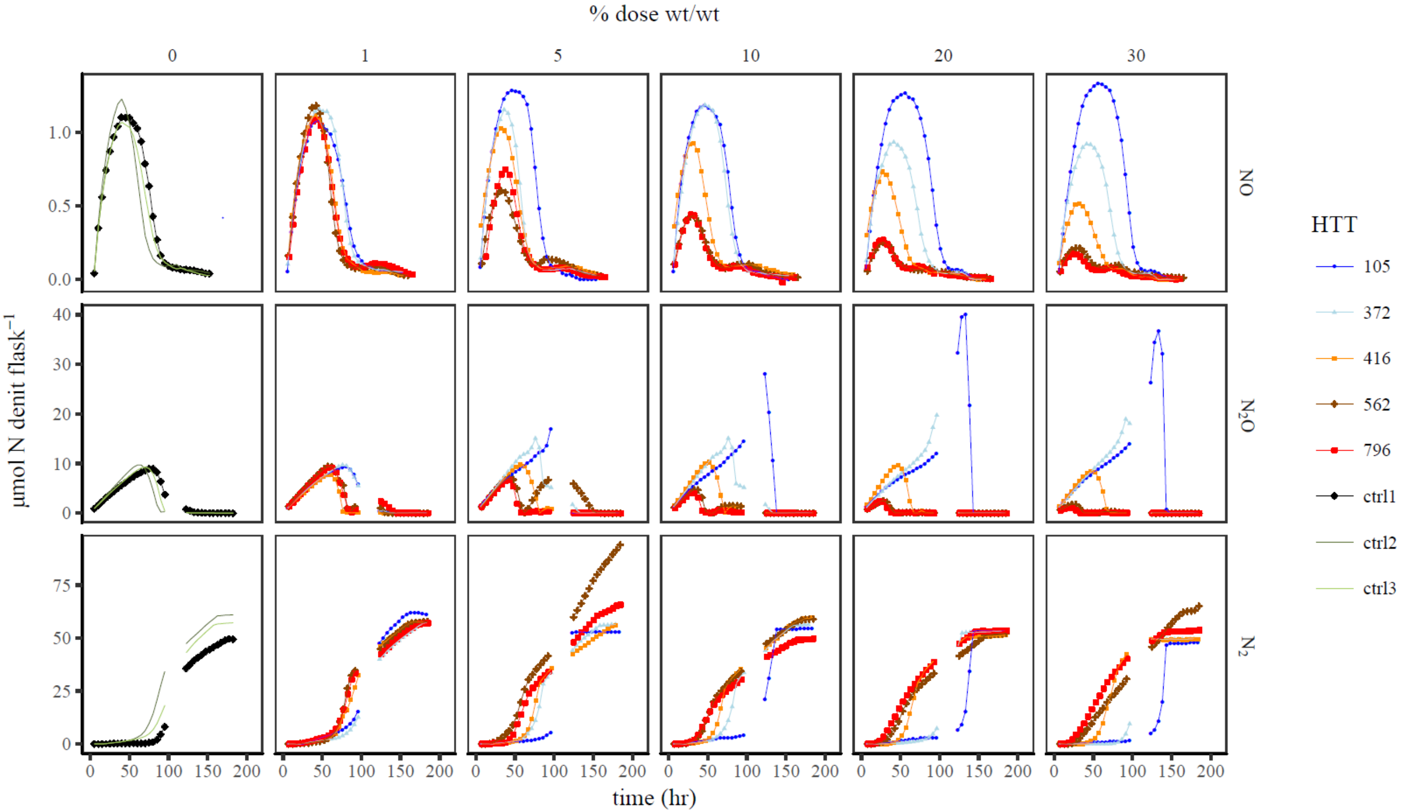

Fig S4 a. Gas kinetics for peat. N_2 values are corrected for leakage and desorption.

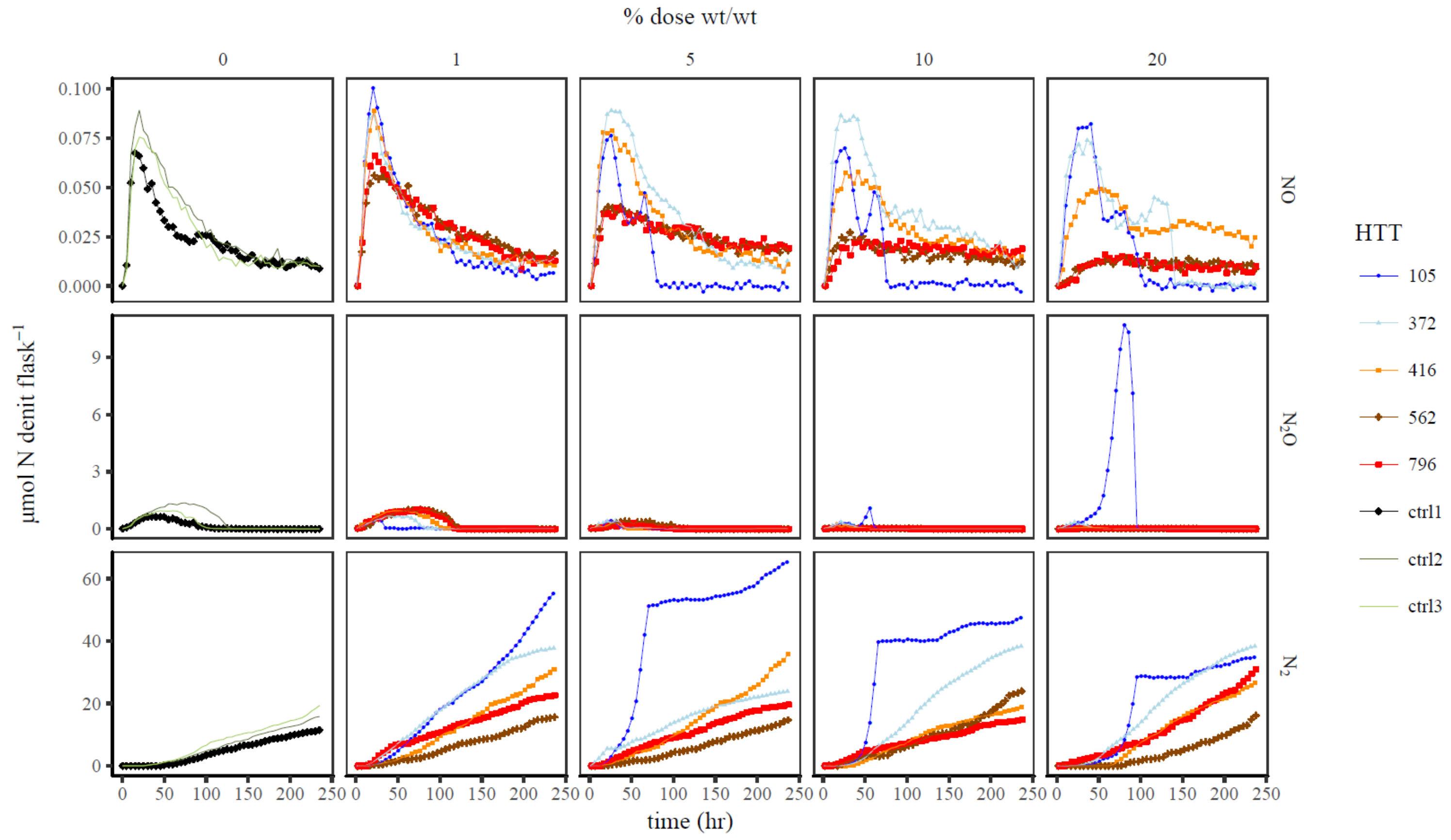

Fig S4 b. Gas kinetics for mineral soil. N_2 values are corrected for leakage and desorption.

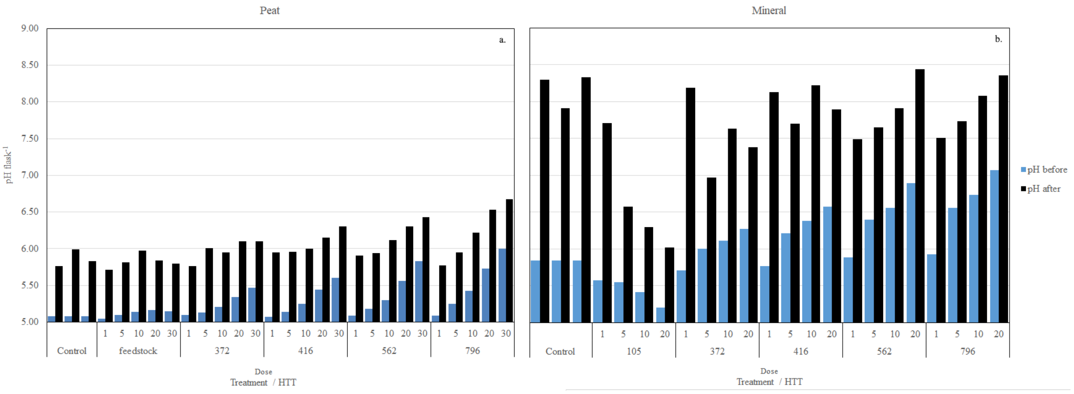

Figure S5. Bar plot of pH measured before and after the incubation for (a) peat and (b) mineral soil.

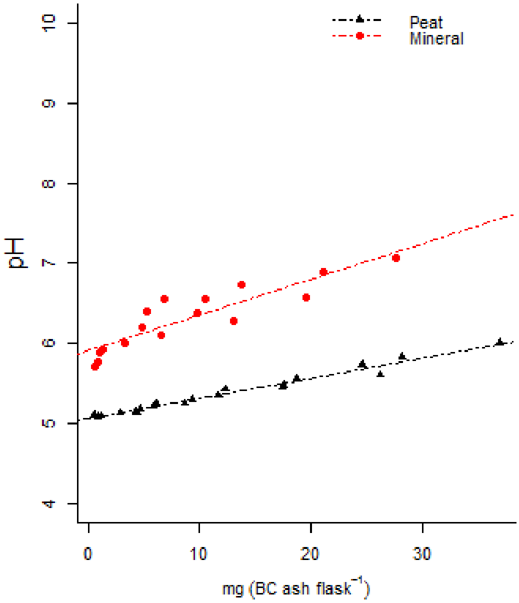

Figure S6. Scatter plot and linear regression of pH values measured in biochar amended soil slurries before incubation and ash content of the biochar. Shown are the complete range of biochar and biochar doses for mineral and peat soil excluding control and feedstock treatments (Linear fit: Peat R^2 0.98; Mineral soil $R^2 = 0.81$).

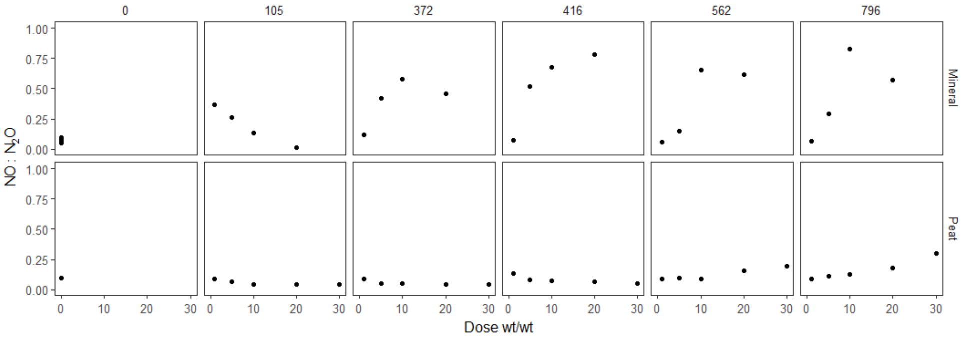

Fig S7. NO:N_2O ratio plotted by dose and HTT

4. Analysis of meta data from Cayuela et al 2014; 2015

The meta data available in the supplementary material from Cayuela et al. (2015) were used to further explore whether stimulation of N_2O emission by biochar is a function of the biochar's H:C ratio. A grouping variable was created to differentiate between biochar that increased N_2O emission compared to the control (stim) and biochars that reduced N_2O emission compared to control (inhib). A type II ANOVA was used to test the significance of the relationship while controlling for unbalanced design due to differing numbers of measurements in each group.

Type II anova

	Df	Sum Sq	Mean Sq	F value	Pr(>F)	
BCeffect	1	0.316	0.31608	5.673	0.0183	*
Residuals	172	9.583	0.05572			

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Paper II

Co-composting of biogas digestate and garden waste with biochar: Effect on greenhouse gas production and fertilizer value of the matured compost

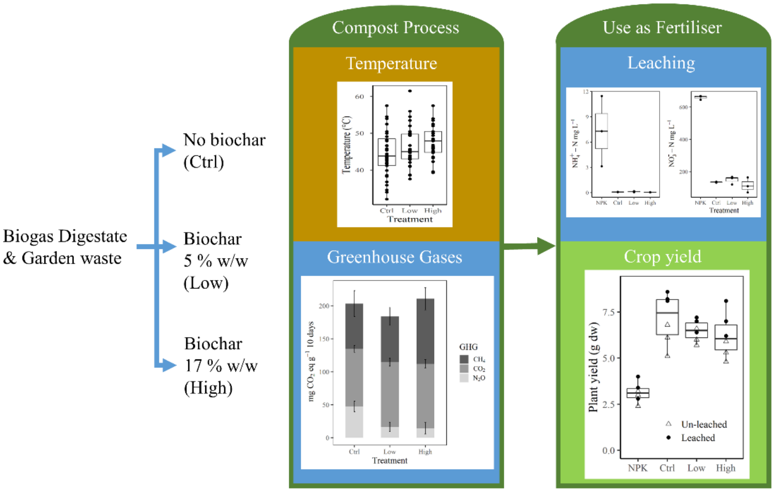
Simon Weldon[1,2*], Pierre-Adrien Rivier[2], Erik J. Joner[2], Claire Coutris[2], Alice Budai[2]

[1]Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, NMBU, 1430 Ås, Norway

[2]Norwegian Institute of Bioeconomy Research (NIBIO), Division of Environment and Natural Resources, Høgskoleveien 7, 1432 Ås, Norway

[*]Corresponding author: simon.weldon@nibio.no

Graphical Abstract



Abstract

Biogas digestate is a nitrogen (N) rich waste product that has potential for application to soil as a fertilizer. Composting of digestate is recognized as an effective step to reduce potentially negative consequences of digestate application to soils. However, the structure of the digestate and the high N content can hinder effective composting. Biochar, which can be produced through the pyrolysis of waste biomass, has shown potential to improve compost structure and increase N retention in soils. We studied biochar effects on the composting process, including greenhouse gas emissions, and the fertilizer value of the compost product including nutrient content, leachability and plant growth. The high Biochar dose (17% w/w) had a significantly positive effect on the maximum temperature and appeared to improve temperature stability during composting with less variability between replicates. Biochar addition reduced cumulative N_2O emission by 65-70 %, but had no significant effect on CO_2 and CH_4 emission. Biochar did not contribute to greater retention of nitrogen (N) contained in the digestate, but had a dilution effect on both N content and mineral nutrients. Fertilisation with compost enhanced plant growth and nutrient retention in soil compared to mineral fertilisation (NPK), but biochar had no additional effects on these parameters. Our results show that biochar improves the composting of digestate with no subsequent negative effects on plants.

Keywords: biochar fertilizer, nutrient leaching, nutrient availability, carbon storage, methane.

1 Introduction

Recycling of organic wastes using anaerobic digestion is an increasingly important strategy to derive energy and organic products from resources that are otherwise underutilized (Holm-Nielsen et al., 2009). One of the key challenges with anaerobic digestion is the production of digestate, which is a nitrogen (N) rich waste product. Direct application of digestate to land can be problematic because it may contain phytotoxic compounds, has a strong odor and may require sterilization (Alburquerque et al., 2012; Bustamante et al., 2012; Tigini et al., 2016; Walker et al., 2009). For this reason, dewatering and composting has been proposed as a method to treat digestate prior to use as a fertilizer (Bustamante et al., 2012). However, composting of dewatered digestate is difficult due to the physical properties of the digestate, which can result in anaerobic conditions with enhanced emissions of greenhouse gases (GHG) and a slow composting process (Walker et al., 2009).

A solution to mitigate this effect of poor feedstock structure is to add a bulking agent (Maulini-Duran et al., 2014). Traditionally this would include products such as wood chip, which would provide structure and porosity to the compost. In recent years there has been increasing interest in the application of biochar to the composting process. Biochar is produced by the pyrolysis of organic feedstocks and is a highly stable carbon form with a high porosity and relatively high surface area (Batista et al., 2018; Budai et al., 2014). The resistance of biochar to decomposition in soil, and its potential value as a C mitigation tool is the primary reason for the significant interest biochar has attracted over the last two decades (Lehmann, 2007). During that time, biochar research has also identified co-benefits of biochar that make it suited for application to soils to increase plant yield (Jeffery et al., 2011), reduce GHG emissions and improve soil quality and nutrient retention (Borchard et al., 2019). These properties have also raised interest in the application of biochar as an additive to compost (Akdeniz, 2019; Sanchez-Monedero et al., 2018; Wu et al., 2017; Xiao et al., 2017).

Biochar has been shown to improve the composting process through reductions in GHG emissions (Agyarko-Mintah et al., 2017), reductions in maturation time and increasing temperature development and stability (Mao et al., 2018; Waqas et al., 2018). Biochar addition has also been shown to have a direct impact on both microbial abundance and diversity (Wei et al., 2014). The mechanisms proposed to explain this effect range from pH effects (Awasthi et al., 2016), increased oxygen infiltration (Awasthi et al., 2017b; Liu et al., 2017), facilitation of redox processes (Agyarko-Mintah et al., 2017) and sorption of substrates as either nutrients (Chen et al., 2010) or gas (Cornelissen et al., 2013). There is also evidence that biochar can have a positive effect on the final compost product, increasing its value as a fertilizer through positive effects on plant yields and nutrient retention (Kammann et al., 2015). However, across the literature, results are variable with both positive, neutral and negative effects of compost biochar mixes on the yield effect of the final product (reviewed by Wang et al. (2019)). Previous studies have suggested that high applications of biochar (>10 % w/v) can have negative consequences for composting process, leading to increased water loss and heat dissipation (Liu et al., 2017). Others have argued that application rates above 20 % (both w/w and w/v) are generally harmful to the composting process (Liu et al., 2017; Xiao et al., 2017).

To our knowledge no one has yet assessed the effect of biochar amendment on both the composting process with digestate and the function of the final product as a fertilizer. Such studies are important in order to identify potential synergies and tradeoffs. We examined the effect of biochar amendments at both low (5 % w/w) and high (17 % w/w) application rate. We used a closed batch composting system consisting of modified consumer grade composting tumblers. The setup allowed for headspace sampling for quantification of GHG and treatment-dependent generation of heat in the individual chambers, mimicking the natural temperature progression encountered when composting larger volumes. We tested the fertilizer properties of the final composts (without and with biochar) against a NPK mineral fertilizer treatment in a plant growth experiment with spring onions, using a loamy soil with low soil organic carbon. Due to the low carbon content of the soil, we also tested the impact of a leaching event on both plant yield and the loss of nutrients.

We hypothesized that, 1) Biochar addition to composting would improve the key measurables of the composting process, increasing maximum temperature and reducing GHG production. 2) Co-composting with biochar would result in a product that has higher nutrient content. 3) Biochar amendment would further improve the retention of the nutrients in the compost product after addition to soil. 4) Nutrients stabilized by biochar are plant available, and the presence of biochar does not reduce plant yield. And 5) The effects on composting process and fertilizer value of the final product would depend on biochar application rate.

2 Materials and methods

2.1 Input materials for composting

Biogas digestate, garden waste and biochar were used in the composting experiment. Dewatered biogas digestate (dry matter content 29 %) was collected from a biogas plant at Vormsund, Norway, using food waste as substrate for biogas production. The digestate was used in the experiment the day following its sampling at the biogas plant. Characteristics of the digestate are presented in Table 1. Fresh garden waste was collected at a municipal waste facility at Bølstad, Southern Norway, where it had been coarsely ground and sieved to remove large twigs and branches. This material was used immediately after collection to avoid spontaneous composting prior to mixing of test materials. The garden waste had a dry matter content of 50 %. Biochar used in this experiment was made from mixed wood and pyrolyzed by Novo Carbo using Pyreg technology at 550 °C Highest Heating Temperature (HTT) (detailed characterization in Table S1). It had a dry matter content of 58 % upon addition to the experiment.

Each experimental unit (compost chamber) received a mixture of garden waste, digestate and biochar, in the following proportions: 40 L freshly ground garden waste (9 kg fresh weight (fw), 4.5 kg dry weight (dw)), 20 L biogas digestate (12.5 kg fw, 3.6 kg dw), and either 5 % (0.70 kg fw, to 0.41 kg dw) or 17 % (2.79 kg fw, 1.62 kg dw) biochar by dry weight. A control without biochar was also included in the experiment.

Table 1. Key properties of biogas digestate and biochar.

	Digestate	Biochar
pH (H_2O)	8.9	8.0
Loss on ignition (%)	71.1	83.9
Density (g L^{-1})	n/a	262
Dry matter content (%)	27	58
Total Nitrogen (g kg^{-1} dw)	49.6	1.2
Phosphorus (P-AL) (mg 100 g^{-1} dw)	710	200
Potassium (K-AL) (mg 100 g^{-1} dw)	384	800

2.2 Experimental set-up of the composting experiment

The composting experiment was conducted in rotating composting units (tumblers), each consisting of two separate 135 L chambers with insulated walls (Joraform 270, Sweden). The chamber side walls each had two sections of 10 cm^2 aeration holes. Three replicate chambers were used for the 5 % and 17 % biochar treatments, and four replicate chambers for the control treatment without biochar, using in total 10 chambers from 5 tumblers. The reason for the additional control chamber was to avoid having a tumbler with only one filled chamber, and potentially different neighbor effects.

The experiment was started on June 20th 2019 (day 0), when ambient temperatures varied from 14-22 °C, and temperatures inside the chambers were continuously recorded using Decagon's ECH2O dataloggers. Greenhouse gases were monitored daily for 10 days. After the initial GHG measurement period, composts were left to mature for four months in the tumblers, turning them once every second week during the whole period for mixing and aeration. At the end of the maturation phase, composts were individually homogenized, sieved at 4 mm to remove any remaining twigs, and representative samples of each compost were analyzed for physical and chemical parameters by a commercial analytical laboratory (ALS Global) using ISO methods. The mature composts were then stored at 4 °C in the dark for 5 months until use in the plant growth experiment.

2.3 GHG measurement

Based on the results of a preliminary experiment, gas sampling was optimized to achieve a representative and reproducible sampling of the compost chambers. First, temperature sensors were removed, and all tumblers rotated five times, before opening them and aerating the headspace with a fan for 30 s. Then chambers were made airtight, and a syringe was used through a sampling port to collect gas samples from the headspace at intervals of 10 min over a period of 30 min. Samples were stored in evacuated glass vials for analysis within 1 week of the end of the sampling period. Carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4) concentrations were determined by gas chromatography (GC Agilent 7890A, Agilent Technologies, Germany), using a thermal conductivity detector (TCD) for CO_2 and N_2O concentrations above 4 ppm, a flame ionization detector (FID) for CH_4, and an electron capture detector (ECD) for N_2O concentrations below 4 ppm. Two standard gas mixes with certified CO_2, CH_4 and N_2O concentrations were analyzed every 8 samples, to enable the conversion of peak areas into ppm. The low standard contained 398.6 ppm CO_2, 1.96 ppm CH_4, and 0.549 ppm N_2O, and the high standard 2004.8 ppm CO_2, 99.5 ppm CH_4, and 4.9 ppm N_2O.

2.4 Plant growth experiment with compost

A loamy sand soil collected on a farm in Southern Norway (Skjærgaarden, N59.3540, E010.4469) was air dried, sieved at 4 mm, and homogenized before use in the plant growth experiment. Soil chemical and physical characteristics, analyzed by a commercial analytical laboratory (ALS Global) using ISO methods, are presented in Table 2. The main production on this farm, spring onion (*Allium fistulosum*), was the plant species chosen for the experiment. Spring onion seeds were sown in seedling palettes using a potting mix containing peat and transplanted to the experimental pots after 6 weeks. Each pot received 2.7 kg dw equivalent soil and three seedlings. Pots were watered at 65 % of the soil maximum water holding capacity (WHC_{max}). WHC_{max}, calculated following Margesin and Schinner (2005)), was 410 mL per kg soil dw. The application of the compost treatments was based on their N content in order to achieve 300 mg total N per kg soil dw. A treatment with mineral fertilizer (NPK 18-3-15), added to achieve 200 mg kg^{-1} total N, was added to the experimental set-up, and referred to as NPK control. A higher fertilisation level was used in pots amended with compost compared to those amended with mineral fertilizer, because the fraction of the total N available to plants is lower in compost than in mineral fertilizer (Suzuki et al., 1990). We had four treatments (NPK control, compost control, compost with 5 % biochar, compost with 17 % biochar) and six replicates per treatment. Plants were watered every third day the first three weeks, and every second day the following three weeks as plants were getting bigger and evapotranspiration higher. Temperatures in the greenhouse were set at 22 °C during daytime (6 AM-8 PM) and 15 °C at night (8 PM-6 AM) to mimic Norwegian summer conditions. Plants were harvested at maturity, and the fresh and dry (60 °C overnight) weight of the edible part (stem and bulb without roots) recorded. The physical and chemical characteristics of the various compost mixes were analyzed by a commercial analytical laboratory (ALS Global) using ISO methods. It included plant available P, K, Ca, Mg and Na extracted using ammonium lactate (Egner et al., 1960) and reported as –AL in Tables 2 and 3.

Table 2. Key properties of the potting soil used in the pot experiment. P-AL and K-AL correspond to plant available P and K extracted using ammonium lactate.

	Soil
pH (H_2O)	5.8
Sand (%)	76
Silt (%)	14
Clay (%)	10
Loss on ignition (%)	5.6
C:N	14
Density (g L^{-1})	1400
Total Nitrogen (g 100 g^{-1} dw)	0.18
Phosphorus (P-AL) (mg 100 g^{-1} dw)	13
Potassium (K-AL) (mg 100 g^{-1} dw)	11

2.5 Nutrient availability

Three out of six replicates per treatment were submitted to a leaching event corresponding to 400 mL water above the WHC_{max}, (equivalent to 10 mm of precipitation). Pots that were not subjected to leaching were watered the same day to 95 % of the WHC_{max} so that the plants experienced comparable soil oxygen levels. These leaching events occurred two weeks prior to harvest, at the beginning of a sunny day to minimize any potential stress due to excess watering. Leachates were collected from each pot, filtered at 0.45 µm and stored at -22 °C until analysis. Ammonium (NH_4-N) and nitrate (NO_3-N) concentrations were measured by spectrophotometric methods using a SEAL analyzer, with a limit of detection of 0.01 mg N L^{-1}.

2.6 Statistical analysis

Comparisons of treatments were undertaken using an ANOVA, followed by post hoc Tukey test for pairwise examination of treatments. In order to understand the relationship between the biochar effect on temperature and GHG production, linear regression using a generalized linear model (GLM) was used to examine the relationship between temperature measured in the chambers and GHG production. We chose a GLM to address the highly skewed nature of the GHG response variables and specified a Gaussian distribution with a log link function (R core team, 2019).

3 Results and Discussion

3.1 Effects of biochar addition on composting dynamics

Composting temperature

In all compost treatments there was a rapid onset of compost heating, with peak temperatures observed after only 4 days (Fig.1). This is comparable to other studies that observed the onset of thermophilic composting after only 1 day of composting (e.g. Chen et al. (2010)). The high biochar addition significantly increased the maximum temperature reached over the course of the measurement period of 10 days compared with control (Fig.1d, ANOVA: F = 3.13, p = 0.048), but there was no significant difference between either the high and low treatments or the low treatments and the control. There appeared to be a higher degree of variability in the max temperature between replicates in both the control and low biochar treatment compared with the control (Fig.1 a,b,c). Biochar addition to compost has been shown to increase microbial respiration (Steiner et al., 2011) and compost temperatures, resulting in an acceleration of the composting process (Waqas et al., 2018). This has been explained by biochar effects on compost physical properties such as aeration (Awasthi et al., 2017a), and reductions of anaerobic clump formation (Sanchez-Garcia et al., 2015). In our study, visual observations suggested that Biochar reduced clump formation observed as digestate adhering to the more structured garden waste in the control treatment.

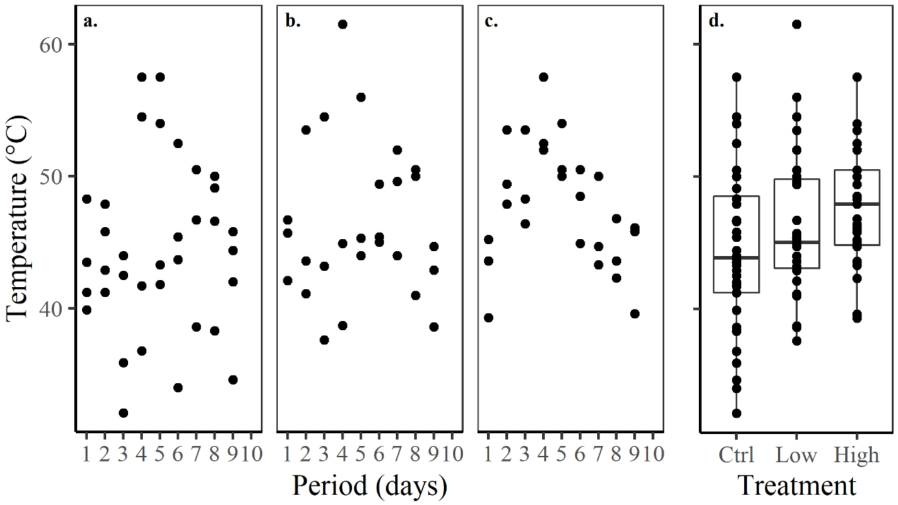


Figure 1. Point plots showing daily maximum temperature prior to GHG measurement in each tumbler in (a) Compost control (Ctrl, n=4); (b) Compost with 5 % biochar (Low, n=3); (c) Compost with 17 % biochar (High, n=3). Plot (d) is a boxplot of max temperatures summarising differences between treatments.

1.1.1. Greenhouse gas emissions

Both CO_2 and CH_4 were initially high in all treatments with a peak from day 1 of the measurements (Fig 2a and c). Peak CO_2 emissions measured on day 1 likely correlate with the relative abundance of easily degradable organic matter at the start of the composting process (de Bertoldi et al., 1983). Variability in this initial flux between treatments is largely responsible for the visible differences in cumulative emissions of CO_2 and CH_4 between the treatments (Fig 2c and d). CH_4 production was especially high at the second sampling point in the high biochar treatment, further contributing to the high cumulative CH_4 emission of this treatment (Fig 2f). Both CO_2 and CH_4 emissions were positively correlated with maximum temperature, except the first day of the 10-day composting period (Table S2). The shift from the early mesophilic to thermophilic phase, which generally occurs after the first day of composting, results in a variable response of microbial turnover to compost temperature (de Bertoldi et al., 1983). We saw no significant effect of treatment on either CO_2 or CH_4 emission despite the effect of treatment on temperature development. Sanchez-Garcia et al. (2015) also saw a significant effect of temperature and a non-significant effect of biochar treatment on CO_2 emissions in a poultry manure compost although they also reported a higher CH_4 emission from biochar amended compost. Studies of biochar and compost mixes have shown contradictory effects of biochar addition on both CO_2 and CH_4 with both higher (Czekala et al., 2016; Sanchez-Garcia et al., 2015) and lower emissions following biochar addition (Awasthi et al., 2017a; Chowdhury et al., 2014; Vandecasteele et al., 2016). These contrasting effects could be explained by the variability in the components of the different composting mixes and perhaps the methods by which these materials were composted.

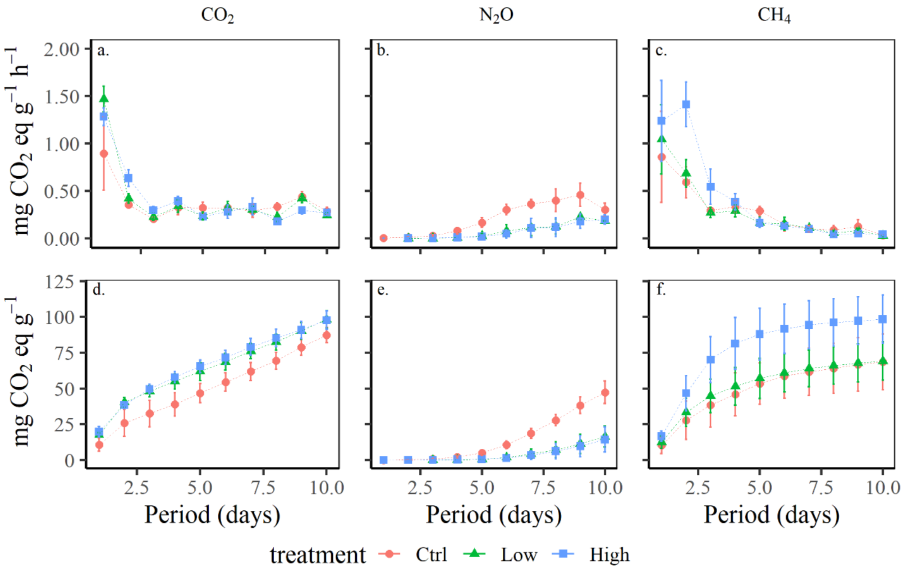


Figure 2. GHG measurements from the composting process throughout the measurement period of 10 days. Top: Mean measured gas flux dynamics of CO_2 (a), N_2O (b), and CH_4 (c). Bottom: Mean cumulative emissions of CO_2 (d), N_2O (e), and CH_4 (f). All values are presented in mg CO_2 equivalents g dw compost^{-1} (h^{-1}) based on 100 years using emission factors of 298× for N_2O and 28× for CH_4. Colors and shape represent treatments, bars represent standard error (n=4 Ctrl; n=3 biochar treatments Low and High).

There was a clear and significant effect of biochar addition on N_2O emission, with a consistently lower N_2O production in the biochar treatments compared to the control compost (Fig 2b). However, there was no evidence of a dose effect and there was no correlation with temperature (Table S2). N_2O emission increased towards the end of the measurement period in all treatments, but more strongly in control compost. N_2O production in this study was limited to the period following the peak in heating and the onset of cooling, while others have measured N_2O production during the thermophilic phase (Sanchez-Garcia et al., 2015). Biochar addition to compost has been shown to have either a negligible effect on N_2O emissions (Sanchez-Garcia et al., 2015) or to reduce these emissions by as much as 98 % relative to a control (Awasthi et al., 2017a). In our study we saw an average cumulative reduction by 65-70 % (Low to High biochar) relative to the control (Fig 3). N_2O emission in the maturation phase of composting may occur through both denitrification and nitrification mediated pathways (Sanchez-Garcia et al., 2015), and biochar is thought to affect these processes differently. Biochar effects on denitrification mediated N_2O emissions are well documented (Borchard et al., 2019) and due to a reduction in the $N_2O/(N_2O+N_2)$ product ratio

(Weldon et al., 2019). The mechanisms responsible for the biochar effect on nitrification mediated N_2O emissions are less well studied. He et al. (2021) showed evidence that biochar simultaneously improves denitrification processes through greater N_2O consumption potential and also through a lower ammonium production potential and lower nitrite consumption potential, resulting in lower net N_2O emission. This suggests that the N_2O emission reductions in our study could have been influenced by both compost aeration and by more direct effects of biochar on microbial nitrogen turnover. Since the N_2O emissions, unlike the CO_2 and CH_4 emissions, were clearly a function of treatment, supports the argument that biochar addition was directly impacting the nitrogen turnover rather than simply altering the aeration of the compost.

Differences between treatments in total GHG emission as CO_2 equivalents based on the cumulative values are shown in Figure 3. Biochar addition clearly reduced N_2O emissions by 65-70 % for both the low and high biochar dose, while slightly increasing CO_2 emissions by 12-13 % relative to the control. The high biochar dose led to the highest increase (44 %) in cumulative CH_4 emissions, resulting in this treatment contributing with the highest total cumulative GHG emissions, 3 % higher than the control, while the low biochar treatment was 10 % lower than the control. However, owing to the high variability in GHG measurements, the total cumulative GHG emissions in CO_2 equivalents was not statistically different across treatments.

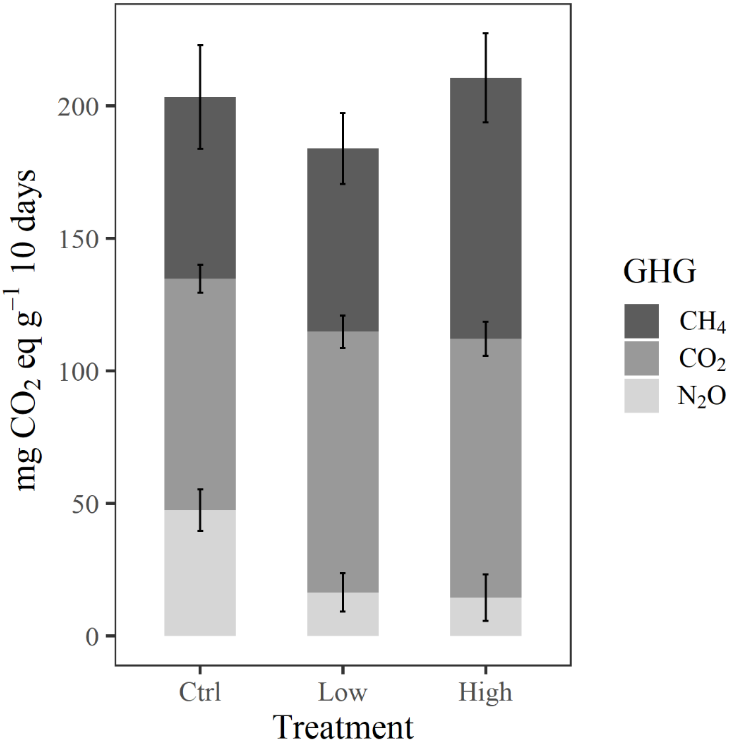


Figure 3. Stacked boxplot of the mean cumulative GHG emissions in CO_2 equivalents (eCO_2). Error bars are standard error (Control compost, n=4; compost with 5 and 17 % biochar, n=3).

Total accumulated GHG emissions in CO_2 equivalents highlights that the N_2O emission reduction is a significant factor governing the total GHG reduction potential of biochar. The lack of a biochar dose effect on N_2O emission combined with the moderate increase in CO_2 and CH_4 in the high biochar treatment suggests that a low biochar amendment is sufficient to achieve a total reduction in GHG emission from green waste and digestate compost.

3.2 Fertilisation potential of compost and biochar-amended compost

Fertilizer value of the mature composts

We saw no evidence that biochar improved the nutrient retention capacity of the final compost since there were no significant differences between the treatments in NH_4-N content, NO_x-N content and K content (Table 3). Biochar has previously been shown to reduce the loss of mineral N through reduced NH_3 emissions (Malinska et al., 2014; Awasthi et al., 2016) and higher NO_3^- and NH_4^+ retention (Kammann et al., 2015; Lehmann et al., 2006). Kahn et al., 2016 found that the increase in N retention of co-composted biochar was relative to initial N content of the parent material, with larger retention the lower the initial N content. Sarkhot et al. (2012) found that biochar could hold 8 % N following mixing in manure. The lack of a significant effect of biochar on mineral N retention in our study may be due to the high initial N content of the digestate and the inclusion of garden waste, which may have performed a similar function to biochar as a porous organic media.

The high biochar compost had significantly higher C/N ratio and TOC than the other treatments, reflecting the significantly larger proportion of biochar. There was also a significant dilution effect of the biochar addition in the high biochar treatment, as shown by the lower concentrations of total N, total P, plant available P, Mg, Ca and Na (P-AL, Mg-AL, Ca-AL, Na-AL), and ash (Table 3). Compared to concentrations in control compost, these elements showed 8-14 % dilution in the compost with 5 % biochar, and 19-29 % dilution in the compost with 17 % biochar. For most physical and chemical parameters, the low biochar treatment was not significantly different from the control. Dilution effects were accounted for during the fertilisation experiment by using compost volumes with similar total N content.

Table 3. Physical and chemical properties of the matured composts (Ctrl: without biochar, Low: 5 % biochar, High: 17 % biochar). P-AL, K-AL, Mg-AL, Ca-AL and Na-AL correspond to plant available P, K, Mg, Ca and Na extracted using ammonium lactate. Results are provided as mean and standard error in parentheses (n=4 for Ctrl, n=3 for Low and High). Means with different letters are statistically different (Tukey, $p < 0.05$).

	Ctrl	**Low**	**High**
pH (H_2O)	8.1 (0.2)a	8.0 (0.3)a	8.5 (0.3)a
C/N	7.8 (0.3)a	8.3 (0.48)a	13.4 (0.43)b
Total N (g $100g^{-1}$ dw)	3.4 (0.1)b	3.4 (0.14)b	2.6 (0.14)a
NH_4-N (mg kg^{-1} dw)	9.9 (2.2)a	12.7 (3.1)a	7.9 (3.1)a
NO_x-N (mg kg^{-1} dw)	2233 (366)a	1733 (517)a	983 (517)a
Total Organic C (% dw)	26 (1.0)a	27 (1.4)a	35 (1.4)b
P-AL (mg $100g^{-1}$ dw)	550 (19)b	503 (27)ab	443 (27)a
Total P (g $100g^{-1}$ dw)	1.2 (0.04)b	1.1 (0.06)b	0.8 (0.06)a
K-AL (mg $100g^{-1}$ dw)	393 (17)a	387 (24)a	403 (24)a
Mg-AL (mg $100g^{-1}$ dw)	193 (6)b	173 (8)b	147 (8)a
Ca-AL (mg $100g^{-1}$ dw)	4600 (193)b	3933 (274)ab	3667 (274)a
Na-AL (mg $100g^{-1}$ dw)	160 (4)c	140 (5)b	113 (5)a
Dry matter content (g L^{-1})	171 (4)a	173 (6)a	163 (6)a
Dry matter content (%)	37.4 (1.8)a	38.6 (2.6)a	33.6 (2.6)a
Ash content (% dw)	39.5 (0.9)b	37.1 (1.2)ab	34.5 (1.2)a
Loss on ignition (% dw)	60.5 (0.9)a	62.9 (1.2)ab	65.5(1.2)b

3.3 Nutrient leaching and plant yield

A leaching treatment during the plant-growth experiment was used to test the hypothesis that biochar would reduce leaching of plant nutrients (Fig 4a and b). The addition of biochar to compost did not result in greater retention of either ammonium or nitrate than observed in soil amended with compost without biochar, as similar amounts of NH_4-N ($p = 0.09$) and NO_3-N ($p = 0.44$) were leached in all compost treatments. By contrast, there was significantly more ammonium ($p = 0.006$) and nitrate ($p < 0.001$) leached from the NPK fertilized soil compared to compost-amended treatments.

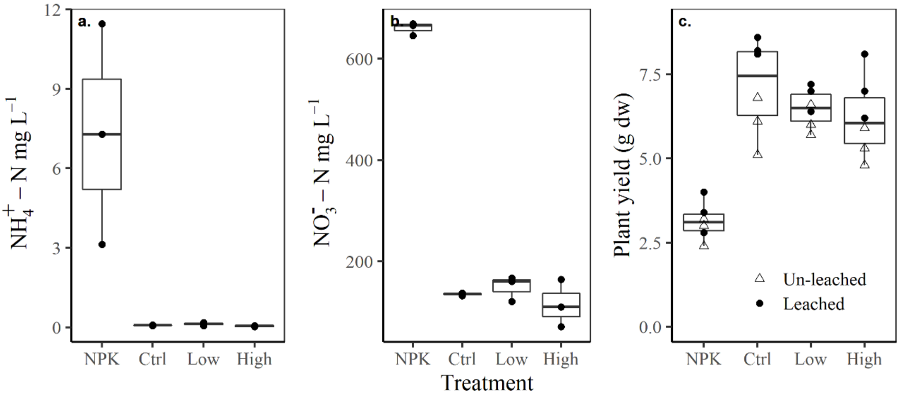


Figure 4. Total leached NH_4-N (a) and NO_3-N (b) following two leaching events. (c) Plant yield at maturity (g dw) showing the results from a leached and un-leached treatment in pots fertilized with mineral fertilizer (NPK), compost without biochar (Ctrl), compost with 5 % biochar (Low), and compost with 17 % biochar (High).

All compost treatments, including biochar amended compost, resulted in significantly higher yield of spring onion (6.62 ± 1.11 g dw, mean ± SD) than observed with the NPK mineral fertilizer (3.13 ± 0.55 g dw). Yield studies, comparing mineral fertilisation to compost addition, have shown inconsistent effects with both positive, negative and neutral effects (Agegnehu et al., 2015; Bass et al., 2016; Herencia et al., 2007; Schmidt et al., 2014). Variability in crop yield responses to compost addition are likely an interaction between crop type (Bass et al., 2016) and native soil properties (Schulz et al., 2013). The soil used in this study was taken from a field in intensive vegetable production. For Norwegian conditions, soil pH was moderately low (pH 5.8) and P concentration was high, which is a consequence of high long-term application of mineral compound fertiliser. As a sandy soil (76 % sand) it was expected to have a low capacity for nutrient and moisture retention. Compost addition to soil has been shown to have significant effects on soil physical and chemical properties. The addition of compost, rich in stabilized organic matter, can increase total SOM content and improve soil bulk density and water holding capacity (Carter et al., 2004; Ramos, 2017). The effect of increased SOM has been shown to have a positive effect on plant yield due to better access to nutrients and better root development through lower bulk density of the soil (Agegnehu et al., 2015). High pH compost like the compost in this study can also have a significant liming effect on soil (Alburquerque et al., 2011; Schulz et al., 2013) with consequences for nutrient availability and retention. A combination of these effects likely explains why compost amendment had a significant and positive effect on plant yield in our study. This is further supported by the significantly higher leaching losses of both NO_3^- and NH_4^+ in the NPK treatment, which is likely a consequence of the poor nutrient holding capacity of the agricultural soil used. We also observed that the leached pots had significantly higher yield than the un-leached pots, suggesting that the leached nutrients were not the primary cause of the observed difference between the yield in the NPK treatment and the compost treatment.

One of our hypotheses was that biochar would improve the fertilisation effect of compost mixture and reduce leaching. Our study showed no significant difference in the yield effect of compost addition at any level of biochar addition ($p = 0.35$, Fig 4c). Yield effect of biochar addition to soils have been shown to be higher in low pH soils with low SOC (Biederman and Harpole, 2013; Jeffery et al., 2011) such as the soil used in this study. However, the dominant effects of biochar in these soils are related to increases in SOC, pH and the application of plant nutrients in the ash fraction (Jeffery et al., 2011). Our analysis of the final compost and biochar mixes confirmed that biochar addition did not result in a significantly higher pH of the final material, and we saw evidence of both mineral and N dilution by the added biochar. Other studies have suggested that biochar additives to compost can influence both pH (Waqas et al., 2018) and the retention of nutrients (Kammann et al., 2015). Banegas et al. (2007) showed that bulking agents such as sawdust can result in a significant nutrient dilution effect at high mixing ratios, similar to the effect we see here with the high biochar treatment. It is possible that our enclosed batch composting resulted in reduced nutrient leaching when compared with larger scale open windrow composting. It is also possible that the dilution effect is more apparent in the composting of high N feedstocks such as digestate (Banegas et al., 2007).

Our results agree with the findings of Wang et al. (2019) who found that across 14 similar studies, increases in crop yield were best explained by compost addition and that biochar addition to compost had no discernible additive effect on yield. Because of the dilution effect of biochar addition this can be seen as a challenge, due to the higher application requirement at higher biochar mixing ratios to meet the N requirements of the crop. However, it also presents an opportunity through the increased carbon storage potential of the amendment.

Our application of 17 % biochar (by weight) with the high biochar treatment is at the higher limit of application that has been seen to have a positive effect on compost properties (Liu et al., 2017; Xiao et al., 2017). The final compost product from the 5 % biochar treatment, which was more similar to the un-amended compost, did not lead to a significant dilution of nutrients, and resulted in a lower total GHG burden.

3.4 Conclusions

Our study confirmed that composted biogas digestate can act as an effective fertiliser for vegetable crops in SOC poor, low pH soils. Biochar addition to the composting process increased the thermal stability of composting through effects on compost temperature development. Relative temperature stability across replicates suggests that biochar additives can ensure that the composting process consistently reaches temperatures sufficient to ensure hygenization of the compost. Addition of low amounts of biochar also reduced the emissions of N_2O during composting, while emissions of CO_2 and CH_4 were not affected. Increasing the amount of biochar increased CO_2 and CH_4 emissions due to higher compost temperatures, suggesting a higher microbial turnover in the high biochar treatment. We argue that this effect is likely linked to the biochar effect on compost structure, which was highly influenced by the viscous properties of the digestate. In the fully matured compost there was evidence of a dilution effect of the added biochar in the high biochar treatment for both N and mineral nutrients. There was no significant effect of biochar addition to compost on the yield of spring onion, suggesting that biochar did not improve the fertiliser property of the final product in our composting system. However, biochar also had no negative effects on plant yield and all compost products performed significantly better in this C poor, low pH soil than mineral fertiliser. This shows that biochar addition to compost can improve the composting process while not negatively impacting the fertiliser properties of the final product. Long-term studies are needed to understand whether repeated applications of biochar amended compost have positive consequence beyond these immediate effects. Life cycle assessments will also enable us to understand how biochar addition can contribute to the total GHG mitigation effect of this process.

Author Contributions

Simon Weldon: Conceptualization, Experimental plan, Statistical analysis, First draft article, reviewing and editing. **Pierre-Adrien Rivier:** Conceptualization, Experimental plan, Experimental work, reviewing and editing. **Claire Coutris:** Experimental plan, Experimental work, reviewing and editing: **Erik Joner:** Experimental plan, reviewing and editing. **Alice Budai:** Conceptualization, Experimental plan, reviewing and editing, funding acquisition.

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Supplementary information

Co-composting of biogas digestate and garden waste with biochar: Effect on greenhouse gas production and fertilizer value of the matured compost

Simon Weldon[1,2*], Pierre-Adrien Rivier[2], Erik J. Joner[2], Claire Coutris[2], Alice Budai[2]

[1]Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, NMBU, 1430 Ås, Norway

[2]Norwegian Institute of Bioeconomy Research (NIBIO), Division of Environment and Natural Resources, Høgskoleveien 7, 1432 Ås, Norway

[*]Corresponding author: simon.weldon@nibio.no

Table S1. Key properties of the potting soil used in the plant experiment. P-AL and K-AL correspond to plant available P and K extracted using ammonium lactate.

	Soil
pH (H_2O)	5.8
Sand (%)	76
Silt (%)	14
Clay (%)	10
Loss on ignition (%)	5.6
C:N	14
Density (g L^{-1})	1400
Total Nitrogen (g 100 g^{-1} dw)	0.18
Phosphorus (P-AL) (mg 100 g^{-1} dw)	13
Potassium (K-AL) (mg 100 g^{-1} dw)	11

Table S2. Biochar properties analysed by Eurofins following the standard Biochar analysis package.

Biochar property	**Unit**	**Measurement**
Ash content (550°C)	% (w/w)	16.1
Total organic carbon	% (w/w)	72.3
Total nitrogen	% (w/w)	1.21
Hydrogen	% (w/w)	2.6
Oxygen	% (w/w)	8.7
Total inorganic carbon (TIC)	% (w/w)	0.7
H/C_{org} ratio (calculated)	Molar	0.44
O/C ratio (calculated)	Molar	0.089
pH	in H_2O	8.0
Conductivity	µS/cm	615
Phosphorus	mg kg^{-1}	2000
Potassium (K)	mg kg^{-1}	8000
Sulphur (S), total	mg kg^{-1}	400
Calcium (Ca)	mg kg^{-1}	26000

Biochar property	**Unit**	**Measurement**
Magnesium (Mg)	mg kg^{-1}	3000
Iron (Fe)	mg kg^{-1}	3000
Boron (B)	mg kg^{-1}	24
Manganese (Mn)	mg kg^{-1}	2320
Silicon (Si)	mg kg^{-1}	32000
Sodium (Na)	mg kg^{-1}	1000
Heavy metals		
Arsenic (As)	mg kg^{-1}	1.1
Lead (Pb)	mg kg^{-1}	11
Cadmium (Cd)	mg kg^{-1}	0.3
Copper (Cu)	mg kg^{-1}	16
Nickel (Ni)	mg kg^{-1}	11
Mercury (Hg)	mg kg^{-1}	< 0.07
Zinc (Zn)	mg kg^{-1}	229
Chromium (Cr)	mg kg^{-1}	12
Poly Aromatic Hydrocarbon (PAH) content		
Naphthalene	mg kg^{-1}	2
Acenaphthylene	mg kg^{-1}	< 0.1
Acenaphthene	mg kg^{-1}	< 0.1
Fluorene	mg kg^{-1}	< 0.1
Phenanthrene	mg kg^{-1}	< 0.1
Anthracene	mg kg^{-1}	< 0.1
Fluoranthene	mg kg^{-1}	< 0.1
Pyrene	mg kg^{-1}	< 0.1
Benz(a)anthracene	mg kg^{-1}	< 0.1
Chrysene	mg kg^{-1}	< 0.1
Benzo(b)fluoranthene	mg kg^{-1}	< 0.1
Benzo(k)fluoranthene	mg kg^{-1}	< 0.1
Benzo(a)pyrene	mg kg^{-1}	< 0.1
Indeno(1,2,3-cd)pyrene	mg kg^{-1}	< 0.1
Dibenz(a,h)anthracene	mg kg^{-1}	< 0.1
Benzo(g,h,i)perylene	mg kg^{-1}	< 0.1
Total 16 EPA-PAH excl. LOQ	mg kg^{-1}	2

Table S3. Output from the 3 GLM models run on the GHG data excluding day 1 measurements.

	CO_2			CH_4			N_2O		
Predictors	*Estimates*	*std. Error*	*p*	*Estimates*	*std. Error*	*p*	*Estimates*	*std. Error*	*p*
(Intercept)	-3.56	0.36	<0.001	-0.01	1.01	0.996	0.63	0.29	0.036
Max temp (ºC)	0.02	0.01	0.003	0.04	0.02	0.069	0	0.01	0.523
Low Biochar (5 %)	-0.03	0.1	0.774	-0.2	0.3	0.492	-0.28	0.09	0.002
High biochar (17 %)	-0.02	0.11	0.825	0.1	0.3	0.745	-0.3	0.09	0.001
Observations	79			79			79		
R^2 (Nagelkerke)	0.128			0.117			0.187		

Paper III

Enhancing plant N uptake with biochar-based fertilizers: beyond sorption

Daniel P. Rasse[a*], Simon Weldon[a,b], Erik Joner[a], Stephen Joseph[c,d], Claudia I. Kammann[e], Xiaoyu Liu[d], Adam O'Toole[a], Genxing Pan[d], N. Pelin Kocatürk-Schumacher[a,f]

[*]**Corresponding Author:** Daniel.rasse@nibio.no

[a] Department of Biogeochemistry and Soil Quality, Norwegian Institute of Bioeconomy Research (NIBIO), Høgskoleveien 7, NO-1431 Ås, Norway

[b] Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, NMBU, Ås, Norway

[c] University of New South Wales, School of Material Science and Engineering, NSW 2052, Australia; ISEM and School of Physics, University of Wollongong, Wollongong, NSW 2522, Australia

[d] Institute of Resource, Ecosystem and Environment of Agriculture, and Center of Biochar and Green Agriculture, Nanjing Agricultural University, Nanjing 210095, China

[e] Department of Applied Ecology, Hochschule Geisenheim University, 65366 Geisenheim, Germany

[f] Faculty of Science and Technology (REALTEK), Norwegian University of Life Sciences (NMBU), P.O. Box N-1432, Ås, Norway

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Abstract

Background Biochar-based fertilizer products (BCF) have been reported to increase both crop yield and N-use efficiency. Such positive effects are often assumed to result from the slow-release of N adsorbed on BCF structures. However, a careful review of the literature suggests that actual mechanisms remain uncertain, which hampers the development of efficient BCF products.

Scope Here, we aim at assessing the BCF mechanisms responsible for enhanced N uptake by plants, and evaluate the potential for further improvement. We review the capacity of biochar structures to adsorb and release N forms, the biochar properties supporting this effect, and the methods that have been proposed to enhance this effect.

Conclusions Current biochar products show insufficient sorption capacity for the retention of N forms to support the production of slow-release BCFs of high enough N concentration. Substantial slow-release effects appear to require conventional coating technology. Sorption capacity can be improved through activation and additives, but not to the extent needed for concentrated BCFs. Positive effects of concentrated BCFs, containing a minor fraction of biochar, suggest hormone-like effects on plant growth. These effects require further research. By contrast to concentrated BCFs, biochar products with enhanced sorption are needed for the efficient recycling of N in organic waste streams, i.e. the production of organic BCFs. This will most likely be achieved through combination of biochar with clay and organic additives, for which biochar macroporosity might be an overlooked key parameter. Developing this technology requires research emphasizing quantitative aspects of nutrient dynamics.

Keywords: Biochar, Biochar compound fertilizer, Fertilizer, Ammonium, Sorption, Slow release

Abbreviations: BCF: Biochar Compound Fertilizer; **BC:** Biochar; **BCac:** Activated Biochar; **BCun:** Unmodified biochar ; **BCen:** Enhanced biochar; **Agrichar:** Biochar modified for agricultural application; **N:** Nitrogen; **P:** Phosphorus; **K:** Potassium; **S:** Sulphur; **CEC:** Cation Exchange Capacity; **AEC:** Anion exchange capacity; **NUE:** Nitrogen Use Efficiency; **SOM:** Soil Organic Matter; **DOC:** Dissolved Organic Carbon; **Ag. Waste:** Agro-industrial waste; **Combi:** Biochar mix with other feedstock, minerals or organic compounds.

The rationale for making biochar fertilizers

The main rationale for making biochar-based fertilizers (BCF) is that positive interactions between nutrients and biochar in soils can be enhanced through application as a combined product. Retaining nutrients in soils in a plant-available form is considered a key property of biochar amendments (Lehmann 2007). Two decades ago, the highly fertile Terra Preta soils of the Amazonas were found to contain exceptionally high charcoal contents (Glaser et al. 2001). Charcoal was later proven to be a major component of the nutrient sorption capacity of certain soil types (Mao et al. 2012). These observations suggested that adding biochar to soil could substantially enhance the retention of plant-available nutrients. Biochar-mediated retention and release could in part explain the reported increases in nutrient use efficiency (Chen et al. 2019; Shi et al. 2020; Zhang et al. 2016; Zheng et al. 2013), decreases in NO_3^- leaching (Borchard et al. 2019; Chen et al. 2019; Liu et al. 2019a; Zheng et al. 2013) and decreases in N_2O emissions (Borchard et al. 2019; He et al. 2017). These positives effects are expected to be greater when nutrients are loaded on biochar surfaces prior to soil application, i.e. through BCF technology, and the rationale for this is two-fold. First, in BCF all nutrients are interacting with the biochar surfaces, while nutrients applied to biochar-amended soil have more limited chances for interaction, notably as the distribution of biochar plowed into soil can be quite heterogeneous (O'Toole et al. 2018). Second, nutrient loading onto fresh biochar can be largely enhanced when biochar is intimately mixed with nutrient sources, heated and/or exposed to varying moisture conditions, such as during composting (Hagemann et al. 2017b; Hagemann et al. 2017c; Joseph et al. 2013; Kammann et al. 2015). Such observations suggest that nutrients could be efficiently bound to biochar prior to soil application. How to do this is a key question, and a central theme of the present paper.

Multiple methods have been used to create BCFs, most of this work being conducted in the last decade. The difficulty in describing and classifying these methods partly comes from the multiple steps and choices to be made when developing a BCFs (Fig. 1). BCFs are composed of 2 to 3 categories of ingredients: 1) biomass feedstock, 2) additives, mostly in the form of clay, minerals and organic substrates, 3) nutrient sources of organic or mineral origin. In addition, activation products can be used, some of them, such as phosphoric acid, contributing directly to the composition of the BCF (e.g. Carneiro et al. (2018)). Biomass can also be activated before pyrolysis especially through reaction with phosphoric acid (Zhao et al. 2017) or a mixture of clay and/or $FeSO_4$ (Rawal et al. 2016). These multiple ingredients are combined through a series of successive treatments involving at least two of the following: 1) pyrolysis, including co-pyrolysis with additives, 2) activation of untreated biochar (BCun) with e.g. acids, oxidizers or steam to obtain activated biochars (BCac), 3) mixing of BCun or possibly BCac with additives, to obtain enhanced biochars (BCen) and 4) loading of nutrients onto the BCac or BCen to obtain the BCFs. The mixing and loading phases are sometimes combined as biochar, binding additives and nutrient sources are mixed together.

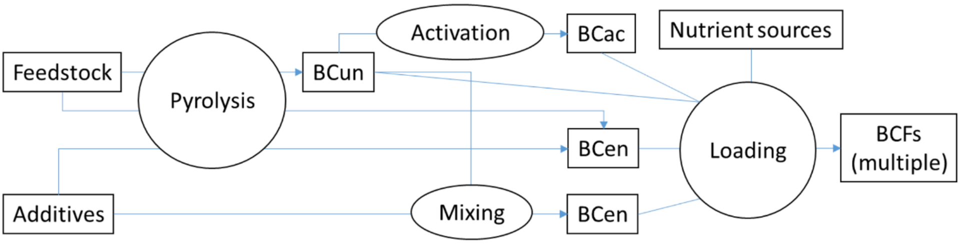

Figure. 1. Simplified representation of BCF production processes, where BCun, BCan and BCen are biochar that are untreated, activated and enhanced, respectively. Material types are in squares, processes in ellipses.

The simplest method for creating a BCF consists of creating a BCun from a feedstock and loading it through mixing in a nutrient solution. Examples of such methods include soaking BCun in a pure nutrient solution such as urea (Magrini-Bair et al. 2009) or ammonium in a synthetic form (Cui et al. 2016; Gai et al. 2014; Hale et al. 2013) or the BC can be applied to a more complex organic residue such as manure or digestate (Kizito et al. 2015; Kocatürk-Schumacher et al. 2017b; Kocatürk-Schumacher et al. 2019). In order to directly increase nutrient retention of the BC, activation steps have been used with some success (Huff et al. 2018). Studies have also explored the addition of additives to the BC in order to increase binding and retention of nutrients, such as bentonite clays and organic binders (Joseph et al. 2013). These additives can be added pre- or post-pyrolysis with pre-pyrolysis application having the advantage that the addition can also result in catalysis of the pyrolysis process (Chen et al. 2017; Qian et al. 2014) but with the potential disadvantage that the properties of the additive can be negatively affected (Ismadji et al. 2016). The final mixing and loading of nutrients onto the BCF has often been made through physical blending (Puga et al. 2020; Shi et al. 2020) and co-torrefaction (Joseph et al. 2015; Nielsen et al. 2014; Ye et al. 2016). When manure solutions are used, mixing with minerals followed by heating treatment has been tested in order to ensure a reaction between the BC surface and the additive (Chia et al. 2010; Chia et al. 2014; Lin et al. 2013).

The examples provided above illustrate the diversity of methods used to produce BCFs, and we will further explore their diversity and significance as we link them to mechanisms in this review. The multiple approaches presented above do not represent a chronological development of the technology. For example, producing more efficient BCFs through the use of clays as additive was already reported in 2010 (Joseph et al. 2010). The industrialization of BCF was firstly initiated in 2012 in China and reached commercial scale by 2017, largely based on conventional steam blending of biochar with mineral urea, phosphate and potassium chloride (Pan et al. 2017; Sun et al. 2018).

The development of BCFs so far appears to have been largely empirical, based on trial and error. Many studies have attempted to justify their approach, often *a posteriori*, by invoking elements of theory such as e.g. sorption and slow release effects as they relate to physico-chemical properties of the composite BCF material. Some elements of theories are well documented, others remain more hypothetical. The magnitude of the reported effects, such as an increase in N use efficiency, has rarely been discussed in light of the theoretical potential of the corresponding BCF-production method. In order to guide product design, we need a better understanding of the mechanisms controlling nutrient loading and release, especially that of nitrogen. In the present study, we review and evaluate these crucial elements and their implications in terms of producing BCFs for plant production and climate-change mitigation.

Conditions for BCFs to be actual fertilizers

To define a biochar product as a BCF it must meet the agreed upon definition of a fertilizer. The International Organization for Standardization (ISO) defines fertilizer as “a substance that contains one or more recognized plant nutrient(s), which is used for its plant nutrient content and is designed for use or claimed to have value in promoting plant growth” (ISO 2015). According to this definition, BCFs can be defined as fertilizers if they contain nutrients; however, ISO also indicates that the nutrient content of the fertilizer should meet the law or regulation of each country or region. In the European Union (EU), a new implementing regulation (EU 2019/2164) on organic production and labelling of organic products has been in force since 2020. According to the new regulation, biochar is defined as a “pyrolysis product made from a wide variety of organic materials of plant origin” and is listed in Annex I as an authorized fertilizer. This means that biochar can be used in Europe in organic farming as a fertilizer/soil conditioner. However, it is still not yet authorized as an EU fertilizing product according to EU Regulation 2019/1009 for making fertilizers available on the internal market. This is expected to change in the coming years as the Regulation obliges the European Commission to assess struvite, biochar and ash-based products (STRUBIAS) and biochar to be included as a new component material category in an extended Annex II.

In this regulation, the requirements for several fertilizing product categories are set out. Table 1 summarizes the requirements and contaminant limits for possible fertilizer and soil improver categories for biochar fertilizers according to EU Regulation 2019/1009, if they were listed as authorized fertilizers.

Table 1. An overview of requirements and contaminant limits for possible fertilizer and soil improver categories for biochar fertilizers according to EU Regulation 2019/1009.

Categories	Min content in solid form (% by mass)		Max contaminant limits (mg kg^{-1} dry matter)							
	C_{org}	N	Cd*	Cr	Hg	Ni	Pb	As	Cu	Zn
Fertilizers										
Organic	15	2.5	1.5	2	1	50	120	40	300	800
Organo-mineral	7.5	2	3	2	1	50	120	40	600	1500
Inorganic macronutrient	1	10**	3	2	1	100	120	40	600	1500
Soil improvers										
Organic soil improver	7.5	n/a	1.5	2	1	50	120	40	300	800
Inorganic soil improver	n/a	n/a	1.5	2	1	100	120	40	300	800

*Max limit for Cd concentration depends on the P content of the fertilizer.

**Minimum N content of a straight solid inorganic macronutrient fertilizer, which contains only one declared macronutrient (nitrogen (N)).

In China, biochar based fertilizers (NY/T 3041-2016, Ministry of Agriculture China) and biochar based organic fertilizer (NY/T 3618-2020, Ministry of Agriculture China) are currently (in 2021) authorized for use in agriculture. As a key ingredient (at least of 5% stable carbon) in such fertilizers, biochar or agrichar, is defined as the solid residue rich in stable organic carbon obtained via oxygen-limited pyrolysis of crop residues at a temperature range of 400 ºC – 700 ºC. Minimum content of major nutrients of N, P_2O_5 and K_2O is 20% (corresponding to 12,3% of N+P+K) for biochar based fertilizers and 5% for biochar based organic fertilizers, while heavy metals and organics must meet guideline values regulated for fertilizers (Table 2). However, these values are still in debate and need to be updated. Production of biochar and biochar fertilizers are nationally authorized and regulated for development in rural industry in conjunction with poverty reduction in undeveloped areas with plenty of biomass feedstocks, and for use in ecological farming, soil improvement and restoration (GB/Z 39121-2020, China State Agency of Market Supervision and Administration 2020).

Table 2. Requirements and contaminant limits regulated for biochar based fertilizer and organic fertilizer respectively with NY/T 3041-2016 and NY/T 3618-2020, Ministry of Agriculture China.

Categories	Min content in solid form (% by mass)		Max contaminant limits (mg kg^{-1} dry matter)				
	Char C[a]	$N+P_2O_5+K_2O$[b]	Cd	Cr	Hg	Pb	As
Biochar based Fertilizer							
Type I	9	20	10	500	5	150	50
Type II	6	30	10	500	5	150	50
Biochar based organic fertilizer							
Type I	10	5	3	150	2	50	15
Type II	5	5	3	150	2	50	15

[a] Char C is measured with CNS Elemental Analyzer after water extraction.

[b] These chemical forms are used per convention only and values should be multiplied by 0.62 to obtain actual sums of elements N + P + K

Reported effects on plants

A number of pot and field studies have tested the effects of BCFs on plant growth, but these are comparatively few compared to the number of trials testing pure biochar. In Fig. 2 (and Tables S1), we summarize the main results from 40 BCF observations from 19 studies and report the percentage change in yield of BCFs compared to a fertilized control. Our analysis excludes studies where biochar and fertilizer were added separately to a soil without prior blending. Average plant yield increased by 24 % with BCFs as compared to fertilized control, with a standard deviation of 23 %. The high variability of the response reflects the diversity of 1) biochar used in the BCF, 2) production methods and 3) experimental conditions in terms of plant species and soil types. The studies used in Fig. 2 span a range of formulation methods and ingredients including: 1) torrefaction of biochar with clay, minerals, inorganic and organic fertilizers; 2) mixing and incubation of biochar with liquid manures, digestate or urine; 3) physical blending of biochar with inorganic fertilizers, including heat treatment of the mixture for improved bonding and coating methods. A full list of data from the studies are included in supplementary information (Table S1) and a summary of chemical properties of BCFs averaged across multiple studies are given in Table 3. Here we see that the C content of BCFs is approximately half that of pure biochar, the latter ranging from 60-90%. In these studies, the BCFs were enriched in N, P, K, and displayed a high pH and a low surface area, the latter probably due to coating or filling of pores with clay and fertilizer (Table 3).

Table 3. Chemical properties of BCFs averaged across multiple studies. n is number of studies, SA is surface area.

n=22 **C (%)**	**n=35** N (%)	**n=26** P (%)	**n=15** K (%)	**n=14** pH	**n=6** SA (m^2 g^{-1})
35.25	8.18	5.18	6.17	7.85	6.33

Mechanisms responsible for stimulation of plant yield by BCFs are still under investigation, but in summary the majority of studies stated either a slow release effect or increased nitrogen use efficiency (NUE), which they partly attributed to: 1) pH-change effects on microbial communities (Nielsen et al. 2014), 2) increased root growth and N uptake (Liu et al. 2020b; Shi et al. 2020; Xiang et al. 2017), 3) increased mycorrhizal root colonization (Blackwell et al. 2015), 4) increased physical retention of dissolved nutrients and reduced leaching (El Sharkawi et al. 2018; Schmidt et al. 2017; Schmidt et al. 2015; Shi et al. 2020; Wen et al. 2017), 5) increased nitrification (Liao et al. 2020), and reduced production of N_2O (Zheng et al. 2017), 7) improved redox conditions and changes in abundance of growth promoting micro-organism (Chew et al. 2020), 8) increased P and K availability (Farrar et al. 2019), and 9) slower diffusion of NH_4^+ and NO_3^- to soil solution (Liao et al. 2020).

A number of studies reported increases in NUE but did not suggest responsible mechanisms (Joseph et al. 2015; Qian et al. 2014; Yao et al. 2015). On average, nutrient use efficiency increased by 34 % ± 27 (n=5). While most of the experiments are controlled with respect to N amounts, it is difficult to simultaneously control for P and K as well, especially when using digestate and other P- and K-rich organic fertilizers. Urea was used in 88 % of formulations where biochar was combined with mineral N fertilizer. Liao et al. (2020) found that yield of oil rapeseed increased by 17 % with a biochar-bentonite-urea BCF compared to urea alone. In general, clay was included as an ingredient in 71 % of the BCF formulations reported, suggesting that interactions between biochar and clay may play a key role in potential yield benefits.

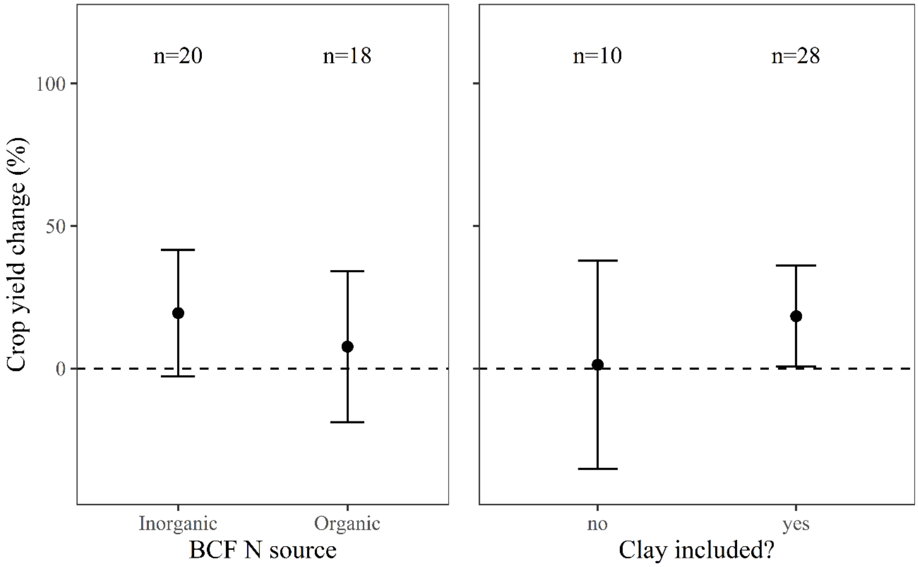

Figure 2. Mean ±SD Crop yield change with BCF compared to a fertilized control, grouped by BCF N source and whether clay was an ingredient (outliers excluded). Based on studies: Zheng et al. (2017), Ye et al. (2020), Yao et al. (2015), Wen et al. (2017), Shi et al. (2020), Qian et al. (2014), Puga et al. (2020), Nielsen et al. (2014), Magrini-Bair et al. (2009), Liao et al. (2020), Kocaturk-Schumacher et al. (2019), Joseph et al. (2015), González et al. (2015), Farrar et al. (2019), El Sharkawi et al. (2018), Chew et al. (2020), Blackwell et al. (2015), Schmidt et al. (2017) [NPK treatment], Liao et al. (2020). (outliers excluded – Schmidt et al. (2015) [306%+], Schmidt et al. (2017) [123%+]

The theory of N-efficient BCFs

Nitrogen use efficiency (NUE) is defined as the ratio between N outputs in harvested products over total field N inputs, i.e. the output-input ratio of N (Zhang et al. 2015). Improvements in fertilizer technology is key to increase NUE (Fageria and Baligar 2005), and it has been reported that BCFs increase NUE compared to soluble mineral fertilizers (Chen et al. 2019; Shi et al. 2020; Zeng et al. 2013). This is an important incentive for the development of BCF products.

Effects of BCF on N-use efficiency, as compared to that of mineral fertilizer, is summarized in Fig. 3. The difference between N inputs and outputs, also referred to as the N surplus, is either stored in the soil or lost from the soil system. When stored in the soil, N surplus can contribute to SOM build-up (Soussana et al. 2017; van Groenigen et al. 2017). However, in the absence of a SOM management strategy, loss can predominate (Zhang et al. 2015). The efficiency of mineral N fertilizers is limited both by gaseous losses of N_2, N_2O and NH_3 and by leaching losses, predominantly as nitrate (Xiang et al. 2020). Biochar-induced reductions in N_2O losses can result from a higher proportion of NO_3^- being converted to N_2 as compared to N_2O (Harter et al. 2013; Weldon et al. 2019), meaning that reductions in N_2O emission do not necessarily indicate a reduction in gaseous N loss. By contrast, runoff and leaching losses of N have been hypothesized early on to be drastically reduced by biochar products (Magrini-Bair et al. 2009). Enhancement of root growth by BCF application is an additional factor that might contribute to improved N capture and retention in soils (Yan et al. 2020).

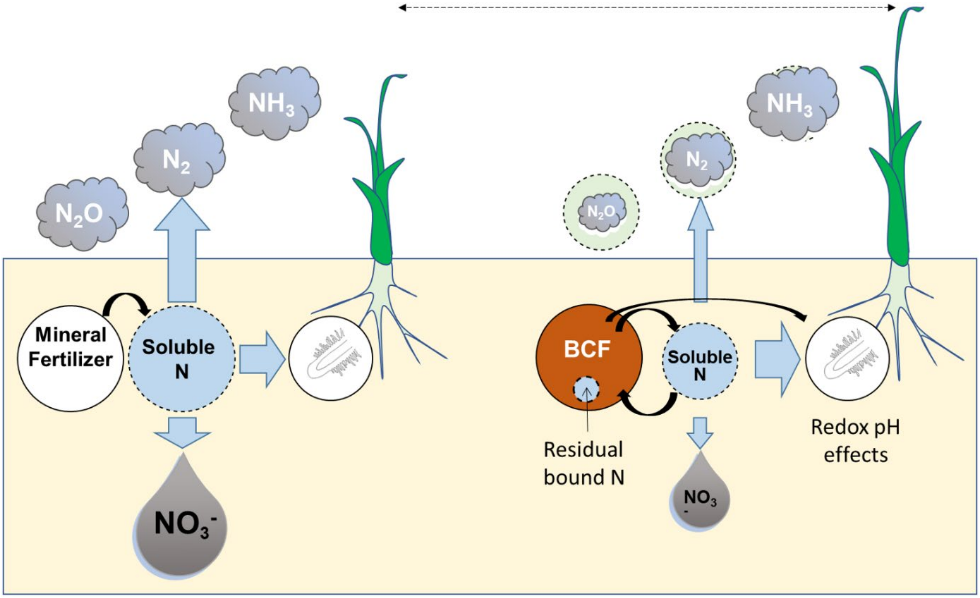

Figure 3. Possible effects of BCF vs. mineral fertilizer on the N-fluxes in an agricultural field. General effects of biochar as soil improvement are not considered as they are not specific to BCF products.

Increase in NUE with BCF has largely been attributed to a putative slow-release effect that biochar matrices have on N fertilizers (Ibrahim et al. 2020). A fertilizer is considered as slow release if it releases less than 15 % and 80 % of its N after 24 h and 28 d, respectively (Jia et al. 2020). A slow-release effect can be obtained either with fertilizer products of limited solubility (ISO. 2015) or through coating with a protective layer that requires hydrolysis and/or biodegradation before the fertilizer is released (ISO 2015; Xiang et al. 2020). Biochar has been tested as an ingredient in coating material for urea, showing promise for improving the slow-release effect, especially when using high-temperature biochars with high surface area (Jia et al. 2020). However, the use of a traditional protective coating on top of the biochar layer appears crucial for obtaining this slow release effect (Jia et al. 2020). Examples of such coatings include starch and polyvinyl alcohol, which have been successfully used to produce slow-release BCFs (Dong et al. 2019; Gwenzi et al. 2018; Liao et al. 2020; Liu et al. 2019b).

Biochar properties supporting fertilizer-based functions

Biochar is often reported to be an exceptional product for retaining nutrients in soils due to its high cation exchange capacity (CEC) and high porosity (Liang et al. 2006; Lychuk et al. 2015; Wong et al. 2019). Assuming that this widely held view is true, a logical hypothesis is that biochar should also make an outstanding support for delivering nutrients to plants in the form of compound fertilizers. Exploring this hypothesis requires first a better understanding of the nature of the CEC and porosity of biochars.

Biochar surfaces can exchange both anions and cations, with the CEC increasing with pH while the anion exchange capacity (AEC) displays the opposite response (Lawrinenko and Laird 2015). The CEC of biochar results from oxygenated functional groups on biochar surfaces such as carbonyl, carboxyl and hydroxyl groups (Suliman et al. 2016). Untreated biochars are high pH products, mostly in the 8-10 pH range (Budai et al. 2014). At desirable pH values for agricultural soils, the CEC largely predominates over the AEC (Silber et al. 2010). Although some of the AEC appears pH independent, its contribution to total ion exchanges remains low (Lawrinenko and Laird 2015; Silber et al. 2010). For this reason it may be expected that biochar capacity for adsorbing cationic nutrients will be of greater significance for the development of a nutrient rich BCF, and therefore we specifically address the CEC of biochar in the following section. Higher CEC values are caused by an abundance of functional groups, while the process of pyrolysis under increasing treatment temperature is largely one of aromatization at the cost of functional groups. This is why the highest CEC of biochar products is often obtained at a fairly low treatment temperature, ~400°C for slow pyrolysis conditions (Amin 2020; Budai et al. 2014; Kameyama et al. 2017; Singh et al. 2020; Wu et al. 2012). It also explains why hydrothermal carbonization and low-temperature carbonization products, obtained at about 250°C, often exhibit a high CEC (Amin 2020; Budai et al. 2014; Mukherjee et al. 2011). However, the stability in soils of ~250°C pyro- and hydrochars is at least an order of magnitude lower than that of biochar produced over 370°C (Budai et al. 2016), making the former products unusable for carbon-sequestration co-benefits.

Ageing in soils increases the CEC of biochars (Lehmann 2007). This effect is attributable to the increased oxidation of surface groups (Liang et al. 2006) and possibly to the binding onto biochar of high-CEC molecular structures having properties similar to those of humic acids (Liang et al. 2006; Wiedner et al. 2015). Very high CEC of biochar has been inferred from the properties of aged charcoal in soils (Liang et al. 2006), while the CEC of fresh biochar is usually rather low (Budai et al. 2014). Studies looking at the short-term increase in the CEC of soil following high-dose biochar application report either no increase (Basso et al. 2013) or only modest increases (Laird et al. 2010), with the largest relative increases reported for soils very low in clay and soil organic carbon and hence low CEC (Cornelissen et al. 2013). It is therefore crucial not to confuse the CEC of fresh biochar with that of its aged forms in soils, especially as we know little about the dynamics and timeframe of the oxidation and loading processes in soils (Lehmann 2007) or organic environments (Hagemann et al. 2017b; Prost et al. 2013). However, observations of biochar in soils have interesting implications for biochar-fertilizer applications, specifically the possibility to increase the CEC of biochar through artificial oxidation and/or coating with high CEC organics, as discussed later.

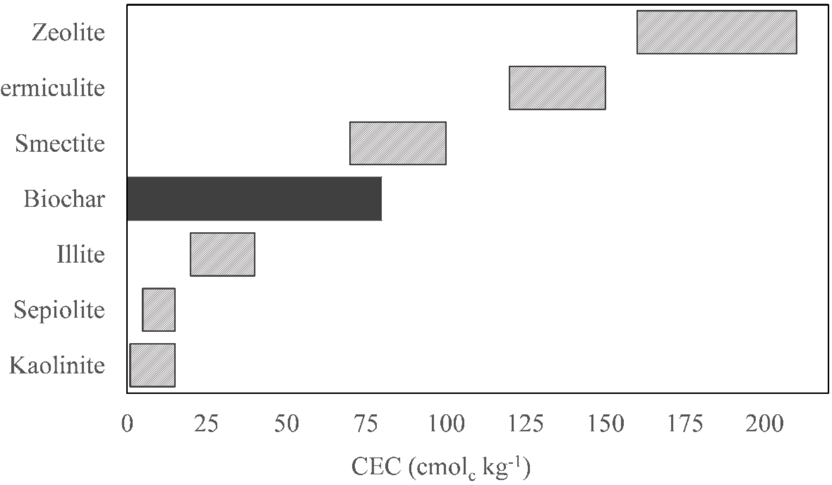

Figure 4. Range of cation exchange capacity (cmol$_c$ kg^{-1}) of various minerals (Koon and Kaufman 1975; Christidis 2013) and biochar (edited from Zwart (2020))

Biochars have a CEC up to 80 cmol$_c$ kg^{-1}, which is considerably lower than that of smectite and vermiculite clays and zeolites (Fig. 4.) (Zwart 2020). Reported CEC of biochar products is quite variable (Table S2, Fig. 5.) due to factors affecting the surface properties of biochar, such as feedstock type and pyrolysis temperature (Mukherjee et al. 2011), but also due to variability and errors in the analytical methods (Munera-Echeverri et al. 2018). Clay minerals and zeolites are known to be effective sorbents for inorganic cations including ammonium from various solutions, due to their high CEC and high specific surface area (Abollino et al. 2008; Christidis 2013). Figure 4 shows that clay minerals cover a wide range of CEC, with kaolinite at the lower end (up to 15 cmol$_c$ kg^{-1}) and vermiculate at the higher end (up to 150 cmol$_c$ kg^{-1}) (Christidis 2013; Shainberg and Levy 2005). Zeolites display even higher CEC values, reaching up to 210 cmol$_c$ kg^{-1} (Koon and Kaufman 1975). Hence, they are extensively used for ammonium removal from wastewaters (Beler Baykal 1998), and also for the recovery of nutrients from various organic waste streams such as human urine (Beler Baykal et al.

2009; Ganrot et al. 2008) and animal manure digestate, retaining up to 25 mg g^{-1} ammonium (Kocatürk-Schumacher et al. 2017b).

In the literature, biochar has often been proposed as a high CEC product, while reporting values that are actually quite modest, such as 18 $cmol_c$ kg^{-1} (Lychuk et al. 2015). By contrast, other natural minerals largely exceed such values (Fig. 4.). The limited CEC of biochar consequently appears to restrict its ability to retain ammonium as compared to some other sorbents (Kocatürk-Schumacher et al. 2017a). This is confirmed by several studies reporting higher removal of ammonium from solutions and a higher concentration of nutrients in the sorbent with zeolite as compared to biochar (Carey et al. 2015; Hina et al. 2015; Kocatürk-Schumacher et al. 2017a).

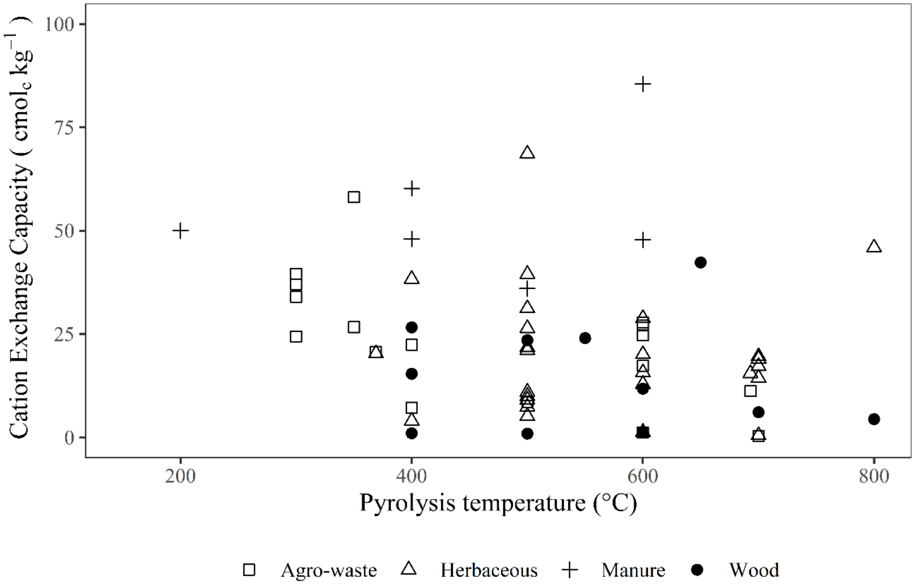

Figure 5. Cation exchange capacity of several biochars produced from various feedstocks and at various pyrolysis temperatures. Based on the studies; Budai et al. (2014), Cui et al. (2016), Gai et al. (2014), Hale et al. (2011), Huff et al. (2018), Jassal et al. (2015), Kocaturk-Schumacher et al. (2019), Li et al. (2018), Mia et al. (2017), Munera-Echeverri et al. (2018), Singh et al. (2020), Zeng et al. (2013), Zheng et al. (2017).

The magnitude of N sorption on biochar surfaces

We undertook a detailed search of the literature to identify studies that quantified the sorption of NH_4^+ and NO_3^- on biochar surfaces based on batch studies (Table S3 and S4). Batch studies are valuable because they represent a highly repeatable and controlled measure for the sorption properties of a material. Our focus was to examine the maximum sorption potential of unmodified biochar across a range of feedstock and pyrolysis temperatures. We converted all values, where necessary, to mg NO_3-N or NH_4-N per g biochar.

A recent meta-analysis of sorption studies conducted on untreated biochar reported an average maximum sorption potential of 11.2 and 1.78 mg N g^{-1} biochar for NH_4^+ and NO_3^- respectively, based on the modelled estimate provided by the Langmuir coefficient Q_{max} (Zhang et al. 2020b). Here, we extend this data set with values reported from single concentration batch studies.

The results for NH_4^+ and NO_3^- maximum sorption potentials reported in the literature are highly skewed (Table 4), suggesting that the median value is a more reliable estimate than the mean. Across studies, the median sorption potential is modest, i.e. 5.58 mg g^{-1} for NH_4-N and 0.18 mg g^{-1} for NO_3-N. However, for both ions, we see relatively higher values reported in individual studies of up to 189 mg g^{-1} NH_4-N (Gao et al. 2015) and 21.6 mg g^{-1} NO_3-N (Jassal et al. 2015).

Table 4. Median values and variability across studies published until January 2021 for the maximum sorption potential of biochar for NH_4^+ and NO_3^- derived from the batch sorption methodology in binary systems.

	0%	25%	Median	75%	100%
NH_4^+- N (mg g^{-1})	-4.03	1.99	5.58	23.8	189.2
NO_3^-- N (mg g^{-1})	-0.08	0.03	0.18	2.68	21.6

Fig. 6. (a,b,c,d) shows that source article (represented by colour) may have a greater impact on the maximum nutrient sorption than either BC highest treatment temperature (HTT) or choice of feedstock. Studies that measure high values report results of similar magnitude across both BC HTT and feedstock gradients, such as in Gao et al. (2015) and Takaya et al. (2016). This may reflect the importance of the experimental set-up and methodology for quantifying N sorption on biochar surfaces, which is deceptively complex. For example,

Wang et al. (2015) showed that NH_3 volatilisation, due to alkalisation by high pH biochar, could result in overestimates of the true sorption potential of char for NH_4^+ by as much as 39%.

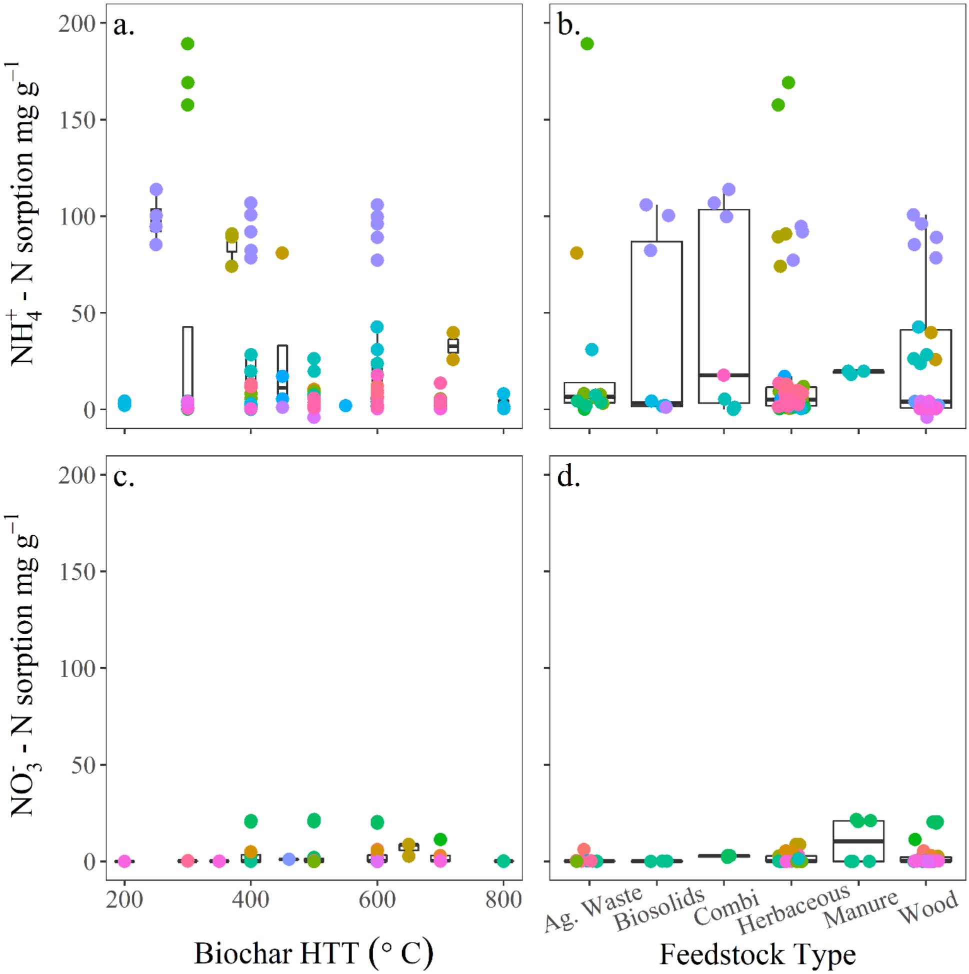

Figure 6. a, b: NH_4^+ maximum sorption. c, d: NO_3^- maximum sorption. a, c: Feedstock type. b, d: BC HTT. Point colours group by study. Feed type defined after Cayuela et al. (2014).

The apparent strong effect of study methodology on the maximum sorption potential of NH_4^+ and NO_3^- makes it difficult to define an accurate value or predict which feedstock or BC HTT combination will yield the best results. It is not clear whether the few high-sorption values in the dataset are outliers due to methodology or if they represent an actual potential (Fig. 6). Repeating such studies would be highly valuable. Due to the high variability and method-dependency of the data, we consider that a conservative estimate for maximum sorption potential of biochar lies between the lower and upper quartiles of the dataset, i.e. 2 – 24 and 0.03 – 3 mg N g^{-1} for NH_4^+ and NO_3^- respectively. Based on these estimates and a required annual fertilisation of 120 kg N ha^{-1} this would result in an expected application rate of between 60 to 5 t ha^{-1} and 4000 to 40 t ha^{-1} of biochar charged with either NH_4^+ or NO_3^- respectively, assuming individual application of either NH_4^+ or NO_3^-.

The importance of surface area and porosity

The high porosity and high surface area of biochars is often quoted as a key element supporting a high exchange capacity for nutrients (e.g. Lychuk et al. (2015)). However, the porosity of biochar is difficult to characterize and study because pore diameters span five orders of magnitude (Brewer et al. 2014). Biochar has a macroporosity inherited from the structure of the plant material it was made from, typically from a few microns to a few tens of micron. This macroporosity is crucial for increasing the retention of plant-available water in soils (Cornelissen et al. 2013; Obia et al. 2016), which is a key beneficial effect of biochar in soils (Razzaghi et al. 2020). This macroporosity, which is inherited from the plant structure, does not appear to be influenced by pyrolysis temperature (Hyvaluoma et al. 2018). Large amounts of solution can remain entrapped in the both the macro and the mesopores of biochars. When considering making BCF, this solution can be a highly concentrated fertilizer solution, which can possibly dry out as concentrated fertilizer deposits in biochar pores. Since the macro-, meso- and nanopores of biochars constitute a labyrinthine structure, asymmetric, hydrated molecules such as nitrate may need time to diffuse from an inner site within a biochar particle to the outside (e.g. alongside a gradient built up by plant roots), depending on moisture and temperature conditions around and in the particle (Conte et al. 2014). The different pore sizes in biochar particles may also separate nutrients in some macropores, mesopores and nanopores from microbial access, since microbes (mostly above 1 µm diameter) will not be able to access such small pores, while plant roots in the vicinity of biochar particles might be able to build up ion-concentration gradients to empty such pores. Such a ‘mole sieve’ effect of biochar, excluding denitrifiers, is one of many explanations for the reduction of N_2O emissions observed when biochar is applied to soil (Borchard et al. 2019; Kammann et al. 2012; Kammann et al. 2015).

Nanoscale porosity governs sorption dynamics and is borne by nanometric to sub-nanometric pores in the polyaromatic structure of biochars (Brewer et al. 2014). This porosity is generally estimated through gas sorption methods, with CO_2 for pores less than a nanometer and N_2 for larger ones (Brewer et al. 2014). There is increasing evidence that, rather than surface area, it is ion exchange mechanisms that are largely responsible for the sorption of major N sources such as NH_4^+ (Fidel et al. 2018), NO_3^- (Heaney et al. 2020) and urea (Singh et al. 2020). Therefore, the significance of biochar surface area for the uptake of nutrients appears uncertain.

Although some early studies suggested that the CEC of biochar and its surface area would both increase with pyrolysis temperature (Lehmann 2007), we now know that it is not the case because of the aromatization trade-off between loss of functional groups and gain in surface area (Budai et al. 2014; Singh et al. 2020). It is likely that for NH_4^+, CEC is the dominant factor. For urea sorption, Singh et al. (2020)report that maximum sorption is obtained with BC HTT at 450 °C, and they further argue that this temperature corresponds to an optimum between CEC and surface area for sorption. Slow pyrolysis biochars produced at around 400 °C appear therefore to have the highest potential for sorbing cations such as NH_4^+.

Improvement through acid and base treatments and oxidations

As previously discussed, studies that attempted to sorb nutrients such as NH_4^+ and NO_3^- on untreated biochar structures generally reported fairly low values (Table 4; Fig. 6.). Such low values for N retention on unmodified biochar do not meet expectations for a BCF product. For this reason, efforts have been put into modifying biochar in order to optimise nutrient retention. Several methodologies, including treatments with steam as physical activation, and chemical activation have been proposed to modify both the physical and chemical properties of the biochars (Sizmur et al. 2017). Chemical activation with acids, bases and salts have been undertaken both as the post treatment of biochars and as pretreatments of the biomass prior to pyrolysis (Blackwell et al. 2015).

Interestingly, pre-treatment of biomass before pyrolysis contributes to higher yields of biochar, higher proportions of P, K, S and N compounds, higher C contents e.g. when impregnated with potassium salts (Masek et al. 2019), higher surface area and porosity, as well as a higher concentrations of surface functional groups (Chu et al. 2018). The activation can result in the increased ability of biochar to adsorb cations, anions and organic molecules. Huff et al. (2018) reported that the CEC of pine wood biomass produced at 400 °C doubled from about 15 to 30 $\mathrm{cmol_c\ kg^{-1}}$ through ozone treatment. Acid treatment of biochars enriched with clay and Fe may increase surface area, CEC and silica content through leaching out of impurities and changes to the surface charge (Lin et al. 2013) but further research is needed to verify such findings.

A considerable amount of research has been published over the last 15 years regarding changes in biochar properties as a result of post-pyrolysis activation. Laboratory trials have been carried out using strong acids such as HNO_3 and H_2SO_4 (Liu et al. 2012; Qian and Chen 2014) and weak organic acids such as citric and malic acids (Heaney et al. 2020; Lonappan et al. 2020). Most base treatments have been carried out using NaOH and KOH (Liu et al. 2012; Petrovic et al. 2016) and salt treatments have relied on chlorides (Zhang et al. 2020a).

Activation of biochar using acid and alkali solutions might be expensive at large scale and requires careful disposal of the activation media (Sizmur et al. 2017). Oxidation with hydrogen peroxide (Mia et al. 2017; Wang et al. 2015; Xue et al. 2012) and ozonation (Huff et al. 2018) have also been proposed as alternative post-treatments to increase sorption capacity.

Chemical activation of biochar leads to higher porosity and CEC, more oxygen functional groups as well as a higher concentration of water extractable organic compounds (Lawrinenko et al. 2016; Lin et al. 2012). Asada et al. (2006) reported an increased ammonium sorption up to 10 mg NH_4-N g^{-1} as a result of H_2SO_4 activation of bamboo biochar. Similarly, activation of corncob biochar with both HNO_3 and NaOH resulted in ammonium retention up to 12.8 mg NH_4-N g^{-1} (Nguyen et al. 2019). Wang et al. (2016) reported that the ammonium retention capacity of the most strongly oxidized biochar using H_2O_2 increased to 5 mg NH_4-N $g^{-1,}$ which was >4 times more than the untreated biochar. Even though literature findings suggest an improved ammonium retention on biochar as a result of post- treatment with activation and oxidation treatment, the amount of ammonium retention still appears limited.

In summary, surface treatment of biochar with acids, bases and oxidants has the potential to modify the surface properties of biochar, which can improve nutrient retention. However, there is little research examining the consequences of these treatments on other desirable properties of the BC. Washing of char, especially with strong acids, bases and oxidants has the potential to leach potentially valuable components off the char. This can include the mineral ash, which is largely responsible for the observed liming effect of biochar (Fidel et al. 2017), and dissolved organic carbon (DOC), which could be responsible for mediating sorption of nutrients (Mia et al. 2017) or otherwise stimulating plant growth and development (Liu et al. 2020a). Additionally, severe chemical oxidation may have detrimental effects on the biochar porous structure and could alter its stability in soil (Duan et al. 2019; Li et al. 2019). This means that application of these techniques requires to carefully consider the potential trade-offs associated with these treatments in light of the desirable properties of the BCF.

Improvement through mineral and clay addition

The properties of biochars can be improved through the addition of minerals either as a pretreatment of the biomass or a post treatment of the biochar (Chia et al. 2014; Farrar et al. 2019). Mineral and organo-mineral enhanced biochars have been shown to increase yields at application rates of less than 1 t ha^{-1} (Blackwell et al. 2015). Rawal et al. (2016) found that the addition of clay and iron sulphate to bamboo biomass prior to pyrolysis increased both the concentrations of condensed aromatic, acidic, and phenolic carbon species, and the pore volume of the biochar structures. They also found that iron-oxide nanoparticles formed inside the pores of the biochar and that these were either ferromagnetic at low temperatures or superparamagnetic at higher temperatures. Some of these effects might be beneficial to the N cycle, however they also report that co-pyrolysis with clay and iron increased N volatilization losses from the BCF. Further analysis (Reynolds et al. 2018) showed that the clay and iron pretreatment resulted in an increase in the concentration of water soluble organic compounds, and notably N containing species especially when kaolinite was used. Viglašová et al. (2018) found that pretreating bamboo with montmorillonite and pyrolysing at HTT of 460°C doubled the maximum adsorption of nitrate.

Dieguez-Alonso et al. (2019) reported an increase in micro-porosity and changes in values of redox and Zeta potential of 400 °C and 700 °C softwood biochars when pretreated with $AlCl_3$, $Cu(OH)_2$, $FeSO_4$, KCl, $MgCl_2$ or $Mg(OH)_2$. They also measured an increased adsorption capacity for PO_4^{3-} and NO_3^-, the latter increasing from 0.1 to nearly 2 mg N g^{-1} biochar. Similarly, higher nitrate removal efficiency was obtained by incorporating Mg/Fe double hydroxides into wheat straw biochar (Xue et al. 2016) and Fe/Ni nanoparticles on sugar cane bagasse biochar (Li et al. 2017). Other studies have shown improvements in specific properties by adding zero valent iron, basalt, or amorphous silica.

Clay-biochar composite have been designed and tested for their ability to sorb NH_4^+ (Chen et al. 2017; Huang et al. 2020; Ismadji et al. 2016). Chen et al. (2017) studying a bamboo biochar-montmorillonite composite reported an increase in the maximum sorption capacity for NH_4^+ of 412 % from 2.44 mg g^{-1} to 12.5 mg g^{-1}. In a study by Ismadji et al. (2016) a cassava peal biochar combined with bentonite resulted in a 149 % increase in NH_4^+ sorption, from 9.49 mg g^{-1} to 23.67 mg g^{-1}. Chen et al. (2017) concluded that the addition of clay prior to pyrolysis acted as an acid catalyst, which fostered reduction processes; however they do not report the sorption capacity of the clay alone. Ismadji et al. (2016) identified a composite effect where the combination of BC and bentonite resulted in a higher sorption capacity than the BC and bentonite alone. Yao et al. (2014) reported that clay addition increased the sorption capacity of biochar for methylene blue. They also observed that the effect was more pronounced with bagasse biochar than with bamboo or hickory biochars, and with montmorillonite than kaolinite clay. To increase binding of clay to biochar particles Huang et al. (2020) used Na_2SiO_3. This suggests that the type of clay, the type of char and the binding treatment all substantially influence the sorption capacity of the resulting product. Liao et al. (2020) suggest that bentonite fixed inside biochar pores swells in contact with water and thereby slows down the diffusion of urea from the BCF to the soil solution. The clay treatment does not appear to substantially increase the surface area of the biochar, but it increases its capacity for ion exchange (Yao et al. 2014). When combining chicken manure with biochar through torrefaction, Lin et al. (2013) report that addition of clay helped conserve N in the resulting BCF. The use of bentonite in BCF increased yield while reducing NO_3^- content of pepper plants (Yao et al. 2015). Darby et al. (2016) reported that BCF with clay and chicken manure did not significantly increase N_2O emissions as comparted to the unfertilized control.

Improvement with organic coating

The interaction of biochar with organic matter in soils has long been postulated to have a significant role in the development of biochar effects on plant yield and nutrient retention (Hagemann et al. 2017b; Kammann et al. 2015; Lehmann et al. 2002; Liang et al. 2006; Sarkhot et al. 2013). The organic coating of biochar is often cited alongside other natural aging processes to explain the greater nutrient retention potential of aged biochar (Fischer and Glaser 2012; Hagemann et al. 2017a; Liang et al. 2006). However, so far research has focused primarily on the oxidation of biochar to explain the effects of aging on biochar properties (Liang et al. 2013; Wang et al. 2015). Very little mechanistic work has been undertaken to understand the significance of organic coatings for mediating these effects and how they might be exploited in the creation of a commercially viable BCF. Here we consider what is known about the effects of biochar and organic matter interactions on the uptake and retention of NH_4^+ and NO_3^-.

Ammonium is a prime candidate for sorption to biochar due to both the alkalinity and the generally larger CEC than AEC of biochar. However, as we have already discussed, the CEC of many unmodified biochars is relatively low in comparison to that of soil organic matter. There is some evidence suggesting that the sorption capacity of biochar for NH_4^+ increases when organic molecules rich in functional groups bind to biochar surfaces. Early studies of biochar and NH_4^+ retention report higher retention in solutions containing both NH_4^+ and organic matter (Lehmann et al. 2002; Sarkhot et al. 2013). Sarkhot et al. (2013) observed a two-fold increase in ammonium sorption (up to 5.3 mg NH_4^+ g^{-1} biochar) when biochar was mixed in manure slurry as compared to pure solution of similar NH_4^+ concentration. Similarly, Lehmann et al. (2002) reported increased ammonium adsorption on biochar in the presence of DOC from manure extracts. Increase in ammonium sorption in both studies is explained by co-adsorption of ammonium and dissolved organic matter. Although these organic molecules could also compete for and occlude the same polar functional groups responsible for the biochar CEC, it is thought that the net result is an increase in the sorption capacity of the biochar for plant nutrients (Conte and A. Laudicina 2017). How to translate and optimize this effect in an industrial process is a key research question for making high-sorption BCFs.

As we have already noted, untreated biochars are usually alkaline and carry predominantly negatively charged surfaces that do not favour adsorption of anions; thus, biochars have in general very low nitrate or phosphate adsorption/retention capacity (Hale et al. 2013; Hollister et al. 2013). On the other hand, a meta-analysis of 120 datasets revealed that biochar consistently and significantly reduced nitrate leaching in studies longer than 30 days, with more pronounced effects for biochars with high C/N ratios and production temperature >500 °C (Borchard et al. 2019). A reconciling hypothesis, supported by recent studies, is that nitrate retention capacity of biochars can increase in the presence of organic substrates or low-molecular weight organic acids, both in lower-pH solution and in soils over time.

Soils amended with large quantities of biochar (1.5 to 6% w/w) have been shown to retain nitrate as compared to no-biochar controls (Chen et al. 2019; Haider et al. 2015). Khan et al. (2016) demonstrated that the CEC of biochar increased during co-composting for a hardwood-shaving biochar from about 3 to about 18 $cmol_c$ kg^{-1}. Prost et al. (2013) showed that the surfaces of co-composted biochar acquired dissolved organic molecules and nutrients from the compost. Kammann et al. (2015) observed that a co-composted wood biochar increased plant growth as compared to a no-biochar control, while an untreated biochar did not. The authors further demonstrated that the co-composted biochar had captured both anionic and cationic nutrients, with the largest fraction as nitrate (up to 5.3 g nitrate-N kg^{-1}). The latter was slowly released with electro ultrafiltration or with repeated water and KCl extractions. The cumulative nitrate and also phosphate release was highly correlated (with $R^2>0.99$) to the concomitant release of DOC from the co-composted biochar particles (Kammann et al. 2015). Hagemann et al. (2017c) confirmed this nitrate "capture" phenomenon with different woody and sewage-sludge biochars, with a ~700 °C wood biochar having the largest effect. Hagemann et al. (2017b) were able to demonstrate that an organic coating rich in N and N-containing functional groups forms on biochar particles during co-composting, and Joseph et al. (2018) showed that clay minerals and organo-mineral complexes improve the ability of biochar particles to capture nutrients. Nitrate anions may be trapped in DOC- or clay-clogged biochar nanopores, retarding their release to the surrounding soil (Joseph et al. 2018).

The results reported here may serve as a starting point to develop biochar products with enhanced environmental N effects, such as reduced nitrate leaching and N_2O emissions. However, the positive effects of organic coatings on nitrate retention reported here have generally been obtained in studies using large biochar applications (>1 w/w %). Although some studies report large relative enhancements of nitrate retention, the values obtained remain low in absolute terms (below 5 mg NO_3-N per g biochar). The same applies to increased NH_4^+ retention, the increase is comparatively large but remains limited in absolute values. Biochar coated with organics are currently in the low range of biochar/N ratio when considering BCFs (Fig. 6.), and substantial improvement would be needed towards actual fertilizer applications. The technology of organic coatings might be better suited for biochar amendments for environmental applications than for BCFs, but at this point we know too little to exclude that significant breakthroughs could be made towards BCF applications, and more research is clearly needed on this topic.

Biochar-mediated uptake of nutrients

As we have previously discussed, BCF can increase the NUE of plants (Chen et al. 2019; Shi et al. 2020; Zeng et al. 2013). This increase can result in part from the many positive effects that biochar has in soils, such as increasing water-holding capacity, nutrient retention and increased pH. Such improvements can lead to apparent increases in NUE, i.e. bigger plants absorb larger quantities of N to grow. However, these effects are not specific to BCF products, but to biochar in general. We have also seen that a main effect of BCF on NUE is thought to be mediated by the sorption and retention of N on biochar surfaces, thereby improving the soil N cycle. However, sorption-like processes are not the only possible mechanisms leading to an enhancement of NUE with BCF. In this section we investigate how biochar applied in fairly low amounts like in BCF may trigger plant responses that also result in a more efficient uptake of nutrients by crops.

Nutrient availability in soil is affected by microbial communities (Brussaard et al. 2007), which can be affected by the presence of biochar (Budai et al. 2016). This suggests that the interaction between BCF and soil microbes might affect the availability of native soil nutrients as well as the uptake of the nutrient applied with the BCF. Ye et al. (2016) observed that a biochar-treated compost increased total soil nitrate more than compost alone, and attributed this effect to the stimulation of soil nitrifier populations. In the same study, however, they also noted that biochar/compost addition, which had a relatively high pH, reduced the amount of plant available P. Similar studies also revealed that BCFs applied at low rates (100-1000 kg ha^{-1}) can increase root colonization by arbuscular mycorrhizal fungi (Blackwell et al. 2015), increase the abundance of nitrogen fixing bacteria and increase the bioavailability of phosphate, potassium and nitrogen (Nielsen et al. 2014). Chew et al. (2020) measured an increase in rice biomass using a BCF containing urea, Fe_2O_3 and apatite. They attributed this effect to increased soil pH, Eh and a shift in microbial community composition. They also discovered that the BCF treatment induced changes to the root membrane potential of the rice, which they hypothesized resulted in greater potential nutrient uptake by the plant.

In addition to the proposed biochar effect on root uptake, studies have also measured an increase in root development following biochar addition (Xiang et al. 2017). This is especially true in infertile soils or in rain fed regions, where more abundant root hairs can increase the ability of plants to access nutrients in soil (Liu et al. 2020b). There is some discussion regarding the mechanism by which biochar stimulates root development. The most basic explanation is that the biochar addition alters soil physical properties allowing better root development without the adverse effects of physical barriers such as soil compaction (Omondi et al. 2016). However, recent studies have suggested that the soluble components of biochar may play a more important role in stimulating plant root growth following biochar addition (Kolton et al. 2017; Lou et al. 2016). Liu et al. (2020a) investigated the effect on maize growth of different biochar components such as water-soluble biochar extract, mineral nutrients in ash and washed biochar. They found that the addition of water-soluble biochar extract promoted maize growth accompanied with greater root size, longer root hairs and more root tips. It was hypothesized that this effect was due to the presence in the biochar of hormone-like substances, which promoted root development. However, further studies are needed to verify this effect using a range of soil conditions, different biochar feedstocks and pyrolysis conditions.

Implications for biochar-based fertilizer design

Sorption and desorption of N on biochar surfaces is a rapid process often occurring on timescales of less than a day (Kizito et al. 2015; Wang et al. 2020). This suggests that, contrary to coating technology, desorption is not a suitable mechanism for slow-release effects on the time scale needed for agricultural purposes. Despite this, sorption of mineral N on biochar surfaces is often cited as a process that also generates slow-release effects (Cai et al. 2016; Dong et al. 2019; Ibrahim et al. 2020; Manikandan and Subramanian 2013). Kang et al. (2018) have shown that the kinetics of sorption of hydrophobic organic compounds is considerably slowed down as the size of biochar particles increases, suggesting that large biochar-fertilizer particles might experience reduced desorption rates. In some instances, desorption of NH_4^+ and NO_3^- from biochar appears incomplete at the first extraction (Gong et al. 2019; Haider et al. 2016), suggesting that desorption might require successive steps. In a soil environment, alternate wetting and drying cycles could regularly disrupt diffusion out of biochar particles, suggesting that a slow-release effect might be generated through limited desorption-diffusion from larger biochar-fertilizer particles in soils. However, a strongly bound N fraction remaining in the biochar structure by the end of plant growth would reduce N-use efficiency, at least in the first year of application. The kinetics of N release from BCF in soils in relation to soil parameters such as moisture and soil properties is understudied and not well understood, and should be a research priority.

A universal BCF recipe would require an ideal biochar, activated and/or enhanced, adsorbing very large quantities of nutrients, notably N forms, and then desorb these nutrients in soil in a slow release fashion. Such an ideal product would work both for mineral and organic sources of nutrients. The fundamental property of this biochar would be outstanding sorption capacity potentially borne by superior values for CEC and surface-area and inducing a slow-release desorption. As we have seen in this review, such a product does not exist and might not be achievable within the techno-economic constraints of fertilizer production. The CEC of current biochar products is too low to make concentrated fertilizer products based on sorption processes alone, and activation methods would need to increase CEC by one or two orders of magnitude to result in sufficiently concentrated fertilizer products (Fig. 7), while current studies generally report only modest increases. In addition, subjecting biochar to oxidative and acid treatments might negatively impact its long-term stability in soil (Duan et al. 2019), a risk that needs to be better evaluated. Enhancement of sorption with higher CEC products such as clay appears more promising, but remains below desirable values for future sorbents, which should display BC:N ratios between 50:1 to 5:1 (Fig. 7). Limitations of the total sorption capacity and the slow release effect must be carefully considered when designing biochar-fertilizer products.

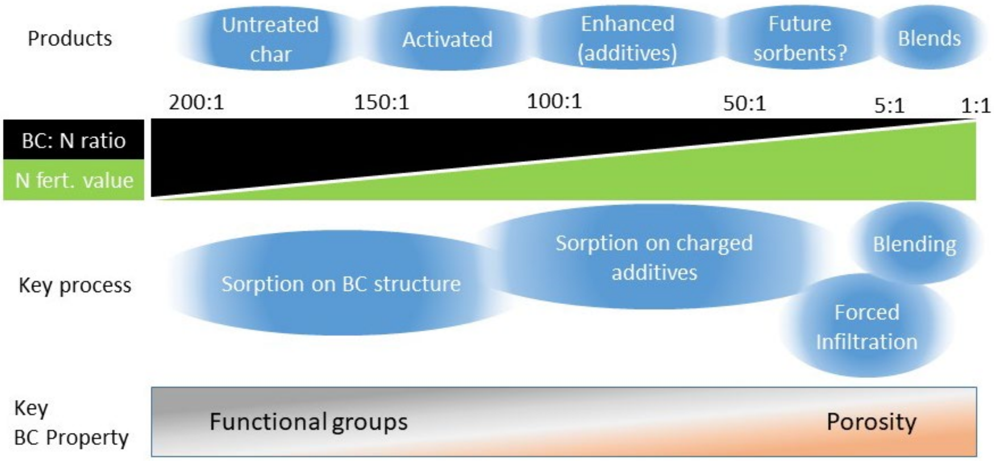

Figure 7. Schematic representation of the amount of biochar needed fix one unit of N, its fertilization value, and the corresponding products, key processes and biochar properties.

Separate technologies will need to be developed for BCFs made with concentrated nutrient sources (mostly mineral) on the one hand, and for applications aiming at recycling N forms from organic waste streams, such as manures, slurries and digestate, on the other hand. A balanced mineral NPK fertilizer contains typically 15 % N, thereby requiring application rates of about 1 ton ha^{-1} for delivering 150 kg N ha^{-1}. For a concentrated fertilizer product, for example in pellet or granule form, a 50% biochar mix is likely an upper limit, i.e. one ton of biochar per ha. Current concentrated BCFs contain as little as 20 % biochar in the fertilizer mix (Shi et al. 2020). For such products, the main effect is not thought to come from adsorption of nutrients, but would rather result from root-growth promoting factors, increases in soil pH and Eh and stimulation of beneficial micro-organisms, which all result in an increase in uptake of specific nutrients. By contrast, biochar products aiming at capturing N forms from organic waste streams, such as manures, slurries and anaerobic digestates, need to be applied at higher rates. Assuming an enhanced biochar consistently adsorbing 20 g NH_4-N per kg, i.e. 4 times that of the current median values (Table 4), application rates would approximate 8 t biochar per ha for a standard fertilization of 150 kg N per ha.

Our conclusions also highlight a need to reevaluate which biochar properties should be targeted for improvement in order to produce BCFs. Many recent studies have focused on CEC, sorption capacity and surface area of biochar structures, however the importance of these properties for BCF production might have been overstated. In the case of physical blends, sorption processes are not supportive of very high nutrient loading. More importantly, this might also be the case for applications geared towards sorption of nutrients from organic waste streams. As we have seen, the CEC of the carbonaceous structure of untreated biochar is fairly low, and improvement through activation for adding functional groups has only limited impact. A more promising venue seems to be the addition of high-CEC clay and organic additives, as suggested by studies of the naturally-occurring coating of biochars in soils and compost (Hagemann et al. 2017b; Kammann et al. 2015) and clay effects on BCF properties (Viglašová et al. 2018). In this context, porosity appears as a key property controlling the coating of clay and organics within biochar structures. The most commonly reported porosity is microporosity, which is routinely measured through BET surface area methods. However, as we have previously discussed, microporosity is most relevant for sorption of gasses and small molecules. By contrast, a high macroporosity, i.e. the porosity partially inherited from the biomass structure, might be essential for mass loading of larger organic and mineral structures within biochars and also possibly for microbial colonization, which might facilitate coating processes. High macroporosity might also be key for adding specific products in concentrated BCFs, such as those based on infiltration of molten urea in biochar particles (Xiang et al. 2020). Cleary, more research is needed on optimizing the macroporosity of biochar toward making N-efficient BCFs.

The value of biochar as a fertilizer additive has largely been placed on its ability to retain nutrients, mostly through mechanisms broadly referred to as sorption. However, our current analysis does not support such a paradigm. There is little doubt that quality slow-release BCFs can be produced through well proven encapsulation and coating technology (Sim et al., 2021), however it is much less clear that the added-value of biochar in such products is directly linked to their intrinsic capacity to retain nutrients. We do no question that aging biochar in soils can play an important environmental role through retaining low-concentration nutrients, but these environmental applications are quite far from those of BCF, which require an immediacy of production and the fixation of concentrated fertilizer sources.

In order to make progress with developing BCF technology, we need to better understand the non-nutrient-retention benefits of low-dose biochar in soils, such as hormone-like effects and microbial and redox effects. At the same time, we should not give up on reaching substantially higher nutrient retention capacity, because enhanced biochars will be key to recycling N in organic waste streams, which is a highly desired outcome for sustainable agriculture and a circular economy. This will most likely be reached through clay and organic additives, for which macroporosity might be an overlooked key parameter.

Evaluating biochar products with the goal of making BCF is a challenging task, as the nutrient retention capacity and the release dynamics need to be precisely quantified and linked to biochar properties. Faced with this difficulty, the majority of studies appear to report relative effects, e.g. relative to an initial dose or to a control, but do not attempt quantitative budgeting applicable to realistic agronomic treatments. For this reason, a cursory read though the literature gives a false sense that high sorption BCF could easily be developed with existing products. By contrast, to support the development of this technology, we need standardized and quantitative methods for measuring nutrient retention and release dynamics and link these to biochar properties. Mechanisms of action and dose responses need to be more systematically studied in order to devise products that combine positive effects and can be used within realistic agronomic management practices.

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Supplementary information: Enhancing plant N uptake with biochar-based fertilizers: beyond sorption

Supplementary information contains the results of 4 separate literature reviews. All literature reviews were undertaken using the web of science and a cut-off date of December 2020. Literature reviews were conducted on the following topics:

1. Studies that quantify the yield effects of Biochar Compound Fertiliser (BCF).
2. Studies quantifying the Cation Exchange Capacity (CEC) of fresh unmodified biochar.
3. Studies quantifying the sorption capacity of fresh unmodified biochar for NH_4^+-N based on the batch sorption technique in synthetic solutions.
4. Studies quantifying the sorption capacity of fresh unmodified biochar for NO_3^-‾N based on the batch sorption technique in synthetic solutions.

Table S1. Percentage yield change in a variety of crops due to BCF application compared to a fertilized control

Crop type	BCF ingredients	BCF app. rate (kg ha^{-1})	BCF-N (%)	Crop yield change (%)	Author
Rice	200 g DM wheat straw, 15 g urea, 15 g betonite, 5 g Fe_2O_3, 5g $FeSO_4.7H_2O$	NA	2.7	67	Chew et al. 2020
Wheat	BMC5: 30% biochar, 36% clay, 23% chicken litter, 11% minerals $CaCO_3$, rock	100	1.2	45	Joseph et al. 2015

Crop type	BCF ingredients	BCF app. rate (kg ha^{-1})	BCF-N (%)	Crop yield change (%)	Author
	phosphate, $MnSO_4$, Ilmenite				
Wheat	BMC5: 30% biochar, 36% clay, 23% chicken litter, 11% minerals $CaCO_3$, rock phosphate, $MnSO_4$, Ilmenite	200	1.2	22	Joseph et al. 2015
Wheat	BMC6: 30% biochar, 36% clay, 23% chicken litter, 11% minerals $CaCO_3$, rock phosphate, $MnSO_4$, Ilmenite	100	0.97	46	Joseph et al. 2015
Wheat	BMC6: 30% biochar, 36% clay, 23% chicken litter, 11% minerals $CaCO_3$, rock phosphate, $MnSO_4$, Ilmenite	200	0.97	23	Joseph et al. 2015
Wheat	BMC7: 30% biochar, 36% clay, 23% chicken litter, 11% minerals $CaCO_3$, rock phosphate, $MnSO_4$, Ilmenite	100	1.3	0	Joseph et al. 2015

Crop type	BCF ingredients	BCF app. rate (kg ha^{-1})	BCF-N (%)	Crop yield change (%)	Author
Wheat	BMC7: 30% biochar, 36% clay, 23% chicken litter, 11% minerals $CaCO_3$, rock phosphate, $MnSO_4$, Ilmenite	200	1.3	45	Joseph et al. 2015
Wheat	BMC8: 30% biochar, 36% clay, 23% chicken litter, 11% minerals $CaCO_3$, rock phosphate, $MnSO_4$, Ilmenite	100	1	10	Joseph et al. 2015
Wheat	BMC8: 30% biochar, 36% clay, 23% chicken litter, 11% minerals $CaCO_3$, rock phosphate, $MnSO_4$, Ilmenite	200	1	44	Joseph et al. 2015
Rye grass	Biochar and Anaerobic digestate (10 mg NH_4^+-N g biochar)	NA	1	-18	Kocatürk-Schumacher et al., 2019
Rye grass	Biochar and Anaerobic digestate (10 mg NH_4^+-N g biochar)	NA	1	-33	Kocatürk-Schumacher et al., 2019

Crop type	**BCF ingredients**	**BCF app. rate (kg ha^{-1})**	**BCF-N (%)**	**Crop yield change (%)**	**Author**
Rye grass	Biochar and Anaerobic digestate (40 mg NH_4^+-N g biochar)	NA	4	-20	Kocatürk-Schumacher et al., 2019
Rye grass	Biochar and Anaerobic digestate (40 mg NH_4^+-N g biochar)	NA	4	-40	Kocatürk-Schumacher et al., 2019
Zea Mays	50 g Biochar, 25 g urea (aqueous), 50 g fast pyrolyis oil (final mixture weight after heating 88 g)	?	6.9	-11	Magrini-Bair et al. 2009
Zea Mays	EB7: H_3PO_4 activated biochar, 30% chicken litter, 30% kaolin clay, rock phosphate , basalt dust and dolomite	1100	0.62	1.9	Nielsen et al. 2014
Zea Mays	EB17: H3PO4 activated biochar, 30% chicken litter, 30% kaolin clay, rock phosphate , basalt dust and dolomite	5440	1.24	1.2	Nielsen et al. 2014

Crop type	**BCF ingredients**	**BCF app. rate (kg ha^{-1})**	**BCF-N (%)**	**Crop yield change (%)**	**Author**
Zea Mays	51% Biochar, 22% urea, 22% betonite, 5% maize flour	?	10	21	Puga et al. 2020
Zea Mays	40% Biochar, 33% Urea, 22% betonite, 5% maize flour	?	17	8	Puga et al. 2020
Zea Mays	29% Biochar, 44% urea, 22% betonite, 5% maize flour	408	20	-2	Puga et al. 2020
Rice	Manure compost BC, $(NH_4)_2(HPO_4)$, KCl, bentonite	450	18	13	Qian et al. 2014
Rice	Maize straw BC, $(NH_4)_2(HPO_4)$, KCl, betonite	450	18	10.4	Qian et al. 2014
Rice	Municipal waste BC, $(NH_4)_2(HPO_4)$, KCl, bentonite	450	18	31	Qian et al. 2014
Rice	Peanut husk BC, $(NH_4)_2(HPO_4)$, KCl, betonite	450	18	28	Qian et al. 2014
Zea Mays	Biochar, urea, bentonite, sepiolite (ratio 5:10:6:3) were mixed and stabilized	?	16	14	Shi et al. 2020

Crop type	BCF ingredients	BCF app. rate (kg ha^{-1})	BCF-N (%)	Crop yield change (%)	Author
	as firm aggregated granules, then the mix was sprayed with wood vinegar				
Pakchoi	H_3PO_4 activated biochar, 30% chicken litter, 30% kaolin clay, rock phosphate , basalt dust and dolomite + compost	1500	1	-7.9	Ye et al. 2020
Zea Mays	Biochar, $(NH_4)_2(HPO_4)$, KCl, bentonite	?	18	10.7	Zheng et al. 2017
Wheat	30% biochar, 23% chicken litter, 36% kaolin clay, 11% CaCO3, Rock phosphate, Ilmenite, $MnSO_4$	5000	1.2	16	Blackwell et al. 2015
Sorghum	Biochar, clay, organic matter + microbe mix	300	1.2	0	Blackwell et al. 2015
Wheat	Biochar and Urea and coated with sodium alginate, cellulose, acetate and ethyl cellulose	?	26	-17	Gonzalez et al. 2015

Table S2. Cation exchange capacity of several biochars produced from various feedstocks and at various pyrolysis temperatures.

Feedstock	BC HTT (°C)	CEC ($\mathrm{cmol_c\ kg^{-1}}$)	Reference
Corncob	369	20.7	Budai et al., 2014
Corncob	693	11.2	Budai et al., 2014
Miscanthus	369	20.3	Budai et al., 2014
Miscanthus	693	15.5	Budai et al., 2014
C. indica	500	26.4	Cui et al., 2016
P. purpureum Schum	500	39.5	Cui et al., 2016
T. dealbata	500	10	Cui et al., 2016
Z. caduciflora	500	7.4	Cui et al., 2016
P. australis	500	11	Cui et al., 2016
V. zizanioides	500	9.1	Cui et al., 2016
Wheat straw	400	4	Gai et al., 2014
Wheat straw	500	5.1	Gai et al., 2014
Wheat straw	600	1.3	Gai et al., 2014
Wheat straw	700	0.5	Gai et al., 2014
Corn straw	400	38.3	Gai et al., 2014
Corn straw	500	68.6	Gai et al., 2014
Corn straw	600	20.1	Gai et al., 2014
Corn straw	700	19	Gai et al., 2014
Peanut shell	400	7.2	Gai et al., 2014
Peanut shell	500	8.5	Gai et al., 2014
Peanut shell	600	1.2	Gai et al., 2014

Feedstock	BC HTT (°C)	CEC (cmol$_c$ kg^{-1})	Reference
Peanut shell	700	0.3	Gai et al., 2014
Corn stover residues	600	27.8	Hale et al., 2011
Cacao shell	300	37	Hale et al., 2013
Corn cob	300	34	Hale et al., 2013
Pine wood	400	15.4	Huff et al., 2018
Poultry litter	400	48	Jassal et al., 2015
Poultry litter	500	36	Jassal et al., 2015
Poultry litter	600	47.8	Jassal et al., 2015
Spruce, pine, fir wood	400	1	Jassal et al., 2015
Spruce, pine, fir wood	500	0.9	Jassal et al., 2016
Spruce, pine, fir wood	600	1.3	Jassal et al., 2017
Holm oak wood	650	42.3	Kocatürk et al., 2019
Switchgrass	800	45.9	Li et al., 2018
Biosolids	800	14.5	Li et al., 2018
Water Oak	400	26.6	Li et al., 2018
Water Oak	800	4.4	Li et al., 2018
Eucalyptus	550	24	Mia et al., 2017
Pigeon pea	600	27.1	Munera-Echeverri et al., 2018
Cacao shell	350	58.1	Munera-Echeverri et al., 2018
Corncob	400	22.4	Munera-Echeverri et al., 2018
Rice husk	350	26.7	Munera-Echeverri et al., 2018
Rice husk	300	24.4	Singh et al., 2020
Rice husk	600	17.3	Singh et al., 2020

Feedstock	BC HTT (°C)	CEC ($\text{cmol}_c\ \text{kg}^{-1}$)	Reference
Rice straw	300	39.6	Singh et al., 2020
Rice straw	600	24.7	Singh et al., 2020
T. dealbata	500	31.2	Zeng et al., 2013
T. dealbata	600	28.8	Zeng et al., 2013
T. dealbata	700	19.6	Zeng et al., 2013
V. zizanioides	500	21.1	Zeng et al., 2013
V. zizanioides	600	15.7	Zeng et al., 2013
V. zizanioides	700	14.4	Zeng et al., 2013
Phragmites sp. S. rosthornii	500	21.8	Zeng et al., 2013
Phragmites sp. S. rosthornii	600	12.9	Zeng et al., 2013
Phragmites sp. S. rosthornii	700	17.2	Zeng et al., 2013
S. rosthornii Seemen	500	23.5	Zeng et al., 2013
S. rosthornii Seemen	600	11.8	Zeng et al., 2013
S. rosthornii Seemen	700	6.1	Zeng et al., 2013
Horse manure and compost	200	50	Zhang et al., 2016
Horse manure and compost	400	60.2	Zhang et al., 2016
Horse manure and compost	600	85.5	Zhang et al., 2016

Table S3. Published values for maximum NH_4^+-N sorption derived from either the Langmuir sorption isotherm or through a basic maximum determination following batch sorption.

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NH_4^+- N (mg g^{-1})**	**Reference**
Rice straw	Herbaceous	400	Lang	11.48	Chandra et al., 2020
Rice straw	Herbaceous	600	Lang	12.19	Chandra et al., 2020
Bamboo powder	Herbaceous	400	Lang	1.90	Chen et al., 2017
C. indica	Herbaceous	500	Lang	10.38	Cui et al., 2016
P. purpureum Schum	Herbaceous	500	Lang	5.72	Cui et al., 2016
T. dealbata	Herbaceous	500	Lang	3.83	Cui et al., 2016
P. australis	Herbaceous	500	Lang	2.19	Cui et al., 2016
Z. caduciflora	Herbaceous	500	Lang	1.87	Cui et al., 2016
V. zizanioides	Herbaceous	500	Lang	1.65	Cui et al., 2016
Bamboo	Herbaceous	600	Lang	0.66	Ding et al., 2010
Greeen waste	Ag. waste	450	Lang	80.91	Esfanbod et al., 2017
Eucalyptus	Wood	720	Lang	25.77	Esfanbod et al., 2017
Eucalyptus	Wood	720	Lang	39.83	Esfanbod et al., 2017
Bamboo	Herbaceous	370	Lang	90.86	Fan et al., 2019
Bamboo	Herbaceous	370	Lang	89.32	Fan et al., 2019

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NH_4^+- N (mg g^{-1})**	**Reference**
Bamboo	Herbaceous	370	Lang	74.06	Fan et al., 2019
corn stover	Herbaceous	400	Lang	0.95	Fidel et al., 2018
corn stover	Herbaceous	500	Lang	1.05	Fidel et al., 2018
corn stover	Herbaceous	600	Lang	0.56	Fidel et al., 2018
Wheat straw	Herbaceous	400	Lang	5.70	Gai et al., 2014
Wheat straw	Herbaceous	500	Lang	3.64	Gai et al., 2014
Wheat straw	Herbaceous	600	Lang	2.46	Gai et al., 2014
Wheat straw	Herbaceous	700	Lang	2.06	Gai et al., 2014
Corn straw	Herbaceous	400	Lang	12.02	Gai et al., 2014
Corn straw	Herbaceous	500	Lang	9.37	Gai et al., 2014
Corn straw	Herbaceous	600	Lang	6.70	Gai et al., 2014
Corn straw	Herbaceous	700	Lang	5.58	Gai et al., 2014
peanut shell	Ag. waste	400	Lang	8.18	Gai et al., 2014
peanut shell	Ag. waste	500	Lang	7.72	Gai et al., 2014
peanut shell	Ag. waste	600	Lang	6.05	Gai et al., 2014
peanut shell	Ag. waste	700	Lang	3.12	Gai et al., 2014
Corn Stover	Herbaceous	300	Lang	157.50	Gao et al., 2015
peanut shell	Ag. waste	300	Lang	189.23	Gao et al., 2015
Corn cob	Herbaceous	300	Lang	169.09	Gao et al., 2015
Rice husk	Ag. waste	300	Lang	0.19	Hale et al., 2013
Corn cob	Herbaceous	300	Lang	0.44	Hale et al., 2013

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NH_4^+- N ($mg\ g^{-1}$)**	**Reference**
Giant reed	Herbaceous	500	Lang	0.94	Hou et al., 2016
Giant reed	Herbaceous	500	Lang	1.09	Hou et al., 2016
Giant reed	Herbaceous	500	Lang	1.16	Hou et al., 2016
Orange peel	Ag. waste	300	Lang	3.66	Hu et al., 2020
Pineapple peel	Ag. waste	300	Lang	4.36	Hu et al., 2020
pitaya peel	Ag. waste	400	Lang	2.06	Hu et al., 2020
cassava peel	Ag. waste	500	Lang	7.38	Ismadji et al., 2016
Poultry litter	Manure	400	Batch	19.80	Jassal et al., 2015
Poultry litter	Manure	500	Batch	19.80	Jassal et al., 2015
Poultry litter	Manure	600	Batch	18.10	Jassal et al., 2015
Softwood chips (spruce)	Wood	400	Batch	28.40	Jassal et al., 2015
Softwood chips (spruce)	Wood	500	Batch	26.30	Jassal et al., 2015
Softwood chips (spruce)	Wood	600	Batch	23.80	Jassal et al., 2015
Blend of both	Combi	400	Batch	0.00	Jassal et al., 2015
Blend of both	Combi	500	Batch	1.10	Jassal et al., 2015
Blend of both	Combi	600	Batch	5.40	Jassal et al., 2015
Rice husk	Ag. waste	600	Batch	30.96	Kizito et al., 2015
Wood	Wood	600	Batch	42.65	Kizito et al., 2015

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NH_4^+- N (mg g^{-1})**	**Reference**
Swtichgrass	Herbaceous	Raw	Lang	1.06	Li et al., 2018
Swtichgrass	Herbaceous	200	Lang	2.94	Li et al., 2018
Swtichgrass	Herbaceous	400	Lang	3.12	Li et al., 2018
Swtichgrass	Herbaceous	600	Lang	4.05	Li et al., 2018
Swtichgrass	Herbaceous	800	Lang	8.14	Li et al., 2018
Water Oak	Herbaceous	Raw	Lang	1.19	Li et al., 2018
Water Oak	Herbaceous	200	Lang	2.04	Li et al., 2018
Water Oak	Herbaceous	400	Lang	2.97	Li et al., 2018
Water Oak	Herbaceous	600	Lang	1.46	Li et al., 2018
Water Oak	Herbaceous	800	Lang	0.44	Li et al., 2018
Biosolids	Biosolids	Raw	Lang	33.67	Li et al., 2018
Biosolids	Biosolids	200	Lang	4.34	Li et al., 2018
Biosolids	Biosolids	400	Lang	2.15	Li et al., 2018
Biosolids	Biosolids	600	Lang	1.70	Li et al., 2018
Biosolids	Biosolids	800	Lang	1.54	Li et al., 2018
Eucalyptus	Wood	550	Lang	1.99	Mia et al., 2017
Bamboo	Herbaceous	450	Lang	5.44	Qin et al., 2020
Bamboo	Herbaceous	450	Lang	17.11	Qin et al., 2020
Mixed hard wood shavings	Wood	300	Batch	2.18	Sarkhot et al., 2013

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NH_4^+- N (mg g^{-1})**	**Reference**
Mixed hard wood shavings	Wood	300	Batch	4.12	Sarkhot et al., 2013
Oak wood	Wood	250	Batch	85.32	Takaya et al., 2016
Greenhouse waste	Herbaceous	250	Batch	94.66	Takaya et al., 2016
Municipal waste	Combi	250	Batch	113.87	Takaya et al., 2016
Presscake from AD	Biosolids	250	Batch	100.33	Takaya et al., 2016
Oak wood (Commercial)	Wood	400	Batch	78.48	Takaya et al., 2016
Oak wood	Wood	400	Batch	100.64	Takaya et al., 2016
Greenhouse waste	Herbaceous	400	Batch	91.93	Takaya et al., 2016
Municipal waste	Combi	400	Batch	106.79	Takaya et al., 2016
Presscake from AD	Biosolids	400	Batch	82.29	Takaya et al., 2016
Oak wood (Commercial)	Wood	600	Batch	88.98	Takaya et al., 2016
Oak wood	Wood	600	Batch	96.06	Takaya et al., 2016
Greenhouse waste	Herbaceous	600	Batch	77.23	Takaya et al., 2016
Municipal waste	Combi	600	Batch	99.79	Takaya et al., 2016
Presscake from AD	Biosolids	600	Batch	105.93	Takaya et al., 2016
Anaerobic digester sludge	Biosolids	450	Lang	1.18	Tang et al., 2019
Oak sawdust	Wood	300	Lang	4.13	Wang et al., 2015a

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NH_4^+- N (mg g^{-1})**	**Reference**
Maple wood	Wood	500	Lang	0.88	Wang et al., 2015a
Maple wood	Wood	500	Lang	-4.03	Wang et al., 2015a
Oak sawdust	Wood	300	Lang	4.13	Wang et al., 2015b
Maple wood	Wood	300	Batch	0.68	Wang et al., 2016
Maple wood	Wood	400	Batch	0.45	Wang et al., 2016
Maple wood	Wood	500	Batch	0.40	Wang et al., 2016
Maple wood	Wood	600	Batch	0.36	Wang et al., 2016
Maple wood	Wood	700	Batch	0.36	Wang et al., 2016
Sewage sludge and walnut shell	Combi	600	Lang	17.77	Yin et al., 2019
S. rosthornii Seemen	Herbaceous	500	Lang	2.57	Zeng et al., 2013
S. rosthornii Seemen	Herbaceous	600	Lang	5.78	Zeng et al., 2013
S. rosthornii Seemen	Herbaceous	700	Lang	5.14	Zeng et al., 2013
T. dealbata	Herbaceous	500	Lang	5.83	Zeng et al., 2013
T. dealbata	Herbaceous	600	Lang	8.71	Zeng et al., 2013
T. dealbata	Herbaceous	700	Lang	13.69	Zeng et al., 2013
V. zizanioides	Herbaceous	500	Lang	1.45	Zeng et al., 2013
V. zizanioides	Herbaceous	600	Lang	2.43	Zeng et al., 2013

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NH_4^+- N (mg g^{-1})**	**Reference**
V. zizanioides	Herbaceous	700	Lang	3.39	Zeng et al., 2013
Phragmites sp. S. rosthornii	Herbaceous	500	Lang	1.72	Zeng et al., 2013
Phragmites sp. S. rosthornii	Herbaceous	600	Lang	1.89	Zeng et al., 2013
Phragmites sp. S. rosthornii	Herbaceous	700	Lang	4.22	Zeng et al., 2013
corncob	Herbaceous	400	Lang	13.14	Zhang et al., 2014
corncob	Herbaceous	400	Lang	11.90	Zhang et al., 2014
corncob	Herbaceous	400	Lang	11.90	Zhang et al., 2014
corncob	Herbaceous	600	Lang	8.48	Zhang et al., 2014
corncob	Herbaceous	600	Lang	9.96	Zhang et al., 2014
corncob	Herbaceous	600	Lang	8.94	Zhang et al., 2014

[2] Quant method refers to method used to determine maximum sorption potential. Batch refers to the determination of maximum sorption using a single high concentration of N solution. Lang refers to the determination of the sorption isotherm using a range of N solution concentrations followed by modelling with the Langmuir sorption isotherm, which provides a coefficient that determines maximum sorption capacity. Both methodologies are batch processes, designations are therefore arbitrary.

Table S4. Published values for maximum NO_3^--N sorption derived from either the Langmuir sorption isotherm or through a basic maximum determination following batch sorption.

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NO_3^-- N (mg g^{-1})**	**Reference**
Date palm	Wood	600	Lang	5.40	Ahmad et al., 2018
Egg shell	Ag. Waste	600	Lang	6.07	Ahmad et al., 2018
Date palm	Wood	300	Lang	0.40	Alsewaileh et al., 2019
Date palm	Wood	700	Lang	2.96	Alsewaileh et al., 2019
Rice straw	Herbaceous	400	Lang	4.91	Chandra et al., 2020
Rice straw	Herbaceous	600	Lang	5.46	Chandra et al., 2020
Corn stover	Herbaceous	650	Lang	8.68	Chintala et al., 2013
Pine wood	Wood	650	Lang	2.58	Chintala et al., 2013
Switchgrass	Herbaceous	650	Lang	8.75	Chintala et al., 2013
Corn stover	Herbaceous	400	Lang	2.72	Fidel et al., 2018
Corn stover	Herbaceous	500	Lang	1.16	Fidel et al., 2018
Corn stover	Herbaceous	600	Lang	1.71	Fidel et al., 2018
Wheat straw	Herbaceous	500	Lang	-0.06	Gai et al., 2014
Corn straw	Herbaceous	500	Lang	-0.08	Gai et al., 2014
Peanut shell	Ag. Waste	500	Lang	-0.07	Gai et al., 2014
Wood chip	Wood	700	Lang	11.30	Hailegnaw et al., 2019
Poultry litter	Manure	400	Batch	21.00	Jassal et al., 2015
Poultry litter	Manure	500	Batch	21.60	Jassal et al., 2015

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NO_3^-- N (mg g^{-1})**	**Reference**
Poultry litter	Manure	600	Batch	20.60	Jassal et al., 2015
Softwood chips (spruce)	Wood	400	Batch	20.30	Jassal et al., 2015
Softwood chips (spruce)	Wood	500	Batch	20.40	Jassal et al., 2015
Softwood chips (spruce)	Wood	600	Batch	19.70	Jassal et al., 2015
Blend of both	Mix	400	Batch	2.90	Jassal et al., 2015
Blend of both	Mix	500	Batch	2.00	Jassal et al., 2015
Blend of both	Mix	600	Batch	3.00	Jassal et al., 2015
Japanese cedar	Wood	400	Batch	-0.01	Kameyama et al., 2016
Japanese cedar	Wood	600	Batch	0.00	Kameyama et al., 2016
Japanese cedar	Wood	800	Batch	0.23	Kameyama et al., 2016
Japanese cypress	Wood	400	Batch	0.05	Kameyama et al., 2016
Japanese cypress	Wood	600	Batch	0.04	Kameyama et al., 2016
Japanese cypress	Wood	800	Batch	0.23	Kameyama et al., 2016
Moso bamboo	Herbaceous	400	Batch	0.00	Kameyama et al., 2016
Moso bamboo	Herbaceous	600	Batch	-0.02	Kameyama et al., 2016
Moso bamboo	Herbaceous	800	Batch	0.15	Kameyama et al., 2016
Rice husk	Ag. Waste	400	Batch	0.06	Kameyama et al., 2016
Rice husk	Ag. Waste	600	Batch	-0.02	Kameyama et al., 2016
Rice husk	Ag. Waste	800	Batch	0.07	Kameyama et al., 2016
Sugar cane	Herbaceous	400	Batch	0.01	Kameyama et al., 2016

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NO_3^-- N (mg g^{-1})**	**Reference**
Sugar cane	Herbaceous	600	Batch	0.02	Kameyama et al., 2016
Sugar cane	Herbaceous	800	Batch	0.06	Kameyama et al., 2016
Poultry manure	Manure	400	Batch	-0.01	Kameyama et al., 2016
Poultry manure	Manure	600	Batch	0.01	Kameyama et al., 2016
Poultry manure	Manure	800	Batch	0.02	Kameyama et al., 2016
Domestic sludge	Biosolids	400	Batch	0.00	Kameyama et al., 2016
Domestic sludge	Biosolids	600	Batch	0.09	Kameyama et al., 2016
Domestic sludge	Biosolids	800	Batch	0.09	Kameyama et al., 2016
Bamboo powder	Herbaceous	900	Lang	1.25	Mizuta et al., 2004
Rice husk	Ag. Waste	600	Lang	0.11	Shukla et al., 2019
Conocarpus green waste	Wood	600	Lang	0.23	Usman et al., 2016
Conocarpus green waste	Wood	600	Lang	0.23	Usman et al., 2016
Palm kernel shell	Ag. Waste	600	Lang	0.26	Uttran et al., 2018
Bamboo	Herbaceous	460	Lang	1.04	Viglašová et al., 2018
Oak sawdust	Wood	600	Lang	2.02	Wang et al., 2015
Oak sawdust	Wood	600	Lang	-0.08	Wang et al., 2015b
Lignin	Wood	200	Lang	0.03	Yang et al., 2017b
Lignin	Wood	350	Lang	0.09	Yang et al., 2017b

Feedstock	**Feed type**	**BC HTT (°C)**	**Quant. Method**	**NO_3^-- N (mg g^{-1})**	**Reference**
Lignin	Wood	500	Lang	0.11	Yang et al., 2017b
Lignin	Wood	700	Lang	0.18	Yang et al., 2017b
Cellulose	Wood	200	Lang	0.02	Yang et al., 2017b
Cellulose	Wood	350	Lang	0.03	Yang et al., 2017b
Cellulose	Wood	500	Lang	0.03	Yang et al., 2017b
Cellulose	Wood	700	Lang	0.05	Yang et al., 2017b
Rice Straw	Herbaceous	500	Lang	0.03	Yang et al., 2017b
Corn cob	Herbaceous	600	Lang	3.27	Zhao et al., 2017
Phragmites communis	Herbaceous	300	Lang	0.10	Zhou et al., 2019
Sawdust	Wood	300	Lang	0.18	Zhou et al., 2019
Sawdust	Wood	500	Lang	0.35	Zhou et al., 2019
Egg shell	Ag. Waste	300	Lang	0.15	Zhou et al., 2019
Egg shell	Ag. Waste	500	Lang	0.21	Zhou et al., 2019
Egg shell	Ag. Waste	700	Lang	0.32	Zhou et al., 2019

[2] Quant method refers to method used to determine maximum sorption potential. Batch refers to the determination of maximum sorption using a single high concentration of N solution. Lang refers to the determination of the sorption isotherm using a range of N solution concentrations followed by modelling with the Langmuir sorption isotherm, which provides a coefficient that determines maximum sorption capacity. Both methodologies are batch processes, designations are therefore arbitrary.

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Paper IV

A re-analysis of NH_4^+ sorption on biochar: have expectations been too high?

Simon Weldon[1,2*], Bert van der Veen[3], Eva Farkas[2], Nazlı Pelin Kocatürk-Schumacher[2,4], Alba Dieguez-Alonso[5], Alice Budai[1], Daniel Rasse[1]

[1] Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, NMBU, 1430 Ås, Norway

[2] Norwegian Institute of Bioeconomy Research (NIBIO), Division of Environment and Natural Resources, Høgskoleveien 7, 1432 Ås, Norway

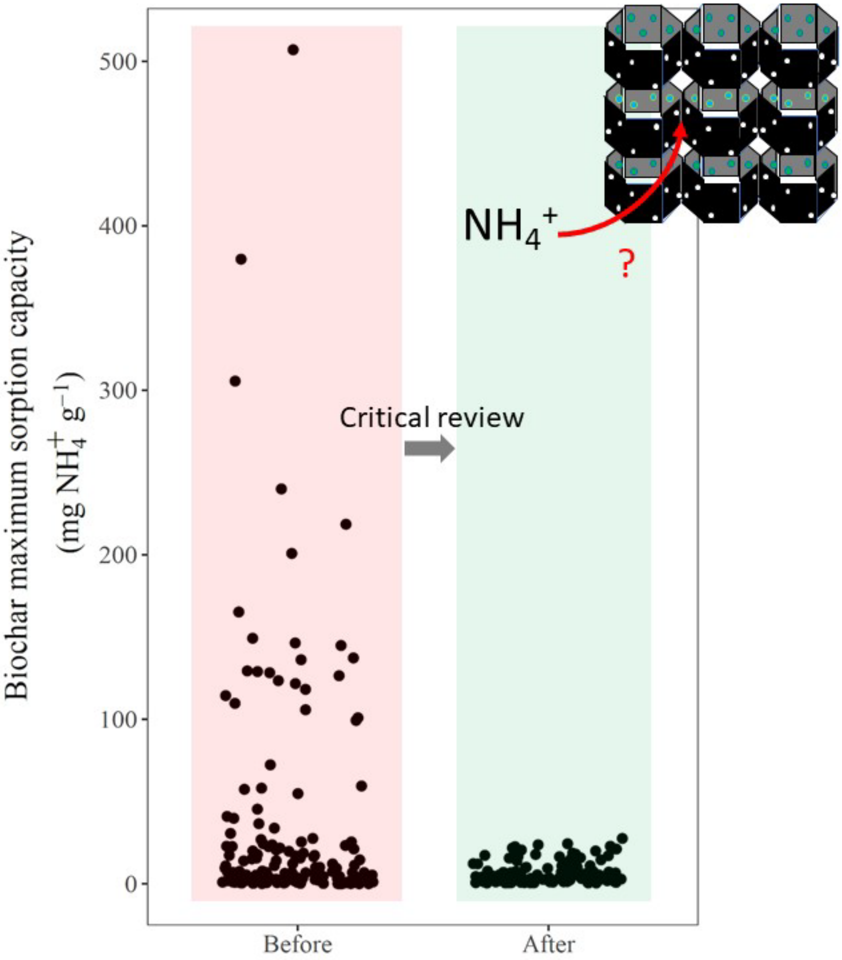
[3] Norwegian Institute of Bioeconomy Research (NIBIO), Division Food Production and Society, Høgskoleveien 7, 1432 Ås, Norway

[4] Faculty of Science and Technology (REALTEK), Norwegian University of Life Sciences (NMBU), 1432, Ås, Norway

[5] Institute of Fluid Dynamics and Thermodynamics, Faculty of Process and Systems Engineering, Otto-von-Guericke University Magdeburg, Universitätsplatz 2, DE-39106 Magdeburg, Germany

[*] Corresponding author: simon.weldon@nibio.no

Graphical Abstract



Abstract

Sorption of nutrients such as NH4+ is often quoted as a critical property of biochar, explaining its value as a soil amendment and a filter material. Published values for NH4+ sorption to biochar range from very low (<0.01 mg NH4+ g-1 biochar), to extremely high (518 mg NH4+ g-1 biochar). Based on this large variability our objective was to identify which feedstock, pyrolysis temperature and activation method maximises the sorption capacity of biochar for NH4+. To do so, we conducted a standardized remodelling exercise of published batch sorption studies using standard Langmuir sorption isotherm. We excluded studies presenting datasets that either could not be reconciled with the standard Langmuir sorption isotherm or generated clear outliers. Our analysis indicates that the magnitude of sorption capacity of unmodified biochar for NH4+ is lower than previously reported, with a median estimate of 4.2 mg NH4+ g-1 biochar and a maximum reported sorption capacity of 22.8 mg NH4+ g-1 biochar. Activation resulted in a significant relative improvement in sorption capacity, but absolute improvements remain modest, with a maximum reported sorption of 27.56 mg NH4+ g-1 biochar for an activated biochar. Methodology appeared to substantially impact sorption estimates, especially practices such as pH control of batch sorption solution and ash removal. A reason why solution pH and ash content might be critical is the major impact they can have on NH3 volatilization losses. Such losses are rarely quantified in sorption studies, although they can greatly bias sorption estimates. Our results support ion exchange as the dominant mechanism by which biochar retains NH4+, although the availability of data consistently quantifying potentially relevant variables was limited.

Abbreviations: CEC: Cation Exchange Capacity; **HTT**: Highest Treatment Temperature; **Agri. Waste:** Agro-industrial waste; **Combi:** Biochar mix with other feedstock, minerals or organic compounds. **N:** Nitrogen; **C.I.:** Confidence Intervals; **GLM:** Generalised Linear Model; **GLMM:** Generalised Linear Mixed Model

1 Introduction

Biochar has received significant attention in the last 20 years as a tool to mitigate climate change and as a green technology to valorise waste products for utility in agriculture and waste management. The study of the *Terra Preta* soils in the Amazonas has been a driving force behind the current interest in biochar (Lehmann, 2007). The high content of pyrogenic C and the high nutrient holding capacity of these soils has raised hope that biochar application to soil could deliver similar benefits over short timescales (Glaser et al., 2001; Glaser et al., 2015). Biochar has been recommended as a tool to both reduce N loss in soils (Al-Wabel et al., 2018) and as media in waste reclamation to stabilise and recover waste N (Huang et al., 2018). Based on its ability to retain nutrients, biochar has also been studied as a component in compound fertilisers (Dong et al., 2019).

An early paradigm of biochar research was that the high nutrient retention capacity of biochar in soils is a function of the ion exchange capacity of the biochar. Ion exchange in soils is composed of both anion and cation exchange capacities (AEC and CEC respectively). At agriculturally relevant pH (≥ 6) biochar is believed to contribute most to the CEC (Beesley et al., 2011; Lehmann et al., 2011) and therefore favour the retention of cationic nutrients such as NH_4^+ (Yao et al., 2012; Zhang et al., 2020). The CEC of biochar can be manipulated through choices relating to pyrolysis method, pyrolysis temperature, feedstock, and pre or post pyrolysis activation (Hassan et al., 2020). Despite this, the range of CEC measured for fresh biochar is low by comparison with materials such as clays or soil organic matter (SOM) (Rasse et al., Unpublished results).

The current paradigm of biochar N retention is that incubation of biochar in compost or soil, often referred to as ageing, is essential to the development of a high nutrient retention on biochar (Joseph et al., 2021). However, relying on field ageing to develop a biochar suited to the task of retaining N is highly impractical for applications such as fertiliser development or filter material in waste management. Efforts have been made to artificially age biochar through the application of post pyrolysis treatments (Wang et al., 2015b), or through the incorporation of biochar with materials such as clay (Ismadji et al., 2016). However, while this does result in large relative increases in sorption capacity, absolute values remain small (Rasse et al., Unpublished results).

Studies have reported high sorption capacity of biochar for NH_4^+ (Gao et al., 2015; Liu et al., 2016; Takaya et al., 2016), which has led to the conclusion that fresh biochar is competitive with other commonly used sorbents in the field of nutrients recovery (Huang et al., 2018). However, a more recent review suggests that this potential might, on average, be more limited (Zhang et al., 2020). The challenge is that the spread of values for biochar sorption capacity of NH_4^+ is large (Rasse et al., Unpublished results) and, although the exceptionally high values represent the minority of studies, these values could be an important indicator of the potential of specific biochar products and the mechanisms by which this potential can be maximised.

It is unclear which biochar properties are responsible for the large range in NH_4^+ sorption values reported for biochars. Several studies have discussed that the predominant mechanism responsible for biochar sorption of NH_4^+ in single solute systems is ion exchange (Zhang et al., 2020). However, as discussed, the CEC of fresh biochar is generally low. Studies have reported NH_4^+ sorption values higher than the measured CEC (Jassal et al., 2015; Fidel et al., 2018), but it is unclear what other biochar properties are responsible for this effect.

A previous study, examining literature values for NH_4^+ sorption to fresh biochar, identified an apparent effect of source article on the magnitude of estimates that appeared to override any effect of either biochar feedstock or pyrolysis temperature (Rasse et al., Unpublished results). Based on this they hypothesised that the estimates for biochar sorption capacity for NH_4^+ may be confounded by study methodology. This may in part be explained by the different methods for determining sorption capacity (Volesky, 2007), or the different mathematical approaches for modelling the sorption behaviour (Barrow, 2008). All these elements have the potential to confound the interpretation of sorption capacity across studies. In addition, a number of reviews have identified errors and inconsistencies in the application of techniques to estimate sorption of solutes to solids (Barrow, 2008; Foo and Hameed, 2010; Tran et al., 2017; Al-Ghouti and Da'ana, 2020; Cherkasov, 2020).

With this quantitative review, we aim to separate the effects of study methodology from those of biochar properties on the biochar sorption capacity for NH_4^+. We further aim to identify properties of the biochar that sustain higher sorption potential for NH_4^+. We begin by undertaking a thorough appraisal of the literature to develop an estimate for the maximum sorption potential. With this conservative dataset we then examine relationships between biochar sorption capacity and biochar properties to identify which variables might best explain the magnitude of biochar sorption capacity.

2 Methodology

2.1 Choice of approach

To understand the relationship between biochar properties and sorption capacity for NH_4^+, we first needed to develop a constrained dataset of estimates for the maximum sorption potential of biochar.

Our approach was to re-model published sorption isotherms using the Langmuir model in order to derive an estimate for the theoretical maximum sorption potential of biochar for NH_4^+. The Langmuir model requires measurements that span saturation (Giles et al., 1960; Calvet, 1989; Barrow, 2008), so by definition, we excluded single-concentration studies where the theoretical maximum sorption cannot be ascertained. We also excluded isotherm studies that did not apply the Langmuir model because it potentially indicated that the datasets were not appropriate for such a modelling, e.g., due to an insufficient measurement range. The remodelling step was required in order to 1) standardise the approach for estimating the Langmuir coefficients and 2) provide a measure of uncertainty in order to quality check the estimates.

2.2 Data collection

Our literature search was conducted on the Web of Science with a cut-off date of February 2020 using the search terms: (Batch Sorption OR Isotherm OR Langmuir OR Freundlich) AND (NH_4^+ OR ammonium) AND (Biochar OR Activated carbon OR Pyrogenic carbon OR black carbon). We identified all studies where measurements used to estimate the Langmuir coefficients were provided (in graphic form) either in the main text or in supplementary information.

Remodelling was conducted according to the classical Langmuir approach to model isotherms (Giles et al., 1960). In short, a fixed amount of sorbent is subjected to increasing concentrations of sorbate in a solution, and the amount of adsorbed sorbate (q_e) is calculated according to Equation 1.

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad \text{Eq 1.}$$

Where C_0 (mg L^{-1}) is the initial concentration of the sorbate solution, C_e (mg L^{-1}) is the equilibrium concentration. V (L) is the solution volume and M (mg) is the mass of the sorbent. Isotherm models are plotted as a function of q_e (mg g^{-1}) against C_e (mg L^{-1}), and we therefore excluded studies where q_e was plotted against C_0.

Relevant figures were copied from documents as .jpg files and digitised manually using Engauge Digitizer (Mitchell et al., 2020). Units were standardised with q_e in mg NH_4^+ g^{-1} biochar and C_e in mg NH_4^+ L^{-1} solution.

2.3 Checking *f*or consistency

We checked all studies for data and unit consistency. Following this consistency check, four studies were removed (Table S2), resulting in a quality-checked collection of 125 isotherms in 31 papers (Table S4).

2.4 Data re-modelling

We applied a standard non-linear modelling approach to estimate the Langmuir coefficients Q_{max} and K_L, which represent the theoretical maximum sorption capacity and the adsorption equilibrium constant, respectively (Eq 2). This non-linear modelling approach is preferred to the linearisation of the Langmuir isotherm, which is commonly used to simplify coefficient estimation (Eq 3).

$$q_e = \frac{Q_{max} K_L C_e}{(1 + K_L C_e)} \qquad \text{Eq 2.}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \qquad \text{Eq 3.}$$

Linearization has been shown to introduce bias and therefore result in poor estimates (Barrow, 2008; Foo and Hameed, 2010; Tran et al., 2017; Al-Ghouti and Da'ana, 2020; Cherkasov, 2020). Our own tests on this dataset confirm that estimates derived by linear vs non-linear methods vary significantly (Fig S3. Supplementary Information). Therefore, we used only the non-linear method for the purpose of this review.

We estimated the non-linear parameters using the *nls* function in the R-package *nlme* (Pinheiro et al., 2019; R Core Team., 2019). We set a condition to accept only positive estimates for the coefficients on the basis that negative values for Q_{max} or K_L confound the theoretical assumptions of the Langmuir model. For the sake of clarity in the text, we distinguish between the previously published and our remodelled estimates for Q_{max} with the terms Q_{pub} and Q_{new}, respectively.

We assessed the fit of the isotherms using the standard error of the estimate. We removed all isotherm models where the standard error of the estimates was greater than the value of the estimate, for any of the coefficients. This resulted in the largest functional subset consisting of 116 isotherms in 29 studies (Table S4).

2.5 Biochar properties

We aimed to model the effect of biochar properties on values of Q_{new}. Due to variability in the availability of the specific variables that were provided in the source articles, we performed the modelling on multiple subsets of the data (subsets defined in Table S4, Supplementary Information). The variables included in the model fitting are reported in Table S3 (Supplementary Information).

We chose source article to represent the apparent effect of study methodology on the response variable and applied this as a random effect. Because we aimed to understand how source article might influence the fit of the biochar parameters, we applied both a Generalised Linear Model (GLM) and Generalised Linear Mixed Model (GLMM), which allowed us to parametrise the model both with and without a random effect. In the fitting of both the GLMs and GLMMs, we chose a gamma distribution with log-link function. We performed model-selection using Akaike's information criterion adjusted for small sample sizes (AICc), and with the *MuMln* R-package (Barton, K., 2020). We considered all models within 2 points AICc difference of the best fitting model as fitting the data equally well (Burnham and Anderson, 2002), and discuss the differences between those models in the results. We used the *glmmTMB* R-package (Brooks et al., 2017) to fit the models both with and without source article as a random effect.

3 Results and discussion

3.1 Spread of the values

Our remodelling and analysis of the 116 isotherms included in 29 studies showed that Q_{new} was lower than 20 mg g^{-1} in the majority of studies (Fig. 1, Table S4). Despite our approach to data discrimination our final dataset contained outliers, represented by two studies consisting of 5 isotherms with Q_{new} values approximately 3 – 10 times the upper quartile of all measurements included in this study. One of the studies reporting these higher values (Fan et al., 2019), estimated a Q_{pub} of 95–116 mg g^{-1} for a commercially produced bamboo biochar at a highest treatment temperature of 370 ºC (solution pH was between 3 and 7). This was higher than the 6.8 – 22.8 mg g^{-1} Q_{pub} range reported for a bamboo biochar produced at 450 ºC HTT (solution pH 6) by Qin et al. (2019). The second outlier study (Yin et al., 2019), estimated Q_{pub} values for a non-activated poplar wood biochar that were approximately 10 times higher than the next two highest estimates for non-activated wood biochar, including a high temperature wood chip (Hailegnaw et al., 2019) and a low temperature Oak sawdust (Wang et al., 2015c). Removal of these values from the dataset reduced the mean and standard deviation of the estimates and reduced the difference between the median and the mean (Table 1). We tested whether we could explain these high outlier values by modelling Q_{new} as a function of available biochar properties such as solution pH, activation, biochar HTT, or feedstock. However, inclusion of these outliers in a GLM resulted in a negative estimate for the pH effect on Q_{new} (GLM: Est.-0.05, C.I. -0.16 – 0.06 see Table S5a Supplementary Information), which is unexpected considering the well documented positive correlation between pH and cation sorption (Fidel et al., 2018). Removing these 2 studies resulted in a positive correlation between pH and Q_{new} as well as a better fitting model (Table S5b Supplementary Information). This observation supports removing these values from our analysis, but it does not preclude that other variables, not available for analysis, might explain these high values.

Table 1. Spread of remodelled sorption coefficients for maximum theoretical sorption capacity Q_{new} values (mg NH_4^+ g^{-1} biochar) summarised by quartiles, median and mean with standard deviation for activated and non-activated biochar. (Subset: 1 (top) and subset 2 (bottom), see Table S4 in Supplementary Information)

		0%	25%	50%	75%	100%	Mean	(sd)
Including outliers (Source article n = 29; Isotherm n = 116)	activated	0.93	2.39	7.24	17.24	59.44	11.61	(12.24)
	not activated	0.49	2.59	4.22	10.96	149.23	11.77	(25.89)
Excluding outliers (Source article n = 27; Isotherm n = 111)	activated	0.93	2.06	6.96	17.04	27.56	9.96	(8.4)
	not activated	0.49	2.57	4.20	9.52	22.82	6.51	(5.92)

A previous quantitative review of the biochar sorption potential for NH_4^+ estimated average values of 14 and 29 mg g^{-1} for non-activated and activated biochars, respectively (Zhang et al., 2020). In Rasse et al (Unpublished results), the mean for non-activated biochars was 31.5 mg g^{-1}, which is 2 folds higher than the estimate by Zhang et al. (2020) for non-activated chars. The reason for this discrepancy is that the study by Rasse et al (Unpublished results) included values excluded by Zhang et al. (2020) in their analysis. Rasse et al., (Unpublished results) identified that the response variable, Q_{max}, was skewed, which informed their decision to interpret the median as a more suitable measure of centre. Applying our current conservative approach however, we find both a low median and mean estimate for our remodelled estimate of Q_{new} for both non-activated and activated char (Table 1), which reduced the degree of skew in the data, further highlighting the influence of the high estimates on the mean.

Our results suggest that the sorption potential of biochar is low even following activation (Table 1). However, we come to this conclusion because we raise doubts over a number of high estimates. While our study suggests that the most likely explanation for these high values are methodological issues, it is also possible that these chars represent exceptional biochar sorbents. For future studies, values outside the range we identify here should be scrutinised more closely to rule out methodological issues and identify biochars with exceptional sorption capacity.

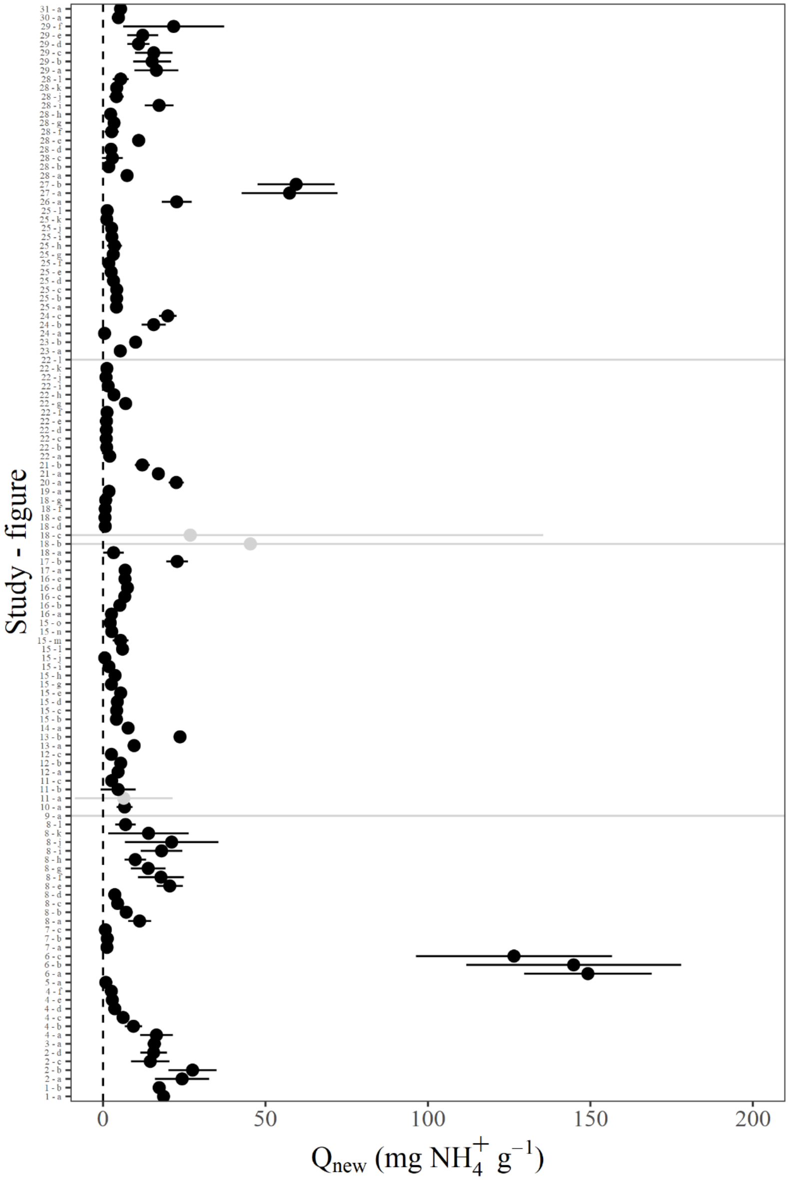


Figure 1. Q_{new} (mg NH_4^+ g^{-1} biochar) values for articles following data discrimination prior to removal of uncertain estimates (subset 2 – see Table S4 Supplementary Information). Y axis labels represent a publication reference followed by a letter differentiating the individual isotherms from each publication. Bars represent 95% confidence intervals and grey colouring represent estimates where the standard error of the estimate was larger than the estimate.

3.2 Relationship between Q_{new} and biochar properties

To explain variations in Q_{new} we extracted the most consistently reported data that quantified biochar properties. This included specific surface area, specific pore volume, CEC, and elemental analysis. However, even for these important properties of the biochar, we found considerable variability in the frequency of reporting. For example, CEC was quantified in only 8 of the 28 studies. Although specific pore volume and specific surface area were quantified by 12 studies consisting of 48 isotherms, measurements were conducted with two different methods, i.e. N_2 or CO_2 adsorption, which are known to quantify different pore sizes and therefore produce substantially different estimated values (Maziarka et al., 2021). The most consistently quantified biochar properties were the elemental contents of O, N, and C, quantified in 13 studies consisting of 72 isotherms. Taking advantage of this larger data pool, we chose to include the molar ratio (O+N):C as an explanatory variable. The molar ratio O:C is used frequently as a proxy for the abundance of negatively charged functional groups on the surface of biochar (Budai et al., 2014). These functional groups are largely responsible for the CEC of biochar (Xiao et al., 2018; Hassan et al., 2020) making this variable a potentially valuable proxy for CEC.

While fitting the GLM we identified several outliers in the value (O+N):C that we traced back to isotherm measurements conducted on eggshell biochar that had an exceptionally high ash content (98 % ± 0.5) (Xu et al., 2019). For this biochar type the interpretation of (O+N):C, as a proxy for negatively charged functional groups on a carbon matrix, is confounded by the abundance of mineral C and O in the ash component of this biochar. This observation highlights the potential confounding effect of mineral oxygen content of ash for the popular interpretation of the molar ratio (O+N):C.

We found that both pH (GLM: Est. 0.13, C.I. 0.00 – 0.25) and activation (GLM: Est. 0.91, C.I. 0.48 – 1.33) of the biochar had a positive relationship with Q_{new} in the model. While Biochar HTT (GLM: Est. -0.001, C.I. -0.001 – 0.0001) had a negative relationship with Q_{new}. (Tables S5b, d, Supplementary Information). We tested the effect of study methodology on our results by running the models both with and without source article as a random effect. Without a random effect, the variable feedstock appeared to be an important explanatory variable with *Wood* biochar resulting in significantly lower estimates for Q_{new} than *Agri. Waste*, *Herbaceous,* and *Combi* biochars in both data subsets (Fig. 2). However, inclusion of source article as a random effect removes the effect of feedstock, highlighting that feedstock is often study specific. For example, only two studies in our dataset compare wood biochar with other feedstock types (Li et al., 2018; Xu et al., 2019).

Estimates for the effect of activation on Q_{new} were relatively large, positive, and consistent throughout all models. The activation methods applied in the available literature can be loosely categorised based on 2 different approaches. Either, use of oxidants, in the form of acids (Boopathy et al., 2013; Wang et al., 2016; Zhu et al., 2016; Mia et al., 2017; Vu et al., 2017; Khalil et al., 2018; Vu et al., 2018), or combination of the biochar with minerals (Wang et al., 2015a; Chen et al., 2017; Gong et al., 2017; Chandra et al., 2020; Xiao et al., 2020). The largest estimates (Q_{new} > 20 mg g^{-1}) included 2 studies applying mineral treatments pre-pyrolysis (Ismadji et al., 2016; Chandra et al., 2020) and a single study applying a HNO_3 treatment post pyrolysis (Vu et al., 2017). Compared with the highest estimate for a non-activated char 22.8 mg g^{-1} (Qin et al., 2019), activation resulted in the highest overall estimate of Q_{new} at 27.6 mg g^{-1} (Xiao et al., 2020). However, the relatively small difference in Q_{new} between the best-performing modified and non-modified biochar show that activating biochar may only provide relatively minor net benefits, potentially at the cost of a more expensive biochar production process.

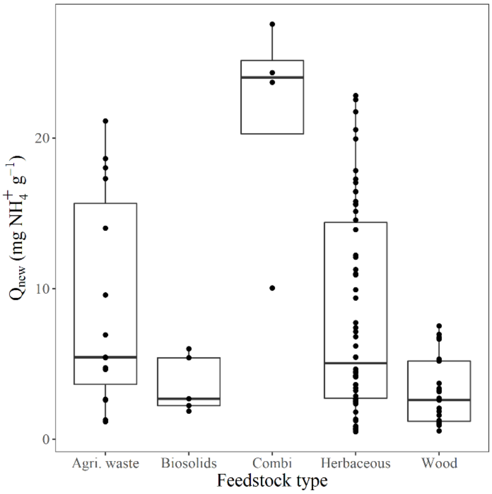


Figure 2. Distribution of Q_{new} values by feedstock. Data are for non-activated biochar only. Based on data subset 4 (Table S4, Supplementary Information) following discrimination process and after removal of outliers.

We included solution pH in our modelling because sorption in solute systems is known to be pH dependent (Fidel et al., 2018). Similar to activation, the effect of solution pH was consistent and positive in all models (Table S5d, Supplementary Information). Although we identify a positive correlation between solution pH and Q_{new}, the effect of pH on NH_4^+/NH_3 speciation is known to result in reduced sorption at high pH due to the lower sorption affinity of NH_3 (Hu et al., 2020). However, our results show consistently higher estimates for Q_{new} in studies where solution pH was higher than the pKb of ammonium (Fig. 3b), which can be attributed to ammonia volatilisation. Ammonia is an important component of N loss in agricultural systems (Sha et al., 2019). NH_3 volatilisation can result in substantial N losses at high pH, which are generally not quantified in sorption studies (Kizito et al., 2015; Wang et al., 2015b; Esfandbod et al., 2017). NH_3 can also chemisorb to biochar surfaces under ambient conditions forming amine groups (Hestrin et al., 2019). Both mechanisms may confound interpretation of the Langmuir isotherm where the assumption is that the change in concentration of the sorbate: 1) directly reflects the amount being sorbed on the biochar through conservation of N mass in the system, and 2) is a function of reversible sorption mechanisms on the surface of the biochar. The loss due to volatilisation, in particular, is not only a function of pH, but also of the salt content of the solution, solution temperature, and the equilibrium between the partial pressure of NH_3 in solution and in the immediate environment at the solution surface. This highlights how methodology can affect the interpretation of NH_4^+ isotherms, including the temperature of the solution, the type of vessel used (related to vessel headspace and closed vs open containers) and if the biochar ash was removed prior to sorption experiments or not.

Despite clear evidence that pH has implications for biochar sorption of NH_4^+ (Vu et al., 2018), we found a significant variability in the methodology applied towards pH control throughout the literature. Biochar is strongly alkaline due to both the predominantly negatively charged carbon surfaces and to the ash content (Fidel et al., 2017). Biochar ash, in particular, is a challenge in sorption experiments due to the potentially high buffering capacity of the secondary carbonates and the confounding effect of competitive cations (Fidel et al., 2013; Fidel et al., 2017; Fidel et al., 2018). We identified that only a minority of studies removed the ash-forming species from biochar. Our results suggest that retaining these ash-forming species in biochar results in higher estimates of Q_{new} (Fig. 3a), which is contrary to the hypothesis that cations in ash may compete with NH_4^+ for binding sites. Alternately, higher estimates of Q_{new} in the presence of ash may have several explanations. For example, co-precipitation of ammonium with mineral components of the biochar ash can result in the formation of insoluble minerals such as struvite (Yin et al., 2018; Fan et al., 2019). Such mechanisms are dependent on the composition of the ash component, which varies with feedstock type (Chintala et al., 2013; Xiao et al., 2018). The potentially high buffering capacity of biochar ash could also make pH control of sorption solutions more challenging.

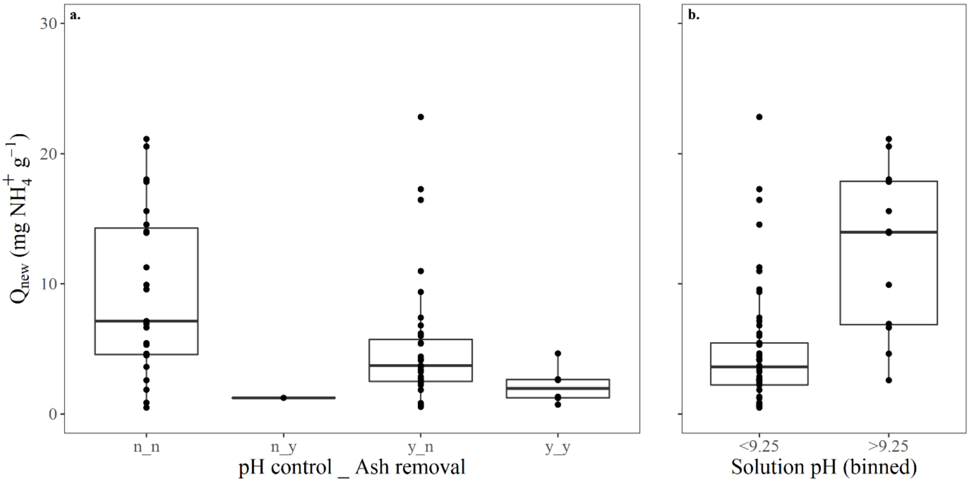


Figure 3. a: Q_{new} as a function of pH control and ash removal excluding activated biochar. b: Q_{new} as a function of solution pH that was binned to represent pH above and below the pKb of ammonium (pH 9.25). Points in both figures show individual measurements. Activated biochars were removed from this data set because activation often involves a washing step.

Increasing biochar HTT resulted in lower estimates of Q_{new} in all data subsets although the effect size was low and HTT did not consistently appear as an explanatory variable in all of the top candidate models. Biochar HTT is a proxy for a range of biochar properties that change both linearly and non-linearly as a function of pyrolysis temperature (Budai et al., 2014). Oxygen and N-containing functional groups are largely involved in ion exchange mechanisms on biochar surfaces and are the primary source of biochar CEC (Xiao et al., 2018). Due to the paucity of CEC data, we applied the elemental molar ratio (O+N):C as a proxy for this functionality. As previously discussed, eggshell biochar confounded this interpretation due to the large amount of mineral O as compared to that contained in the organic C structure. Excluding biochar made from eggshell from our analysis improved the model fit and resulted in a positive effect of (O+N):C on Q_{new} (GLM: Est. 1.18, C.I. 0.32-2.04. see Table S5d). The ratio (O+N):C seemed to explain similar variation in the response as HTT, which was evidenced by the poorer fit of each variable when both were included in the same model. This is likely because HTT is collinear with (O+N):C, although negatively so. Despite the limited number of CEC measurements, CEC was positively correlated with Q_{new} (Fig. 4), but with a high variability in the response. Solution pH appeared to explain some of this variability with a larger difference between measurements of CEC and Q_{new} at solution pH values greater than the pKb of NH_4^+ (Fig. 4 & Fig. S5). This discrepancy between estimates for Q_{max} and CEC has previously been reported in the literature and used as an argument that mechanisms other than ion exchange also contribute to explain Q_{max} (Jassal et al., 2015; Fidel et al., 2018). Although we cannot discard this hypothesis, our results suggest that variability between CEC and Q_{new} could also be a function of methodological choices. Quantification of CEC, as we have already seen with Q_{max}, can also be dependent on methodology, such as pH of solutions and biochar washing prior to measurement (Munera-Echeverri et al., 2018). This may explain why some studies report significantly lower estimates for Q_{max} than for CEC (Fig. 4).

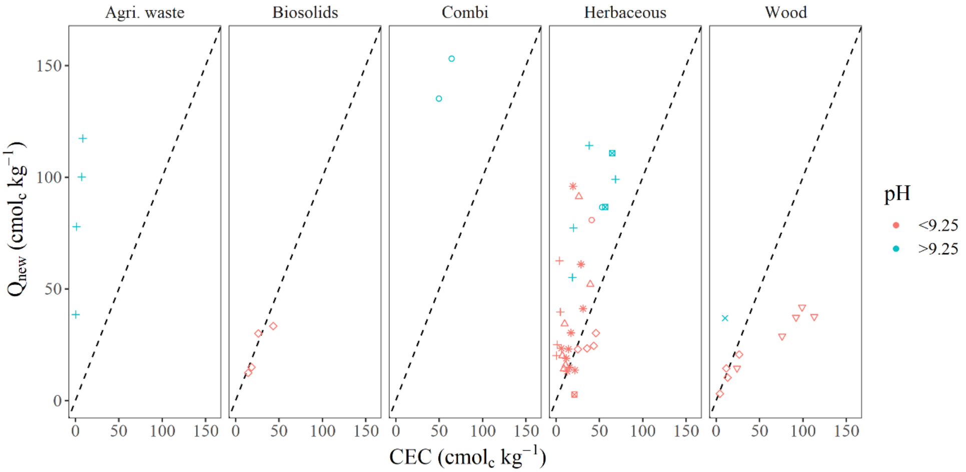


Figure 4. CEC *vs*. Q_{new} in cmol$_c$ kg^{-1}. Symbols refer to study and colour refers to pH. Activated biochars are included and account for 8 of the 53 measurements presented.

Our analysis supports the importance of ion exchange mechanisms for the sorption of NH_4^+ on biochar. This suggests that increasing the density of ion exchange sites is probably the most promising way to increase biochar sorption capacity for NH_4^+. Maximising surface functional groups can be accomplished through choice of pyrolysis temperature, feedstock, and activation procedure. A meta-analysis by Hassan et al. (2020) found that sorption of ionic nutrients was favoured by the abundance of functional groups which was higher at low pyrolysis temperatures. Hassan et al. (2020) also reported greater abundance of functional groups for grass and manure biochar by comparison with wood biochar. This may explain the significantly lower Q_{new} values reported for wood biochars in this study (Fig. 2).

Alternatively, this apparent feedstock effect might also be explained by the quantity and composition of the ash, which is also feedstock-specific. The abundance of functional groups may also be modified through activation via post pyrolysis oxidation with acids and bases (Wang et al., 2015b; Nguyen et al., 2019) or through coating with high-CEC materials such as clay minerals (Ismadji et al., 2016; Chen et al., 2017). Coatings are increasingly seen as a promising method for increasing biochar surface functionality because chemical treatment of biochar may alter the stability of the biochar material (Duan et al., 2019). The few studies reporting values for biochars combined with clay minerals report not only that clay increases the sorption capacity of the biochar, but also that there is a synergistic effect from co-pyrolysis of biochar and clay (Ismadji et al., 2016).

The insufficient reporting in sorption studies of variables such as specific pore volume and specific surface area precludes us from investigation their possible contributions to Q_{max}. Lower measurements of Q_{new} at higher pyrolysis temperatures suggest that total surface area and total porosity, which are often positively correlated with HTT, are not major controllers for sorption of NH_4^+. This is contrary to reports that surface area and porosity may be important for the retention of nutrients such as NH_4^+ (Gong et al., 2019). This may highlight a problem with the general interpretation of total surface area and total pore volume, due to the potential variability in the functional significance of different pore sizes for NH_4^+ sorption. In addition, it is not clear how multiple variables such as porosity, surface area, surface charge, functional groups and biochar mineral components may interact to increase the measured sorption capacity of biochar.

The results of our modelling exercise highlight the need to critically assess the significance of outlier values. We also see the need to standardise biochar measurement methodologies, as highlighted in previous studies (Bachmann et al., 2016; Singh et al., 2017). Here we observe that methodology related to ash removal and pH control, in particular, appear to exert a significant effect.

3.3 Conclusions

Our analysis shows that the range of sorption capacity of fresh, non-activated biochar for NH_4^+ is lower than previously reported. Our approach identified a series of uncertain values in the published literature that corresponded with exceptionally high estimates for the sorption capacity of biochar. Here, we excluded these studies from our analysis, but recommend replicating them. Based on our standardized analysis of Q_{max}, we find that sorption mechanisms on fresh and activated biochar cannot explain the high nutrient retention capacity that has been observed in field-aged and co-composted biochar. This has implications for the modification of biochar for use in specific applications. Development of future biochar sorbents will require estimates based on consistent methodologies for the quantification of sorption capacity. In particular, studies should consider the potential interaction effect of biochar ash on sorption dynamics and interpret results in light of either the inclusion or exclusion of this component of the biochar.

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Author contributions

Simon Weldon: Conceptualisation, Formal analysis, Writing – original draft. **Bert van der Veen,** Formal analysis, Writing – review & editing; **Eva Farkas:** Writing – review & editing; **Nazlı Pelin Kocatürk-Schumacher:** Writing – review & editing **Alba Dieguez-Alonso:** Writing – review & editing **Alice Budai:** Writing – review & editing **Daniel Rasse:** Conceptualisation, Writing – review & editing, Funding acquisition

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Supplementary information

A re-analysis of NH_4^+ sorption on biochar: have expectations been too high?

Simon Weldon[1,2*], Bert van der Veen[3], Eva Farkas[2], Nazlı Pelin Kocatürk-Schumacher[2,4], Alba Dieguez-Alonso[5], Alice Budai[1], Daniel Rasse[1]

[1]Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, NMBU, 1430 Ås, Norway

[2]Norwegian Institute of Bioeconomy Research (NIBIO), Division of Environment and Natural Resources, Høgskoleveien 7, 1432 Ås, Norway

[3]Norwegian Institute of Bioeconomy Research (NIBIO), Division Food Production and Society, Høgskoleveien 7, 1432 Ås, Norway

[4] Faculty of Science and Technology (REALTEK), Norwegian University of Life Sciences (NMBU), 1432, Ås, Norway

[5] Institute of Fluid Dynamics and Thermodynamics, Faculty of Process and Systems Engineering, Otto-von-Guericke University Magdeburg, Universitätsplatz 2, DE-39106 Magdeburg, Germany

[*]Corresponding author: simon.weldon@nibio.no

Table S1. Estimates based on the single batch method excluded from analysis.

Reference	Feedstock	Feed_type	BC HTT (ºC)	N (mg NH_4^+ g^{-1} biochar)
Jassal et al., 2015	Poultry litter	Manure	400	19.8
Jassal et al., 2015	Poultry litter	Manure	500	19.8
Jassal et al., 2015	Poultry litter	Manure	600	18.1
Jassal et al., 2015	Softwood chips (spruce)	Wood	400	28.4
Jassal et al., 2015	Softwood chips (spruce)	Wood	500	26.3
Jassal et al., 2015	Softwood chips (spruce)	Wood	600	23.8
Jassal et al., 2015	Blend of both	Combi	400	0
Jassal et al., 2015	Blend of both	Combi	500	1.1
Jassal et al., 2015	Blend of both	Combi	600	5.4
Kizito et al., 2015	Rice husk	Agri. Waste	600	30.96
Kizito et al., 2015	Wood	Wood	600	42.65
Sarkhot et al., 2013	Mixed hard wood shavings	Wood	300	2.18
Sarkhot et al., 2013	Mixed hard wood shavings	Wood	300	4.12
Takaya et al., 2016	Oak wood	Wood	250	85.32
Takaya et al., 2016	Greenhouse waste	Herbaceous	250	94.66
Takaya et al., 2016	Municipal waste	Combi	250	113.87
Takaya et al., 2016	Presscake from AD	Biosolids	250	100.33
Takaya et al., 2016	Oak wood (Commercial)	Wood	400	78.48
Takaya et al., 2016	Oak wood	Wood	400	100.64
Takaya et al., 2016	Greenhouse waste	Herbaceous	400	91.93
Takaya et al., 2016	Municipal waste	Combi	400	106.79
Takaya et al., 2016	Presscake from AD	Biosolids	400	82.29
Takaya et al., 2016	Oak wood (Commercial)	Wood	600	88.98
Takaya et al., 2016	Oak wood	Wood	600	96.1
Takaya et al., 2016	Greenhouse waste	Herbaceous	600	77.23
Takaya et al., 2016	Municipal waste	Combi	600	99.79
Takaya et al., 2016	Presscake from AD	Biosolids	600	105.93
Wang et al., 2016	Maple wood	Wood	300	0.68
Wang et al., 2016	Maple wood	Wood	400	0.45
Wang et al., 2016	Maple wood	Wood	500	0.40
Wang et al., 2016	Maple wood	Wood	600	0.36
Wang et al., 2016	Maple wood	Wood	700	0.36
		Mean	31.54	(±40.16)
		Median	5.4	

Table S2. Values excluded from initial analysis based on data discrimination process including the reasons for exclusion. Values for Q_{max} are published values. Data was not included in the re-modelling analysis.

Author	Q_{max} **(mg** NH_4^+ **g**$^{-1}$ biochar)	**Feedstock**	**BC HTT (°C)**	**Reason for exclusion**
Kizito et al., 2015	133.3	Wood cuttings	600	Initial concentration presented as Ce. 2 figures with different transformations result in 2 different results.
	71.94	Rice husks	600	
Saleh et al., 2012		Peanut shell		Did not publish coefficients. 2 figures with different transformations result in 2 different results.
Gao et al 2015	202.5	cotton stalks	300	Unit confusion (both mg g^{-1} and mg kg^{-1}). Ce values higher than reported maximum solution concentration.
	243.3	peanut shell	300	
	217.4	corncob	300	
Liu et al 2016	518.9	cotton stalks	300	Unit confusion (both mg g^{-1} and mg kg^{-1}). Ce values higher than reported maximum solution concentration.
	313.9	peanut shell	300	
	373.1	corncob	300	
Median	118.7			
Mean	43.3			

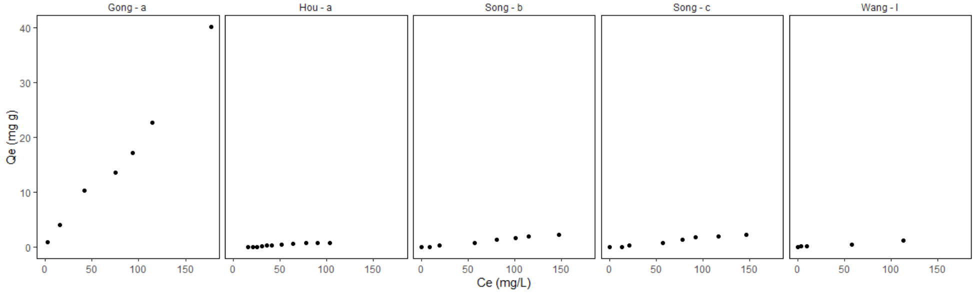

Figure S1 Point plot showing all experimental data that resulted in highly uncertain estimates for Q_{new} that qualified them for exclusion from the final analysis.

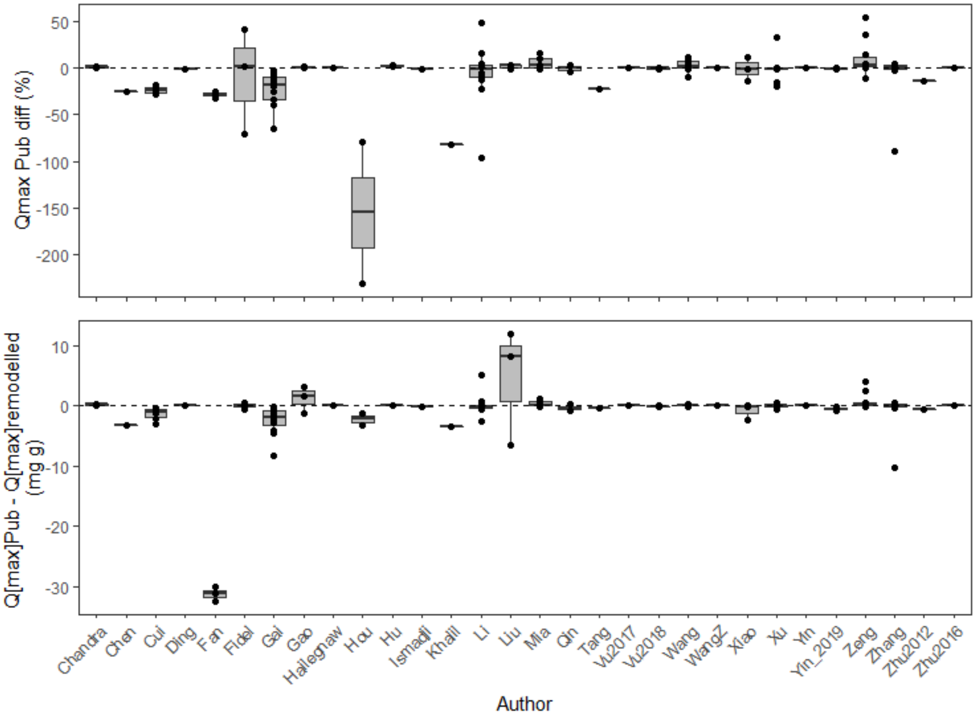

Figure S2. Difference between published Q_{pub} and remodelled Q_{new} both as a function of absolute difference (lower) and relative difference as a percentage of the published value (upper).

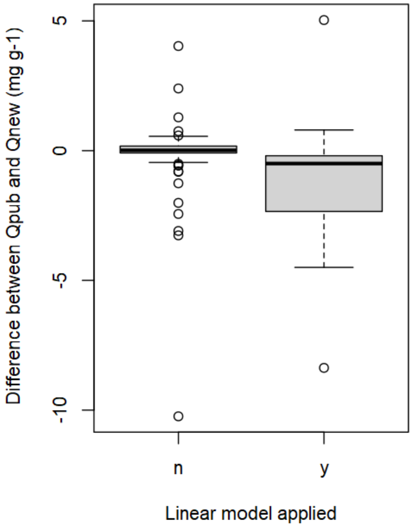

Figure S3. Difference in Q_{pub} vs Q_{new} based on the application of linear (y) vs non-linear (n) modelling approach. Differences are significant based on a one-way Wilcoxon rank sum (W: 1655, $p < 0.001$)

Table S3. Variables included in the final models. Definitions for feedstock are derived from the study by Cayuela et al. (2014).

			Model parametrisation	
Variable	Units	Levels of factor	Sub set 1	Sub set 2
Activation	Factor	Yes, No	+	+
Solution pH	pH		+	+
Biochar HTT	°C		+	+
Feedstock type	Factor	Agri Waste, Biosolids, Combi, Herbaceous, Wood	+	+
(O+N):C	Molar ratio			+

Table S4. Model subsets, reasoning for subsetting and estimates of centre for each subset.

				Q_{new} **estimate of centre (mg g-1)**	
	Isotherms	**Studies**	**Description**	**Median**	**Mean (sd)**
Initial data	**125**	**31**	**Total data pool**	**5.32**	**83137 (917577)**
Subset 1	**116**	**29**	**Following removal of uncertain estimates**	**4.96**	**11.73 (23.09)**
Subset 2	**111**	**27**	**Removing outliers (Q_{new} > 30 mg g^{-1})**	**4.63**	**7.42 (6.79)**
Subset 3	**75**	**13**	**Only studies with measurements of (O+N):C**	**4.22**	**7 (6)**
Subset 4	**72**	**13**	**Excluding Eggshell feedstock**	**4.46**	**7 (6)**

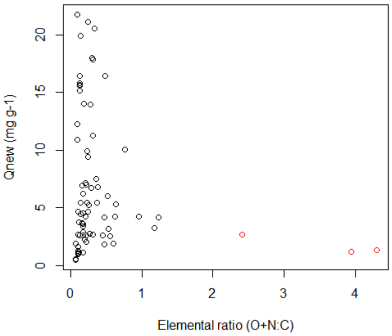

Figure S4. showing the outliers in the estimate of O+N:C relative to our estimate for Q_{new}. Points in red represent the eggshell biochars.

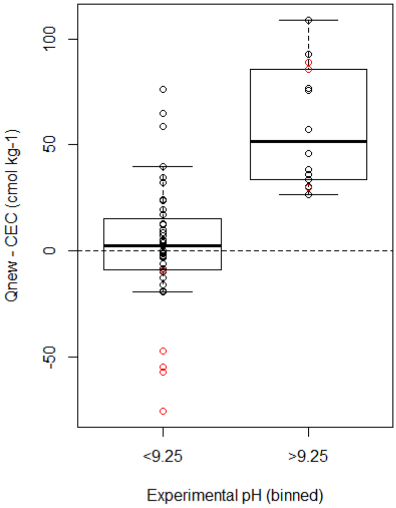

Figure S5. Showing the calculated difference between estimates for Q_{new} and the reported CEC. Points in red represent studies where the biochar ash was removed.

Table S5a Subset 1 with outliers and without random effect.

	Q_nl		**Q_nl**	
Predictors	*Estimates*	*CI*	*Estimates*	*CI*
(Intercept)	4.2	3.34 – 5.05	4.49	3.43 – 5.55
Biochar HTT	0	-0.01 – -0.00	0	-0.01 – -0.00
feed_type [biosolids]	-0.93	-1.95 – 0.09	-1.03	-2.06 – 0.01
feed_type [Combi]	0.83	-0.27 – 1.94	0.85	-0.26 – 1.95
feed_type [Herbaceous]	0.32	-0.25 – 0.88	0.27	-0.30 – 0.84
feed_type [Wood]	-0.51	-1.15 – 0.13	-0.59	-1.25 – 0.07
Solution pH			-0.05	-0.16 – 0.06
Observations	116		116	
AICc	769.56		770.99	

Table S5b Subset 2 without outliers and without random effect

	Q_nl		**Q_nl**	
Predictors	*Estimates*	*CI*	*Estimates*	*CI*
(Intercept)	0.86	-0.17 – 1.88	0.48	-0.46 – 1.43
activation [y]	0.54	0.17 – 0.91	0.55	0.18 – 0.91
Solution pH	0.19	0.09 – 0.29	0.18	0.08 – 0.28
feed_type [biosolids]	-0.47	-1.25 – 0.31	-0.43	-1.22 – 0.36
feed_type [Combi]	0.61	-0.26 – 1.48	0.62	-0.26 – 1.50
feed_type [Herbaceous]	0.09	-0.34 – 0.52	0.07	-0.37 – 0.50
feed_type [Wood]	-0.75	-1.27 – -0.24	-0.79	-1.32 – -0.27
Biochar HTT	0	-0.00 – 0.00		
Observations	111		111	
AICc	632.32		632.69	

Table S5c Subset 2 without outliers and with random effect

	Q_nl		**Q_nl**		**Q_nl**		**Q_nl**	
Predictors	*Est.*	*CI*	*Est.*	*CI*	*Est.*	*CI*	*Est.*	*CI*
(Intercept)	0.96	-0.02 – 1.95	0.8	-0.19 – 1.79	1.52	1.16 – 1.89	1.78	1.19 – 2.37
activation [y]	0.91	0.48 – 1.33	0.9	0.47 – 1.33	0.87	0.44 – 1.31	0.87	0.44 – 1.30
Biochar HTT	-0.001	-0.002 – 0.00					-0.001	-0.00 – 0.00
Solution pH	0.13	0.00 – 0.25	0.09	-0.03 – 0.21				
Random Effects								
σ^2	0.31		0.32		0.32		0.32	
τ_{00}	0.47 $_{auth}$		0.51 $_{auth}$		0.57 $_{auth}$		0.56 $_{auth}$	
ICC	0.6		0.62		0.64		0.64	
N	27 $_{auth}$		27 $_{auth}$		27 $_{auth}$		27 $_{auth}$	
Observations	111		111		111		111	
Marginal R^2 / Conditional R^2	0.180 / 0.673		0.155 / 0.676		0.142 / 0.695		0.150 / 0.693	
AICc	597.764		598.254		598.317		599.335	

Table S5d Subset 4 without eggshell biochar with random effect

	Q_nl		**Q_nl**		**Q_nl**	
Predictors	*Est.*	*CI*	*Est.*	*CI*	*Est.*	*CI*
(Intercept)	0.69	-0.36 – 1.75	0.29	-0.86 – 1.45	-0.01	-1.14 – 1.12
activation [y]	0.91	0.33 – 1.49	0.91	0.35 – 1.47	0.88	0.32 – 1.44
Biochar HTT	0	-0.00 – -0.00	0	-0.00 – 0.00		
Solution pH	0.2	0.07 – 0.33	0.19	0.06 – 0.32	0.15	0.02 – 0.28
O_C_N			0.74	-0.21 – 1.70	1.18	0.32 – 2.04
Random Effects						
σ^2	0.27		0.26		0.27	
τ_{00}	0.33 $_{auth}$		0.36 $_{auth}$		0.42 $_{auth}$	
ICC	0.55		0.58		0.61	
N	13 $_{auth}$		13 $_{auth}$		13 $_{auth}$	
Observations	72		72		72	
Marginal R^2 / Conditional R^2	0.228 / 0.651		0.216 / 0.673		0.185 / 0.684	
AICc	374.509		374.596		375.057	

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NIBIO
NORWEGIAN INSTITUTE OF
BIOECONOMY RESEARCH

Postboks 115
NO-1431 Ås, Norway
www.nibio.no/en

NMBU
Norwegian University
of Life Sciences

Postboks 5003
NO-1432 Ås, Norway
+47 67 23 00 00
www.nmbu.no

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