Biochar, soil and land-use interactions that reduce nitrate leaching and N$_2$O emissions: A meta-analysis

Nils Borchard$^{a,b,⁎}$, Michael Schirrmann$^c$, Maria Luz Cayuela$^d$, Claudia Kammann$^e$, Nicole Wrage-Mönnig$^f$, Jose M. Estavillo$^g$, Teresa Fuertes-Mendizábal$^h$, Gilbert Sigua$^i$, Kurt Spokas$^j$, James A. Ippolito$^j$, Jeff Novak$^h$

$^a$ Center for International Forestry Research, Jalan CIFOR, Situ Gede, Sindang Barang, Bogor 16115, Indonesia
$^b$ Natural Resources Institute Finland (Luke), Latokartanonkaari 9, 00790 Helsinki, Finland
$^c$ Leibniz Institute for Agricultural Engineering and Bioeconomy, Max-Eyth-Allee 100, 14469 Potsdam, Germany
$^d$ Department of Soil and Water Conservation and Waste Management, CEBAS-CSIC, Campus Universitario de Espinardo, 30100 Murcia, Spain
$^e$ Geisenheim University, Department of Applied Ecology, Von-Lade-Straße 1, 65366 Geisenheim, Germany
$^f$ University of Rostock, Faculty of Agricultural and Environmental Sciences, Grassland and Fodder Sciences, Justus-von-Liebig-Weg 6, 18059 Rostock, Germany
$^g$ University of the Basque Country (UPV/EHU), Department of Applied Ecology, Von-Lade-Straße 1, 65366 Geisenheim, Germany
$^h$ United States Department of Agriculture, Agriculture Research Service, Coastal Plains Research Center, 2611 West Lucas Street, Florence, SC 29501, USA
$^i$ United States Department of Agriculture, Agriculture Research Service, Soil & Water Management Research Unit, 439 Borlaug Hall, 1391 Buford Circle, University of Minnesota, St. Paul, MN 55108, USA
$^j$ Department of Soil and Crop Sciences, C127 Plant Sciences Building, Colorado State University, Fort Collins, CO 80523-1170, USA

HIGHLIGHTS

- N$_2$O emissions were reduced by 38% with biochar.
- Soil NO$_3$ concentrations remained unaffected.
- NO$_3$ leaching was reduced by 13% with biochar.
- Biochar strongly reduced N$_2$O-emission in paddy and sandy soils.

GRAPHICAL ABSTRACT

ABSTRACT

Biochar can reduce both nitrous oxide (N$_2$O) emissions and nitrate (NO$_3$) leaching, but refining biochar’s use for estimating these types of losses remains elusive. For example, biochar properties such as ash content and labile organic compounds may induce transient effects that alter N-based losses. Thus, the aim of this meta-analysis was to assess interactions between biochar-induced effects on N$_2$O emissions and NO$_3$ retention, regarding the duration of experiments as well as soil and land use properties. Data were compiled from 88 peer-reviewed publications resulting in 608 observations up to May 2016 and corresponding response ratios were used to perform a random effects meta-analysis, testing biochar’s impact on cumulative N$_2$O emissions, soil NO$_3$ concentrations and leaching in temperate, semi-arid, sub-tropical, and tropical climate. The overall N$_2$O emissions reduction was 38%, but N$_2$O emission reductions tended to be negligible after one year. Overall, soil NO$_3$ concentrations remained unaffected while NO$_3$ leaching was reduced by 13% with biochar; greater leaching reductions (>26%) occurred over longer experimental times (i.e. >30 days). Biochar had the strongest N$_2$O-emission reducing effect in paddy soils (Anthrosols) and sandy soils (Arenosols). The use of biochar reduced...
1. Introduction

Agriculture accounts for ~60% of global anthropogenic N₂O emissions, largely due to organic and mineral nitrogen (N) fertilizer use and the extended use of legumes either as crops (soy, pea, bean or groundnut) or as green cover (Davidson, 2009; IPCC, 2013; Kammann et al., 2017; Smith et al., 2008). In addition to fertilizer-induced N₂O emissions, excessive N fertilization or inadequate timing of N application not fitting plant demand also leads to N leaching that affects ground and surface water quality, reduces N use efficiency (Ding et al., 2010), and subsequently elevates indirect N₂O emissions (Cooper et al., 2017; Minghua et al., 2017; Tian et al., 2017) e.g. from landscape-draining waterways (Turner et al., 2015).

Soil N₂O emissions and nitrate (NO₃⁻) losses are mainly a result of microbial activities affecting inorganic soil N concentrations via nitrification and denitrification processes, and by abiotic processes (Barnard et al., 2005; Bateman and Baggs, 2005; Cayuela et al., 2014; IPCC, 2006). Nitrification is the transformation of ammonium (NH₄⁺) to NO₃⁻ via nitrite (NO₂⁻), with N₂O being a by-product. Denitrification reduces NO₃⁻ or NO₂⁻ to NO, N₂O, and N₂ (Barnard et al., 2005; Cayuela et al., 2014; Harter et al., 2014; IPCC, 2006; Kammann et al., 2017). Efficiency and productivity of nitrification is mainly affected by availability of N and oxygen while availability of biodegradable organic matter and lack of oxygen govern efficiency and productivity of denitrification (Barnard et al., 2005; Bateman and Baggs, 2005; Linn and Doran, 1984; Granli and Bockman, 1994). Microbes performing nitrification prefer slightly acidic to alkaline soil pH, while soil denitrification is at optimum between pH 4 to 8 (Ahn, 2006; Antoniou et al., 1990; Barnard et al., 2005). Availability of easily biodegradable organic matter stimulates denitrification as it provides energy to maintain microbial metabolism and electrons required to reduce NO₃⁻ (Ahn, 2006; Barnard et al., 2005). Thus, physico-chemical soil properties regulate and organic matter amendments stimulate N₂O emissions.

Recently, biochar has been proposed as an organic carbon (C) soil amendment for reducing leaching of soil compounds (Abdelrahman et al., 2018; O’Connor et al., 2018a) and for improving soil quality (Crane-Droesch et al., 2013; Liu et al., 2013; Mehmoood et al., 2017). Biochar may add both a small mineralizable and a more recalcitrant, less mineralizable C fraction to soils (Wang et al., 2016); additionally, biochar has also been shown to retain NO₃⁻ within its pores (Kammann et al., 2015; Haider et al., 2016, 2017; Hagemann et al., 2017a; Sumaraj and Padhye, 2017). Therefore, applying biochar to soils may affect conditions that control nitrification, denitrification (Cayuela et al., 2014; Kammann et al., 2017; Liu et al., 2018), and other N transformation and loss pathways. In order to evaluate biochars’ overall potential and magnitude for reducing N losses across application locations, agricultural systems, application rates, and time, meta-analyses have been found to be a useful tool (Borenstein et al., 2009).

The first meta-analysis studying biochar impact on soil N₂O emissions showed a mean reduction of 54% (Cayuela et al., 2014); further meta-analyses, particularly those including field studies, have shown lower N₂O reductions ranging between 12 and 32% (Cayuela et al., 2015; Liu et al., 2018; Verhoeven et al., 2017). The meta-analysis published by Liu et al. (2018) was the first study to present biochar impacts on N pools, N fluxes, and the N cycle, but interactions between biochar use and experimental duration, soil types, and land use are still scarcely understood or exclusively assessed for C cycling (Wang et al., 2016; Verhoeven et al., 2017; Duarte-Guardia et al., 2018). Thus, the current meta-analysis differs from previous biochar meta-analyses, because it assesses the impact of biochar on N₂O emissions, NO₃⁻ leaching and final NO₃⁻ concentration in soil based on: (i) experimental duration that affects the C and N cycle (Hagemann et al., 2017b; Wang et al., 2016), (ii) relevance of soil and land use types to provide a basis for spatial (global) assessments (Duarte-Guardia et al., 2018; Werner et al., 2018), and (iii) impact of agricultural practices, such as vegetation type and fertilizer use.

Recently, biochar has been proposed as an organic carbon (C) soil amendment for reducing leaching of soil compounds (Abdelrahman et al., 2018; O’Connor et al., 2018a) and for improving soil quality (Crane-Droesch et al., 2013; Liu et al., 2013; Mehmoood et al., 2017). Biochar may add both a small mineralizable and a more recalcitrant, less mineralizable C fraction to soils (Wang et al., 2016); additionally, biochar has also been shown to retain NO₃⁻ within its pores (Kammann et al., 2015; Haider et al., 2016, 2017; Hagemann et al., 2017a; Sumaraj and Padhye, 2017). Therefore, applying biochar to soils may affect conditions that control nitrification, denitrification (Cayuela et al., 2014; Kammann et al., 2017; Liu et al., 2018), and other N transformation and loss pathways. In order to evaluate biochars’ overall potential and magnitude for reducing N losses across application locations, agricultural systems, application rates, and time, meta-analyses have been found to be a useful tool (Borenstein et al., 2009).

The first meta-analysis studying biochar impact on soil N₂O emissions showed a mean reduction of 54% (Cayuela et al., 2014); further meta-analyses, particularly those including field studies, have shown lower N₂O reductions ranging between 12 and 32% (Cayuela et al., 2015; Liu et al., 2018; Verhoeven et al., 2017). The meta-analysis published by Liu et al. (2018) was the first study to present biochar impacts on N pools, N fluxes, and the N cycle, but interactions between biochar use and experimental duration, soil types, and land use are still scarcely understood or exclusively assessed for C cycling (Wang et al., 2016; Verhoeven et al., 2017; Duarte-Guardia et al., 2018). Thus, the current meta-analysis differs from previous biochar meta-analyses, because it assesses the impact of biochar on N₂O emissions, NO₃⁻ leaching and final NO₃⁻ concentration in soil based on: (i) experimental duration that affects the C and N cycle (Hagemann et al., 2017b; Wang et al., 2016), (ii) relevance of soil and land use types to provide a basis for spatial (global) assessments (Duarte-Guardia et al., 2018; Werner et al., 2018), and (iii) impact of agricultural practices, such as vegetation type and fertilizer use.
2. Material and methods

2.1. Data compilation

A comprehensive survey of literature published between January 1, 2010 and May 31, 2016 was conducted, compiling 608 observations from 88 peer-reviewed publications accessed on the ISI Web of Knowledge. By using the term “biochar” in the “topic” field, 3328 publications appeared, but the number was reduced to 88 publications by abstract and full publication screenings (Table S1). Studies were scrutinized using the following inclusion/exclusion quality criteria: They: (i) were conducted in soil (e.g., horticultural substrates were excluded); (ii) included a minimum of three replicates per treatment; (iii) followed a randomized design; (iv) contained a “treatment” and a “control” such that the treatment was the same as the control in all aspects except for the inclusion of biochar; and (v) reported cumulative net N2O emissions, cumulative NO3 leached and/or final NO3 concentrations in soil. Data (i.e., mean values, standard deviation, standard error, number of replicates) on N2O fluxes, NO3 concentration in soil after experiment, and NO3 leaching were collected from tables, from figures by using WebPlotDigitizer software (www.automeris.io/WebPlotDigitizer/), or from contacting the authors directly. The final dataset consists of 608 observations, with 120 observations for nitrate leaching, 146 observations for nitrate concentration in soil after the experiment, and 435 observations for cumulative NO3 emissions (Table S2). Factors controlling N2O emissions, NO3 concentration in soil after the experiments, and cumulative NO3 leaching were also collected from the publications. Once the dataset was completed, it was subjected to a strict quality check and each observation and related predictor variable was checked by at least two researchers independently. When there was a disagreement between the extracted values, the respective study was checked by an additional third researcher and a final correction was reached. Data were then grouped by study length, biochar properties, soil properties, N fertilization, and land use. Grouping was performed in accordance to previous classifications used by Jeffery et al. (2011) and Cayuela et al. (2014) (Table S3), considering a minimum number of observations per group to process reliable data (Table S4).

2.2. Meta-analysis

The effect of biochar treatment on N2O emissions, NO3 concentration, and NO3 leaching was estimated via meta-analysis. As a standardized metric of the effect size, the natural log response ratio (RR) was computed for each experiment (Hedges et al., 1999):

\[
RR = \ln \left( \frac{X_{\text{ctr}}}{X_{\text{trt}}} \right)
\]

which is the ratio between the treatment mean \(X_{\text{trt}}\) and the control mean \(X_{\text{ctr}}\). In the case of N2O emissions, RR is defined as the ratio between the cumulative N2O emissions from the biochar treated soil and the N2O emissions from the non-treated soil in each study. An RR with zero would mean no effect, while a negative or positive RR value would mean a reduction or increase in N2O emissions through biochar treatment, respectively. The logarithm ensures better statistical properties of the effect size distribution and equal influence of nominator and denominator on the metric. The RR was expressed as a percentage change relative to zero. The variance of RR is given as (Hedges et al., 1999):

\[
\text{var}(RR) = \frac{SD_{\text{trt}}^2}{N_{\text{trt}}X_{\text{trt}}^2} + \frac{SD_{\text{ctr}}^2}{N_{\text{ctr}}X_{\text{ctr}}^2},
\]

where SDtrt2 and SDctr2 are the standard deviation and Ntrt and Nctr are the sample sizes of the treatment or control of the experiment. The parameters for calculating RR and var(RR) were extracted from the studies or recalculated when necessary. Funnel plots were used to detect biases in the traits included in the meta-analyses. The funnel plots were symmetric for N2O emissions, NO3 concentration, and NO3 leaching data sets, which indicates absence of publication biases.

The combined effect size over all available studies was estimated with a random effects model. The random effects model was chosen because we did not assume that the underlying true effect size is homogeneous over all included studies due to study conditions and environmental influences, and we further wanted to make generalizations beyond the observed studies (Hedges and Vevea, 1998). The random effects model was estimated with the DerSimonian-Laird estimator (DerSimonian and Laird, 2015). Each study was weighted by the inverse of its sampling error variance (inverse-variance-weighting), which ensures that studies with very small sample sizes do not have a severe influence on the estimates. The overall effect was estimated for cumulative N2O emissions, final NO3 concentration, and cumulative NO3 leaching. For assessing the heterogeneity of the meta-analysis, the I² index was used. The I² index indicates the percentage of the total variability among the effect sizes that can be explained by the between-studies heterogeneity (Huedo-Medina et al., 2006). Furthermore, we explored possible factors and relations influencing the overall effect sizes including study length, biochar properties, soil properties, N fertilization, and land use. These factors were grouped in accordance to previous classifications by Cayuela et al. (2014) and Jeffery et al. (2011) (Tables S3 & S4). Categories with less than two samples were removed from analysis. The subgroup analysis was conducted with a categorical random effects model and summarized in forest plots. All estimates were reported along with 95% confidence intervals. Estimates and confidence intervals were calculated from bootstrapping the random effects models with 1000 bootstrap intervals. Positive publication bias was tested with the Failed Safe N-test that takes into account the tendency of journals to only publish significant results. A fail-safe number was calculated using the Rosenberg method, indicating the number of non-significant or missing studies that one would need to add to the meta-analysis data set to reduce the observed, overall statistically significant results (Rosenberg, 2007).

3. Results

3.1. Percent overall changes and their change over time

Results showed a significant reduction of overall N2O emissions by 38% (\(P < 0.05\); Fig. 1) caused by biochar applications. According to the Failed Safe N-test, the significant N2O reduction is robust against a possible positive publication bias because a huge number of non-significant observations would need to be furthermore included in the meta-analysis (\(>650,000\)) to turn the significant result into a non-significant result (Table S4). However, biochar induced reductions of N2O emissions were of transient nature with a tendency to be negligible within one year (Fig. S1). In spite of a non-significant overall effect on NO3 leaching, biochar significantly and consistently reduced NO3 leaching by 26 to 32% in studies with an experimental time of \(>30\) days (Fig. 1). In parallel, available NO3 in soils decreased over time with significant reductions for experiments conducted for \(>120\) days (Fig. 1).

3.2. Biochars

Results suggest a dependency of biochar feedstock selection and conversion technology on N dynamics (Fig. 2). Biochars produced of wood and lignocellulosic biomass by gasification, slow pyrolysis, and their combination with steam at each heating temperature, reduced soil N2O emissions (\(P < 0.05\)). On the other hand, N2O emissions remained unaffected after application of i) biochars made of manure and biosolids (\(P = 0.095\)) and ii) biochar produced by fast pyrolysis (particle residence time a few seconds; Bruun et al. 2012) and iii) hydrochars produced via hydrothermal carbonization (Libra et al.
Concentrations of $\text{NO}_3^-$ significantly decreased in soils amended with biochars produced at heating temperatures $>500 \degree C$ and with those produced by fast pyrolysis. Biochars produced from lignocellulosic biomass and biochars produced at temperatures of $>500 \degree C$ reduced $\text{NO}_3^-$ leaching. Particle size of biochar particles did not affect $\text{N}_2\text{O}$ emissions, $\text{NO}_3^-$ concentration, and $\text{NO}_3^-$ leaching ($\text{NO}_3^-$ leaching$_\text{biochar}$. $P = 0.069$; Fig. 3). $\text{N}_2\text{O}$ emissions were reduced after biochar application over a broad range of biochar pH, N and C contents, except for biochars consisting of $\approx 460 \text{ g C kg}^{-1}$; a relatively small number of biochar types ($5.9$ to $12.8 \text{ g N kg}^{-1}$ and C/N mass ratio of $100$ to $200$) reduced the $\text{NO}_3^-$ concentration in soil. Exclusively wood biochars characterized by pH values ranging between $7.8$ and $8.9$ increased $\text{NO}_3^-$ concentration in soil, while acidic to neutral ($\text{pH} < 7.8$) and strongly alkaline ($\text{pH} > 9.6$) biochars reduced leaching of $\text{NO}_3^-$. Leaching of $\text{NO}_3^-$ was further reduced by biochars consisting of $\approx 780 \text{ g C kg}^{-1}$, N ranging between $3.3$ and $5.9 \text{ g kg}^{-1}$, and C/N mass ratio of $100$ to $200$.

3.3. Soils

Soil $\text{N}_2\text{O}$ emissions were reduced regardless of soil texture (i.e. clay, silt, sand) as reflected by small data variability ($-34 \pm 8\%$; strongest reduction in soil with $>70\%$ sand: $-47\%$) (Table S4). The concentration of $\text{NO}_3^-$ in soil varied strongly ($-6 \pm 26\%$) among grouped textures (Table S4) and only coarse textured soils (i.e. sand) showed a reduced concentration and leaching of $\text{NO}_3^-$ (Fig. 4).

Biochar reduced $\text{N}_2\text{O}$ emissions at each soil pH and C/N ratio (Fig. 5). However, in soils with SOC concentrations $>24 \text{ g kg}^{-1}$ and total N concentrations $>3 \text{ g kg}^{-1}$, the $\text{N}_2\text{O}$ emission reduction was smallest and not significant. Furthermore, biochar applications reduced soil $\text{NO}_3^-$ concentrations in slightly acidic to neutral soils ($\text{pH} 5.5$ to $7.0$), in soils that contained low SOC concentrations ($<10 \text{ g kg}^{-1}$), and in low total N soils ($<1 \text{ g kg}^{-1}$). Interestingly, soils that were less affected by biochar in terms of soil $\text{NO}_3^-$ concentrations actually showed reduced soil $\text{NO}_3^-$ leaching ($\text{pH} < 5.5$; $10$ to $24 \text{ g C kg}^{-1}$, $0.7$ to $1.7 \text{ g N kg}^{-1}$, C/N mass ratios of $>9.3$ and $>12.4$).

3.4. Soil types and soil management

Man-made soils (i.e. Anthrosols represented in this study exclusively by paddy soils), organic soils (i.e. Histosols), sandy soils (i.e. Arenosols), and soils typical for steppe and sub-humid temperate climate (i.e. Luvisol) showed reduced $\text{NO}_3^-$ emissions after biochar applications (Figs. 7 and 8). Biochar applications reduced $\text{NO}_3^-$ concentration only in Luvisols (i.e., soils of sub-humid temperate climate). Soil $\text{NO}_3^-$ leaching was exclusively reduced in Cambisols (i.e. soils of limited age), and semi-arid soils (i.e. Calcisol, Solonetz) (Figs. 6 and 7). Low biochar application rates of $\approx 10 \text{ Mg ha}^{-1}$ neither affected $\text{N}_2\text{O}$ emissions nor $\text{NO}_3^-$ leaching, but increased $\text{NO}_3^-$ concentration in soils (Fig. 8). Larger biochar application rates (e.g., $\approx 10$ to $20 \text{ Mg ha}^{-1}$) reduced $\text{N}_2\text{O}$ emissions, and tended to reduce $\text{NO}_3^-$ leaching and concentration. $\text{N}_2\text{O}$ emissions, $\text{NO}_3^-$ concentrations in soils, and $\text{NO}_3^-$ leaching remained unaffected for soils managed by application of biochar in combination with organic fertilizers. Compared to unfertilized soils, the $\text{NO}_3^-$ emission mitigation potential of biochars was larger for fertilized soils (reduction of $-46\%$ for mineral fertilizer [e.g. $\text{NH}_4\text{NO}_3$, $\text{NH}_4\text{H}_2\text{SO}_4$, $\text{KNO}_3$], $-34\%$ for urea, $-32\%$ for mixtures of organic and mineral fertilizers, and $-27\%$ for unfertilized soils; Fig. 8). The impact of biochar and fertilizers on $\text{NO}_3^-$ concentration in soils varied, with reduced $\text{NO}_3^-$ concentration for biochar experiments fertilized with mineral N and increased $\text{NO}_3^-$ concentration in soils after use of urea in combination with biochar. Additions of organic fertilizer and...
unfertilized biochar experiments did not affect NO$_3^-$ concentration measured after experiments. Leaching of NO$_3^-$ was reduced by biochar in unfertilized soil and when the fertilizer application rate was below 150 kg N ha$^{-1}$ (Fig. 8). For each N application rate, biochar induced a reduction of N$_2$O emissions, but leaching of NO$_3^-$ progressively increased in response to increased N application rates (i.e. -26% for 150 kg N ha$^{-1}$, -7% for 150–300 kg N ha$^{-1}$, 46% for >300 kg N ha$^{-1}$). Hence, over all N fertilizer application rates, the NO$_3^-$ leaching reduction was not significant (i.e. +3% with mineral fertilizer, -7% with organic fertilizer, and -35% with organo-mineral fertilizer). In parallel to reduced NO$_3^-$ leaching in soils fertilized with <150 kg N ha$^{-1}$, concentration of NO$_3^-$ was also reduced. Larger N application rates showed increased concentration of NO$_3^-$ after application of 150 to 300 kg N ha$^{-1}$, but did not affect NO$_3^-$ concentration after application of >300 kg N ha$^{-1}$.

Except for perennial crops (e.g. fruit trees), N$_2$O emissions at least tended to be reduced in all agronomic experiments (i.e. arable crops with -45% and horticultural cultures with -32%) that cultivated cereals (-31%, P < 0.05), maize (-31%, P = 0.17), rice (-40%, P < 0.05), vegetables (-30%, P = 0.07), and other crops (-35%, P = 0.18) (Fig. 9). Compared to control soils, agricultural soils enriched with biochar were further depleted in NO$_3^-$ while NO$_3^-$ leaching was reduced. Biochar applications to grassland increased NO$_3^-$ concentration in soils, but neither N$_2$O emissions nor NO$_3^-$ leaching were affected.

4. Discussion

Overall, soil N$_2$O emissions and NO$_3^-$ leaching were reduced after biochar applications, while soil NO$_3^-$ concentration remained overall unaffected. These findings are in line with meta-analysis results published by Liu et al. (2018) and Nguyen et al. (2017), except that their findings (based on 796 observations) indicated a significant reduction of 12% in soil NO$_3^-$ concentration. In the current study, reasons for reduced NO$_3^-$ leaching and an at least unaffected concentration of NO$_3^-$ were presumably the result of soil processes affected by biochar and the ability of biochar to reversibly take up and release nitrate (Kammann et al. 2015, Haider et al. 2016, 2017; Hagemann et al. 2017a). Soil properties and processes can be modified by biochar in several ways. Biochar increases soil pH due to its "liming effect" (Clough et al., 2013; Hüppi et al., 2015; Nguyen et al., 2017), which induces a shift of the NH$_4^+$/NH$_3$(g) equilibrium promoting release of NH$_3$ at elevated pH values, biochar-induced NH$_3$ volatilization, particularly from acidic soils, may
have reduced soil NO$_3^-$ concentration and leaching (Liu et al., 2018). Other potential mechanisms explaining NO$_3^-$ concentration and leaching from soil are i) a presumed sorption of NO$_3^-$ on biochar (Nguyen et al., 2017; Sumaraj and Padhye, 2017; Yao et al., 2012), ii) biochar entrapment of NO$_2^-$/NO$_3^-$ (Kammann et al., 2015; Haider et al., 2016, 2017; Hagemann et al., 2017a, b; Pignatello et al., 2006), and iii) stabilization of NO$_3^-$ in biochar pores and organo-mineral coatings on biochars that hampers release, but promotes nitrate capture (Kammann et al., 2015; Hagemann et al., 2017a, b; Haider et al., 2016; Joseph et al., 2017). Thus, biochar can alter processes controlling NO$_3^-$ formation substantially, but its interaction with pathways of NO$_3^-$ stabilization and retention remain elusive.

The same mechanisms may further explain reduced N$_2$O emissions, with multiple processes needing to be considered to explain biochar-induced alteration of N$_2$O emissions. It has been shown that biochar addition can promote the expression of the N$_2$O reductase genes of denitrifiers (NosZ), promoting a complete reduction of NO$_3^-$ to N$_2$ instead of N$_2$O (Wang et al., 2013; Harter et al., 2014), thereby shaping microbial communities (Harter et al., 2016a, b; Krause et al., 2018). Theoretically, the effect can be related to a slight pH increase around biochar particles; it is well known that a higher soil pH promotes a more complete denitrification to N$_2$. On the other hand, a reduction of the nitrate concentration around biochar particles can reduce the concentration of “NO$_3^-$ substrate” for denitrifiers which would be in line with the observation of an increase in the NosZ gene expression. Furthermore, one may assume that biochar adds a fraction of readily degradable organic C sources (Lan et al., 2017; Wang et al., 2016), which induces a reduction of N$_2$O emissions (Barnard et al., 2005; Cayuela et al., 2013; Lan et al., 2017) by microbial growth and N immobilization. These processes impart a complex study matrix upon systems that receive biochar, which may explain the lack of process-based knowledge in the literature.

4.1. Impact of time

Our meta-analysis indicated a transient nature of biochar on N$_2$O emissions reduction, which needs more research regarding the mechanisms, and which needs to be taken into account as a dynamic factor when assessing biochars’ long-term greenhouse gas mitigation potential (Woolf et al., 2010). Factors that affect biochars’ long-term ability to reduce soil N$_2$O emissions includes biochar aging within soil, leading to biochar surface property changes via oxidation and formation of oxygen-containing functional groups (Mia et al., 2017), sorption of natural organic matter leading to clogged biochar pores (Kasozi et al., 2010; Pignatello et al., 2006; Sumaraj and Padhye, 2017; Hagemann et al., 2017b), and formation of organo-mineral complexes coating biochar surfaces (Joseph et al., 2017; Sumaraj and Padhye, 2017). Alteration of surface functional groups will affect electrostatic interactions, reducing the capacity of biochar to sorb NO$_3^-$ (Güereña et al., 2012; Mia et al., 2017; Nguyen et al., 2017) while organo-mineral complexes tend to increase NO$_3^-$ retention by mechanisms still under debate (Hagemann et al., 2017b; Joseph et al., 2017; Nguyen et al., 2017; Sumaraj and Padhye, 2017). Hence, aging of biochar and capturing NO$_3^-$ may explain progressive reduction of NO$_3^-$ concentration in and leaching from soil, which can suppress N$_2$O emissions from denitrification pathways (Bouwman et al., 2002; Cayuela et al., 2013; Pelster et al., 2011).
4.2. Impact of biochar production and properties

Results suggested that N$_2$O emissions remained unaffected after application of N-rich biochars (e.g., manure and biosolids feedstocks) characterized by C/N ratios similar to soil organic matter (C/N: 17 ± 1), while application of N-poor biochars made from wood and lignocellulosic biomass (C/N: 279 ± 13 and 112 ± 5, respectively) reduced N$_2$O emissions, similar to the findings of Liu et al. (2018). Our results further indicate that NO$_3^-$ concentration remained overall unaffected, but Liu et al. (2018), who utilized a larger number of observations, revealed a significant decrease in soil NO$_3^-$ concentration (12%). Our study revealed that NO$_3^-$ concentrations were reduced at N fertilizing rates (<150 kg N ha$^{-1}$) typically applied to biochar experiments as also reviewed by O’Connor et al. (2018b), but increased when N fertilization was higher (150–300 kg N ha$^{-1}$). Similar to previous research (e.g., Clough et al., 2013; Kanthle et al., 2016; Demiraji et al., 2018; Liu et al., 2018), soil NO$_3^-$ leaching was overall reduced by biochar application. Factors that may explain these findings are the availability of easily biodegradable organic C and ash present in biochar, both affecting soil N transformation or nitrate capture by biochar. Biochar produced at temperatures $\leq 500$ °C are almost free of labile organic C while those produced at temperatures $> 500$ °C can contain labile organic material (Keiluweit et al., 2010; Wang et al., 2016; Zimmerman et al., 2011); biochar-borne labile organic C sources may induce microbial immobilization of N or capture NO$_3^-$ by organic coating found on aged biochars (Borchard et al., 2014c; Clough et al., 2013, Hagemann et al., 2017a, b). Applied biochar particles that contain ash are slightly alkaline (i.e. close to 7.8) and provide a spatially limited, but optimal environment for substantially stimulated nitrifier activity (Antoniou et al., 1990; Barnard et al., 2005; Nguyen et al., 2017), which may explain elevated NO$_3^-$ concentrations in soils amended with biochars having pH between 7.8 and 8.9. Another potential pathway for a stimulated nitrifier activity is the sorption of inhibitory phenolic compounds that can reduce or block nitrifier activity e.g. in acidic conifer forest soils (DeLuca et al. 2006).
4.3. Impact of soil type and soil properties

Biochar applications increased NO$_3^-$ concentration in very coarse soils (>80% sand) and soils poor in organic C and N. Although the exact mechanisms are unknown, this could be a result of biochar application that increased total soil organic C and a stimulated stabilization of inherent soil C (Borchard et al., 2014a; Hernández-Sorián et al., 2015; Kasozi et al., 2010; Pignatello et al., 2006), a subsequent accelerated N transformation, and sorption and/or retention of NO$_3^-$ (Nelissen et al., 2012; Clough et al., 2013; Liu et al., 2018). Adding biochar to coarse textured soils typically affects water retention and flow (Ajayi and Horn, 2016; Clough et al., 2013; Petersen et al., 2016), which is assumed to reduce NO$_3^-$ leaching as stated by Liu et al. (2018) and this meta-analysis. When applied to acidic soils and soils rich in soil organic matter, biochar may have induced decomposition of native soil organic matter (Ding et al., 2017; Wang et al., 2016), stimulating soil organic matter mineralization, nitrification, and formation of NO$_3^-$ (e.g. Nelissen et al., 2012). In comparison to findings by Liu et al. (2018), our meta-analysis results showed that NO$_3^-$ emissions remained unaffected in soils rich in organic matter (>24 g kg$^{-1}$), here exclusively grassland soils as compared to other agricultural soils, see below) at elevated NO$_3^-$ concentration in soil stimulating an incomplete reduction of NO$_3^-$ (Barnard et al., 2005); moreover, the complete reduction of NO$_3^-$ to N$_2$ during denitrification was suppressed by low pH-values of these soils. Thus, pH, organic matter and texture are controlling factors explaining biochar-induced formation and retention of NO$_3^-$ in soil and corresponding N$_2$O emissions.

Soils that are well aerated, coarse textured, and typically poor in soil organic matter are Arenosols, while Histosols are rich in organic matter yet may also be anoxic (Driessen et al., 2001). Our results revealed that biochar applications to Arenosols had no effect on NO$_3^-$ concentration and leaching (~14%), but biochar reduced NO$_3^-$ emissions by ~48%. Arenosols are promoting almost complete nitrification of NH$_4^+$ to NO$_3^-$ (Chapin et al., 2011), which biochar evidently enhances in Arenosols (Meusel et al., 2018; Nguyen et al., 2017). Soils naturally known to be a source of N$_2$O emissions are Histosols and paddy soils (i.e. man-made soils or Anthrosols) that emit N$_2$O, especially during transitions of dry-to-flooded or flooded-to-dry soil conditions due to seasonally varying water regimes (Dalal et al., 2003; Kögel-Knabner et al., 2010; Liu et al., 2010; Peng et al., 2011; Schwärzel et al., 2002). Our results revealed that biochar applications to Histosols reduced NO$_3^-$ emissions by ~47%. This N$_2$O emissions reduction may be improved by biochar through i) alteration in soil moisture regime during non-flooded periods (Ajayi and Horn, 2016; Clough et al., 2013; Petersen et al., 2016), ii) a reduction of redox potentials to levels that promote formation of NH$_4^+$, or iii) complete denitrification to N$_2$ (Harter et al., 2014; Barnard et al., 2005; Cayuela et al., 2013; Sumaraj and Padnje, 2017).

4.4. Impact of soil conditioner and land use type

Agricultural land use requires replacement of nutrients by fertilization and can mitigate climate change by sequestering C in soils (Werner et al., 2018; Wollenberg et al., 2016). Biochar is thought to sequester C in soils and stabilize non-charred soil organic C (Abdelrahman et al., 2018; Borchard et al., 2014a; Wollenberg et al., 2016), which may have an impact on nitrification and subsequently on N$_2$O emissions (Nelissen et al. 2012). Our meta-analysis results showed that typical biochar application rates of ~10 Mg ha$^{-1}$ (ranges typically between 5 and 50 Mg ha$^{-1}$; Liu et al., 2013; Lorenz and Lal, 2014) reduced N$_2$O emissions, while NO$_3^-$ concentration and leaching tended to be reduced, similar to results of Liu et al. (2018). Our findings confirm that biochar-induced alterations of mineral N transformations are dose-related as also shown for crop yields and soil organic C dynamics (Crane-Droesch et al., 2013; Ding et al., 2017). Moreover, biochar applications significantly suppressed N$_2$O emissions typically induced by N fertilization (Barnard et al., 2005) indicating biochar could be a valuable mitigation tool to lower emission factors of N fertilizers. Assuming maintained or even increased yields after biochar application (Crane-Droesch et al., 2013), an important factor to consider is that reduced N$_2$O emissions also reduce greenhouse gas emission equivalents per kg produced agricultural crop.

Based on our meta-analysis results, it appears that a fertilizer dose-related mechanism progressively reduced soil NO$_3^-$ leaching and increased soil NO$_3^-$ concentration; this response, however, dropped to a non-significant response at N fertilizer application rates of >300 kg ha$^{-1}$. This effect likely may be due to the limited capacity of biochars to immobilize and entrap NO$_3^-$ (Borchard et al., 2014b; Clough et al., 2013; Hagemann et al., 2017b), explaining the reduced or even maintained NO$_3^-$ leaching for experiments that received >300 kg N ha$^{-1}$ compared to those receiving less N fertilization, and increased NO$_3^-$ concentration after application of >150 kg N ha$^{-1}$ (Borchard et al., 2014b). However, biochar could not prevent leaching of NO$_3^-$ after application rates of >300 kg N ha$^{-1}$. Thus, applying >300 kg N ha$^{-1}$ to biochar amended soils increases the risks associated with N loss by NO$_3^-$ leaching rather than by N$_2$O emissions; mechanisms controlling this finding remain unclear.

Patterns of reduced N$_2$O emissions, NO$_3^-$ concentration and leaching suggest that biochar application reduces N losses from agriculture (i.e. cereals, rice), except for grassland, perennial crops (e.g. gapevine and fruit trees), and forest. Compared to other agricultural soils (pH: 6.3 ± 1.2), biochar applications to Arenosols had no effect on NO$_3^-$ concentration and leaching, while NO$_3^-$ leaching during study affected by cultivated crops (cereals, maize, rice, vegetables, perennials, and other) and land use type (agriculture, grassland, horticulture, and forest). Data are shown as estimated mean effects and their lower and upper confidence intervals (55%). Circle size indicates number of observations (see also Supplementary information). Solid vertical line indicates mean of control treatments and dashed vertical line indicates mean of overall effect. Probability levels are indicated by asterisks (** for P < 0.001; * for P < 0.01, and “ for P < 0.05).
suitable for up-scaling N2O emission reduction estimations and potentially (e.g. texture, soil organic matter, pH) may provide reliable information about 

Considering land use (e.g., paddy soils, grasslands, annual crops) reduced both N2O emissions and NO3 leaching and presumably improves both N use efficiency and mitigates climate change. Considering land use (e.g., paddy soils, grasslands, annual or perennial cropping systems, etc.) in conjunction with soil properties (e.g. texture, soil organic matter, pH) may provide reliable information suitable for up-scaling N2O emission reduction estimations and potentials, and ultimately the best practical scenarios for environmental biochar use. Our results support the notion of a dose-response relationship of biochar application on N2O emission reduction and also NO3 leaching, which hints towards the interesting possibility of using biochar as a carrier matrix for “carbon-fertilizers” as successfully explored by Qian et al. (2014). Using biochar in this way could greatly reduce the required dose of N per hectare, which would improve N use efficiency and reduce the economic barriers for biochar use in agronomy. However, the eco-physiological mechanisms controlling N uptake by plants in soil-biochar-plant systems require further analyses to ensure sustainable N-management.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.10.060.

Acknowledgement

This work is also supported by the USDA/NIFA Interagency Climate Change Grant Proposal number 2014-02114 [Project number 6657–12130-002-08I, Accession number 1003011] under the Multi-Partner Call on Agricultural Greenhouse Gas Research of the FACCE-Joint Programme. The German BLE and FACCE-JPI funded the German participants of the “DesignChar4Food” (D4F) project (CK: Project No. 2814ER01A; NW-M: Project No. 2814ER02A), the Spanish colleagues (JME and TFM) were funded by FACCE-CSA no 276610/MIT04-DESIGN-UPVASC and IT-932-16, and US colleagues (JN, JI and KS) were funded by The USDA-National Institute of Food and Agriculture (Project # 2014–35615-21971), USDA-ARS CHARnet and GRACENet programs – D4F greatly stimulated discussions. MLC was supported by a “Ramón y Cajal” research contract from the Spanish Ministry of Economy and Competitiveness and thanks Fundación Séneca for the project # 19281/IPI/14. Any opinions, findings, or recommendation expressed in this publication are those of the authors and do not necessarily reflect the view of the USDA. Nils Borchard was appointed as integrated expert at CIFOR by the Centre for International Migration and Development (CIM). CIM is a joint operation of the Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH and the International Placement Services of the German Federal Employment Agency. Many thanks owed to Ines Heyer, Lisa Fitkau, and Andreas Haller for the help with compiling data.

References


