Point-by-point response to the reviews

Anonymous Referee #1 (C12-C13) Received and published: 09 February 2015.

The manuscript deals with the effects of freshed and aged biochars from pyrolysis and hydrothermal carbonization on nutrient sorption in agricultural soils. The topic of the manuscript could be of interest to the readers. It certainly falls in the SOILD. However, many parts of manuscript need to be rewritten, some disputable sentences need to be improved. Therefore, I recommend it for publication after major revisions.

1. Please be consistent with some terms like pyrochar, hydrochar, biochar and charcoal. If the authors would like to focus on pyrochar and hydrochar, please use just those terms.

Reply: Both you and reviewer #2 criticized the large number of different terms used. Therefore, we decided to only use the term 'char' when we talk about both char types and to only use the terms 'pyrochar' or 'hydrochar' separately when we talk about one of them. Accordingly, we changed the term 'biochar' in the main title of the paper to 'char'. Additionally we wrote a definitions for these terms in the introduction and how we use them throughout the manuscript (revised manuscript page 2, line 20-32).

2. Page 33, from line 21; please define DOC since it is the first time to be used.

Reply: Thank you for this hint. We defined this abbreviation as 'dissolved organic carbon' (revised manuscript page 4, line 19).

3. Page 37: How was CEC measured?

Reply: We did not measure CEC immediately after shaking the mixtures. We made separate char-soil mixtures for determining CEC. CEC was measured as potential CEC with the standard method after ISO 13536:1995. We corrected our writing and added this to the Materials & Methods section (revised manuscript page 8, line 6-7).

4. Page 39: Statistical analysis is not complete. It is only focused on adsorption processes.

Reply: We hope that we have understood your comment correctly by assuming that you were referring to the statistics on the effects of washing, which was indeed missing in the Material & Methods section and were added in the revised manuscript. Besides the statistical procedures for the adsorption experiments, we tested for differences between unwashed and washed chars with the unpaired t-test (revised manuscript page 9, line 18-19).

5. Page 40: Please give some explanation about Hydro200, Hydro250. The reader needs to be reminded here about those treatments.

Reply: We added a short repetition of the definitions for the used terms in the beginning of the result section (revised manuscript page 9, line 24-26).

6. Page 42, line 26: Is 8-2 % correct???

Reply: We switched the values from lowest to highest (2-8 %) and completed the values with the addition 'depending on the nutrient solution concentration' (revised manuscript page 11, line 14).

7. The results section particularly sorption of phosphorous is very difficult to be understood. It needs to be rewritten.

Reply: We rewrote the entire results section and shortened it considerably (from 2.476 words to 1.982 words) in order to make it more easily readable.

8. Reference list needs to be edited.

Reply: We are not completely sure in which way the reference list needs to be edited. In any case, we used the Corpernicus/SOIL EndNote template for editing the references. Additionally, we did a thorough spell-checking for all names etc. in the reference list.

Anonymous Referee #2 (C74-C76) Received and published: 09 April 2015.

The paper reports a very detailed study on the N and P sorption potential of pyrochars and hydrochars from different feed stocks for two soils. The authors apprehend the sorption potential of fresh chars produced by different procedures from the same feedstocks and also assess the development of the sorption potential in the laboratory after washing and after field ageing for seven month. Their data indicate differences between the different chars as well as for different nutrients and combinations between soils and chars. Feed stock has some influence on nutrient leaching and sorption. The most important finding of this study is the fact, that the increased sorption capacity of biochar for nutrients was very short-lived and strongly reduced after the 7 months field exposure thereby questioning their efficiency to minimize nutrient leaching in temperate zone soils. In my opinion this result should be more put in the focus of the manuscript. At the moment this important result is somewhat diluted by laboratory experiments, which are not really related to this finding.

The study is timely and the data set presented sound and of interest for an international audience. I have some comments, which need to be addressed before the paper may become publishable in soil:

1. Terminology: ‘biochar’ is used as a term, which groups material produced by very different procedures (pyrolysis and hydrothermal carbonization). I would replace this term by just talking of chars when both types of materials are addressed. Biochar is by definition charcoal, which is produced by pyrolyses. I do not agree with the use of this term for material that was produced by hydrothermal carbonization because it confuses the reader.

Reply: Both you and reviewer #1 criticized rightly the large number of different terms used. Therefore, we decide to only use the term ‘char’ when we talk about both char types and to only use the terms ‘pyrochar’ or ‘hydrochar’ separately when we talk about one of them. Additionally, we wrote a definition for these terms in the introduction and how we use them throughout the manuscript (revised manuscript page 2, line 20-32). Accordingly, we changed the term ‘biochar’ in the main title of the paper to ‘char’.

2. The paper is very long and contains a lot of data. While nine chars, produced by different procedures from different feedstocks, were used for laboratory batch experiments, only chars produced from Miscanthus were used for field incubations.

a) This is pointed out in 2.1, where the production procedures are described. This sentence should be moved to point 2.2, where the field experiments are described.

Reply: Thank you for this hint. We moved the production process of the chars used in the field experiment to section 2.2 “Field ageing”.

b) In my opinion, the logic of the paper would benefit, if the authors concentrated either on the laboratory experiments or only on chars produced from Miscanthus feedstocks.

Reply: In this matter, we cannot fully agree with you. If we used laboratory data only, we would conceal information on contrasting field results against better knowledge which does not seem scientifically sound. On the other hand, if we used the *Miscanthus* field data only, we would lose all information on the other feedstocks such as the risk of phosphorous leaching from digestate-based chars (lab data). While further chars certainly should be tested in the field in future, the laboratory results are necessary to decide which ones might be promising and which ones might be risky.

3. The main point of the paper, reduction of nutrient sorption, is seen in the field experiments, but not very evident, when looking at the obtained during the batch experiments. Here, chars from Miscanthus do show very little effects on nutrient removal. In general laboratory experiments should be carried out to elucidate processes, while field experiments are carried out to investigate behavior under natural conditions. I recommend to report first the field data and then some selected data of the laboratory experiments designed to elucidated the processes and generalization underlying the field observations (soil type, feedstock, washing).

Reply: We considered to restructure the paper as recommended, but finally decided to keep the current structure in order to facilitate a better story line: Starting from the variety of effects depending on char type and ending with one field experiments and the question of persistence of the effects. When we would show the field observations first, readers might that the laboratory experiments deem unnecessary. While we can understand your reasoning, we decided to keep the original structure of the paper for the following reasons:

- If we were showing only selected data from the laboratory experiments, we would lose the objective of the design of the lab experiments, i.e. to systematically compare different chars, feedstocks and soils.

- Furthermore, we would lose information on topics which are not relevant *in this specific* field experiment (e.g. on phosphorous leaching), but generally relevant also for further studies.

- In our opinion, the story of the paper is more consistent if the more theoretical laboratory experiments are shown first and the step to the “real world” second.

However, we fooled your suggestion and shifted the focus more towards the field experiment. We extended the discussion on the results of the field experiment and shortened the results section on the laboratory experiments accordingly, to both improve the readability and to avoid lengthening the manuscript.

4. In summary the authors should work on the story of their manuscript, the way that the readers are guided to be persuaded of the main important conclusions of their paper.

Reply: We revised our manuscript in order to better guide the reader through our “story”. We deleted all concentration numbers from the test in the result section to make it more easily and fluently readable. Moreover, we shortened the manuscript, in particular the results section by 20%.

Effects of fresh and aged ~~bio~~chars from pyrolysis and hydrothermal carbonization on nutrient sorption in agricultural soils

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Keywords: Sorption, Pyrochar, Hydrochar, Nitrate, Ammonium, Phosphate, ~~Biochar~~ Char Ageing, ~~Biochar~~ Char Washing

Kommentar [MG1]: REFEREE #1, Comment 1 & REFEREE #2 Comment 1 **Reply:** Both you and reviewer #2 criticized rightly the large number of different terms used. Therefore, we decided to use the term 'char' when we talk about both char types and to use the terms 'pyrochar' or 'hydrochar' separately when we talk about one of them. Furthermore, we decided to change the term 'biochar' in the main title of the paper to 'char'. Additionally we wrote a new definition for this in the introduction and how we use the terms through the manuscript (revised manuscript page 2, line 20-32).

Abstract

Leaching of nutrients from agricultural soils causes major environmental problems that may be reduced with ~~biochar~~ amendments ~~to the soils.~~ of chars derived from pyrolysis (pyrochars) or hydrothermal carbonization (hydrochars) to the soils. ~~Biochars~~ Chars are characterised by a high adsorption capacity, i.e., they may retain nutrients such as nitrate and ammonium. However, ~~bio~~the physico-chemical properties of the chars ~~properties~~ and hence their sorption capacity likely ~~strongly~~ depend on feedstock and the production process. We investigated the nutrient retention capacity of ~~bio~~pyrochars ~~derived from pyrolysis (pyrochar) as well as~~ chars ~~from hydrothermal carbonization (~~ and hydrochars ~~; produced at 200 and 250°C)~~ from three different feedstocks (digestates, *Miscanthus*, woodchips) mixed into different soil substrates (sandy loam and silty loam). Moreover, we investigated the influence of ~~bio~~char degradation on its nutrient retention capacity using a seven-month in-situ field incubation of pyrochar and hydrochar. Pyrochars showed the highest ability to retain nitrate, ammonium and phosphate, with pyrochar from woodchips being particularly efficient in nitrate adsorption. Ammonium adsorption of pyrochars was controlled by the soil type of the soil-~~bio~~char mixture. We found some ammonium retention on sandy soils, but no pyrochar effect or even ammonium leaching from the loamy soil. The phosphate retention capacity of pyrochars strongly depended on the pyrochar feedstock with large phosphate leaching from digestate-derived pyrochar and some adsorption capacity from woodchip-derived pyrochar. Application of hydrochars to agricultural soils caused small, and often not significant, effects on nutrient retention. In contrast, some hydrochars did increase the leaching of nutrients compared to the non-amended control soil. We found a surprisingly rapid loss of the ~~bio~~chars' adsorption capacity after field application of the ~~bio~~chars. For all sites and for hydrochar and pyrochar, the adsorption capacity was reduced by 60-80% to less or no nitrate and ammonium adsorption. Thus, our results cast doubt on the efficiency of ~~bio~~char applications to temperate zone soils to minimize nutrient losses via leaching.

1 Introduction

Excessive application of mineral fertilizers to agricultural soils is one of the major drivers for various threats to the environment (Laird et al., 2010; Liang et al., 2006). An excess of nutrients may induce soil acidification, increase direct and indirect greenhouse gas emissions (Karaca et al., 2004) and cause eutrophication of the receiving water bodies. However, mineral fertilization has also been the major driver for increased global agricultural production during the last decades. Therefore, technologies are required to both decrease nutrient leaching from soils and enhance nutrient use efficiency with the result that less fertilizer is needed. ~~Biochar~~ ~~Char a~~Amendment ~~to~~ of soils with chars is proposed as one promising option to retain nutrients and prevent leaching (Lehmann, 2009).

~~Biochar~~ ~~C~~These chars are ~~is~~ the solid charcoal product derived from the thermal transformation of a variety of organic feedstocks such as digestates, sewage sludge, woods and other forestry or agricultural residues (Hale et al., 2013; Yao et al., 2012). At present, two main ~~production~~ processes for the production of ~~bio~~chars that are intended for application to soil are used: the first production process, slow pyrolysis, is the combustion and conversion of biomass at processing temperatures above 450°C under oxygen-free conditions. ~~Generally~~In the following, the solid product derived from pyrolysis will be termed ~~biochars~~pyrochar. ~~In the following, we will refer to these biochars the solid product derived from pyrolysis as pyrochar to separate it easier from hydrochars (described below).~~ Pyrochars are characterized by a high degree of aromaticity (Keiluweit et al., 2010; Lehmann et al., 2006) and recalcitrance against degradation or mineralization (Glaser et al., 2002). Second, hydrothermal carbonization (HTC) is a low-temperature production process (temperatures between 180 and 300°C) under high pressure (2-2.5 MPa) with water for several hours (Funke and Ziegler, 2010; Libra et al., 2011; Wiedner et al., 2013). In the following, we will refer to the solid product from the HTC as hydrochar. Hydrochars have recently received increasing attention since wet feedstock can also be carbonized without drying pretreatment (Funke and Ziegler, 2010). Hydrochars are characterized by a lower degree of carbonization and thus more aliphatic carbon (C) but smaller amounts of aromatic C and lower specific surface area (SSA) compared to pyrochars (Eibisch et al., 2013; Titirici et al., 2008). Besides general differences between pyrochar and hydrochar, their properties differ strongly depending on the feedstock, carbonization processes parameters, and subsequent thermochemical reactions (Cantrell et al., 2012; Cao et al., 2011; Eibisch et al., 2013; Eibisch et al., 2015; Yao et al., 2012).

Kommentar [MG2]: **REFEREE #2 Comment 1 Reply:** Both you and reviewer #1 criticized rightly the large number of different terms used. Therefore, we decide to use the term 'char' when we talk about both char types and to use the terms 'pyrochar' or 'hydrochar' separately when we talk about one of them. Additionally we wrote a new definition for this in the introduction and how we use the terms through the manuscript. Furthermore, we decided to change the term 'biochar' in the main title of the paper to 'char'. Now we write (revised manuscript page 2, line 20-32).

For the past ten years, the application of ~~biochar derived from~~ pyrochar~~lysis~~, and later ~~from HTC~~on of hydrochar to agricultural soils, has become a centre of attention as an option to store atmospheric C in soil to mitigate global warming. Additionally, a variety of positive co-benefits are attributed to pyrochar amended soils: an increase in water retention capacity (Glaser et al., 2002; Abel et al., 2013), reduction of greenhouse gas emissions such as nitrous oxide (N_2O) and methane (CH_4), and an enhanced crop productivity due to the retention of plant available nutrients in the rhizosphere (Lehmann, 2009), increased soil pH and soil cation exchange capacity (CEC) (Liang et al., 2006), and preservation of toxic compounds (Chen and Yuan, 2011).

Both, pyrochars and hydrochars contain nutrients which can be released slowly into the rhizosphere (Eibisch et al., 2013; Spokas et al., 2011; Taghizadeh-Toosi et al., 2011) but more important is the pyrochars' ability to adsorb nutrients due to its high surface charge density and CEC. The leaching and adsorption of nitrate (NO_3^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}) to various activated C and charcoals has been studied (Bandosz and Petit, 2009; Ding et al., 2010). However, studies concerning the sorption behavior of ~~bio~~pyrochar, and especially hydrochars, are rare. Previous studies focusing on soil~~-bio~~char mixtures have shown that leaching of NO_3^-, NH_4^+, and PO_4^{3-} from soils amended with ~~bio~~pyrochar or hydrochar~~ from pyrolysis and HTC~~ was frequently reduced due to adsorption on the respective ~~bio~~char (Bargmann et al., 2014b; Ding et al., 2010; Laird et al., 2010; Sarkhot et al., 2012). Laird et al. (2010) applied 20 g kg^{-1} pyrochar from hardwood to an agricultural soil, which decreased the leaching of NO_3^- from swine manure by 10%. Yao et al. (2012) reported increased NO_3^- adsorption of up to 4%, but also leaching rates of up to 8% from aqueous solution. Other studies showed that NO_3^- (Castaldi et al., 2011; Hale et al., 2013; Jones et al., 2012), as well as NH_4^+ leaching was decreased by 94% due to pyrochar application to a ferralsol in a 37-day soil column leaching experiment (Lehmann et al., 2003). Furthermore, both NH_4^+ adsorption by up to 15% from aqueous solution, but also leaching up to 4% in to solution was observed (Yao et al., 2012). Also other nutrients which are not particularly prone to leaching, such as PO_4^{3-}, have been reported to be retained by application of pyrochar (Laird et al., 2010; Morales et al., 2013; Xu et al., 2014). For example, Laird et al. (2010) reported up to 70% reduced PO_4^{3-}-P leaching in a soil column experiment mixed with 20 g kg^{-1} pyrochar. In contrast, Yao et al. (2012) observed up to 5% PO_4^{3-}-P leaching from aqueous solution for pyrochars from bamboo and hydrochars from peanut-hull. In summary, these studies implicate a strong variation of leaching or retention behavior of ~~bio~~chars, which seems to depend on feedstock and production process.

~~Biochar~~ Char application has been promised to be multi-beneficial. However, benefits have been tested mostly for ~~bio~~pyrochar~~ from slow pyrolysis~~-amended tropical soils with few comparative studies for temperate soils or hydrochars. This is one of the main reasons why neither pyrochar nor hydrochar application is considered in agricultural practice in the temperate zone at the moment. Even though ~~bio~~chars, especially pyrochars, are relatively stable in soils, an increasing number of studies suggest that biotic and abiotic processes can lead to degradation of ~~bio~~char and thus change its surface properties and sorption behavior (Cheng et al., 2008; Hale et al., 2011; Liu et al., 2013; Steinbeiss et al., 2009). The physical structure and chemical properties of hydrochars result in a lower recalcitrance towards microbial degradation compared to pyrochars (Bargmann et al., 2014a; Hale et al., 2011; Steinbeiss et al., 2009). Furthermore, hydrochars release a higher amount of dissolved organic carbon (DOC) which might be easily mineralized. Hence, soil amended with hydrochars increases microbial-biomass production and immobilization of mineral nitrogen (Bargmann et al., 2014a; Lehmann et al., 2011), and an increased nitrification from NH_4^+ to NO_3^- may occur. Over time, slow ~~bio~~char aging due to oxidation may lead to carboxylic and phenolic functional groups on the chars' surface and thus negative charges. On the other hand, the atomic C content and positive surface charge on the edge sites of aromatic compounds will be reduced (Cheng et al., 2008; Cheng et al., 2006; Glaser et al., 2000). Furthermore, surface oxidation increases CEC per unit C and the charge density (Liang et al., 2006), but a higher

Kommentar [MG3]: **REFEREE #1, Comment 2 - Reply:** Thank you for this hint. We defined this abbreviation as 'dissolved organic carbon' (revised manuscript page 4, line 19).

anion exchange capacity (AEC) has been found for aged pyrochars as well (Mukherjee et al., 2011). At the same time, pyrochars may adsorb organic matter (OM) which blocks ~~bio~~char surfaces and reduces their sorption capacity (Mukherjee et al., 2011). However, so far these long-term changes of ~~bio~~char properties and consecutive functions have been ignored in most ~~bio~~char studies on nutrient retention, which may lead to systematic bias.

In summary, according to the majority of studies (Hale et al., 2013; Knowles et al., 2011; Lehmann et al., 2003; Morales et al., 2013; Xu et al., 2014), ~~bio~~char may be a potential melioration for soils by decreasing nutrient leaching via improved adsorption properties. However, there is only little knowledge of the nutrient sorption potential of pyrochars compared to hydrochars, and the influence of ageing/degradation on nutrient sorption.

The influence of ~~bio~~char properties resulting from different carbonization methods and different feedstock materials on nutrient sorption potential is also insufficiently understood. Furthermore, no systematic comparison of different feedstock materials on nutrient sorption has yet been conducted, and the effect of aging of ~~bio~~chars on their sorption potential has not yet been investigated. ~~Therefore, the~~The objectives of this study are to first determine the nutrient sorption potential of nine different ~~bio~~char-soil mixtures in laboratory batch experiments and to investigate the influence of i) ~~bio~~char type (pyrochar vs. hydrochar), ii) soil type (sandy loam vs. silty loam), and iii) ~~bio~~char feedstock (woodchips, digestate and *Miscanthus*). Secondly, we want to assess the effect of aged vs. fresh ~~bio~~chars (pyrochar and hydrochar from *Miscanthus*) on nutrient sorption potential in a field experiment.

2 Materials and Methods

2.1 Production and general properties of pyrochars and hydrochars and their corresponding feedstocks

The nine ~~bio~~chars that were used for laboratory batch experiments originated from the same setup as the chars described in Eibisch et al. (2013, 2015). They derived from HTC and pyrolysis and were produced from three feedstock materials with different physico-chemical properties (digestates (99% maize), woodchips (95% poplar, 5% willow), and *Miscanthus*). The hydrochars were carbonized with water (1:10, w/w) in a batch reactor for 6 h, 2 MPa at 200 (hereafter referred to as Hydro200) and 250°C (hereafter referred to as Hydro250; SmartCarbon AG, Jettingen, Germany). Pyrochars were produced in a Pyreg reactor (PYREG

Kommentar [MG4]:
REFEREE #2, Comment 2b - Reply:

In this matter, we cannot agree with you. If we used laboratory data only, we would conceal information on contrasting field results against better knowledge which does not seem scientifically sound. On the other hand, if we used the *Miscanthus* data only, we would lose all information on the other feedstocks such as the risk of phosphorous leaching from digestate-based chars. While further chars certainly should be tested in the field in future, the laboratory results are necessary to decide which ones might be promising and which ones might be risky.

REFEREE #2, Comment 3 - Reply:

We are disagreeing with your comment. When we show the field observations first, readers might that the laboratory experiments deem unnecessary. So we did not change the structure of the paper. While we can understand your reasoning, we decided to keep the original structure of the paper for the following reasons:

- If we were showing only selected data from the laboratory experiments, we would lose the objective of the design of the lab experiments, i.e. to systematically compare different chars, feedstocks and soils.

- Furthermore, we would lose information on topics which are not relevant *in this specific* field experiment (e.g. on phosphorous leaching), but generally relevant also for further studies.

- In our opinion, the story of the paper is more consistent if the more theoretical laboratory experiments are shown first and the step to the “real world” second.

However, to shift the focus more towards the field experiment, we extended the discussion of its results and shortened the results section on the laboratory experiments accordingly to both improve the readability and to avoid lengthening the manuscript.

GmbH, Dörth) for 0.75 h at 750°C (designated hereafter as Pyro750). Detailed information on ~~bio~~char preparation and methods of analysis (e.g., specific surface area (SSA), pore volume, average pore size) can be found in Eibisch et al. (2013) and Eibisch et al. (2015).

~~Hydrochar and pyrochar produced from *Miscanthus* was used for the field incubation. The hydrochar was carbonized with water (1:10, w/w) in a tabular reactor (3 m^{-3}) for 11 h, 2 MPa at 200°C by AddLogicLabs / SmartCarbon (Jettingen, Germany). Citric acid was added as catalyst for the dehydration process and to increase the C content in the solid product (Wang et al., 2010). Pyrochars were produced in a Pyreg reactor for 0.75 h at 750°C. Analyzes of general properties of the chars and raw material were carried out by Andrea Kruse (KIT Karlsruhe). All chars were dried at 40°C and sieved ≤2 mm. Basic characteristics of feedstocks, pyrochars, and hydrochars for the laboratory batch and field incubation experiment are listed in Table 1.~~

In order to simulate field ageing, we compared unwashed ~~bio~~chars with washed ~~bio~~chars in the laboratory experiment. Washing was assumed to be capable of simulating ageing of the char as initially bound nutrients or salts would be removed. Washing was carried out by shaking 4.5 g biochar with 1 L deionized water in an overhead-shaker at 9 rpm for 4 h and thereafter solution was filtered with pleated paper filter (Grade: 3 hw; Diameter: 150 mm; 65 g m^{-2}) and filtrate (pyrochar or hydrochar) was dried for 24 h at 105°C. Washing effects were only studied in the pyrochar and hydrochar applied to silty loam mixtures, because highest nutrient leaching or adsorption effects were expected for this soil.

2.2 Field ageing

Hydrochar and pyrochar produced from *Miscanthus* was used for the field incubation. The hydrochar was carbonized with water (1:10, w/w) in a tabular reactor (3 m^{3}) for 11 h, 2 MPa at 200°C by AddLogicLabs / SmartCarbon (Jettingen, Germany). Citric acid was added as catalyst for the dehydration process and to increase the C content in the solid product (Wang et al., 2010). Pyrochars were produced in a Pyreg reactor for 0.75 h at 750°C. Analyzes of general properties of the chars and raw material were carried out by Andrea Kruse (KIT Karlsruhe). All chars were dried at 40°C and sieved ≤2 mm. Basic characteristics of feedstocks, pyrochars, and hydrochars for the laboratory batch and field incubation experiment are listed in Table 1.

Kommentar [MG5]: **REFEREE #2, Comment 2a - Reply:** Thank you for this hint. We moved the production process of the chars used in the field experiment to section 2.2 "Field ageing".

For the investigation of the effect of ageing of the chars in the field, ~~bio~~chars were incubated in-situ at three cropland sites in the North German lowland (mean annual temperature 8.8°C, around 600 mm precipitation). The three sites differ mainly in their soil texture (Table 2) and are located in Bortfeld (sandy loam (SL); 52°28'N, 10°41'E, 80 m a.s.l.), Volkmarsdorf (sandy loam (SL); 52°36'N, 10°89'E, 105 m a.s.l.) and Querenhorst (loamy sand (LS); 52°33'N, 10°96'E, 112 m a.s.l.). All sites were managed according to common regional practice with conventional tillage and fertilizing. Crop rotations were barley (2012), winter wheat (cover crop), sugar beet (2013) (Querenhorst); barley (2012), mustard (cover crop), sugar beet (2013) (Volkmarsdorf); potatoes (2012), sugar beet (2013) (Bortfeld). At all three sites, mini-plots (plot size: 70 × 70 cm; plot depth: 25 cm) were dug out in triplicate in March 2013, and the hydrochar and pyrochar were mixed into the soil in a cement mixer in an amount that aimed to double the soils' C-content (corresponds to around 100 t ha^{-1} ~~bio~~char). The experimental setup was a randomized plot design carried out in three rows for each site so that every row consisted of three treatments: (i) control (soil only), (ii) soil + hydrochar, and (iii) soil + pyrochar. In order to distinguish the soils' C-contents from treated or non-treated soil, and to quantify any blending or attenuation with the surrounding soil, e.g., due to tillage, 105 g Zinc as an inert tracer was added to each treatment in the cement mixer (control, pyrochar + soil, hydrochar + soil). The mini-plots were not fenced off, so the farmers were able to manage the fields exactly like to the rest of the field.

Sampling was carried out twice: the first set of soil samples was taken in March 2013 right after mixing the soil with ~~bio~~chars (T_0). After seven months (October 2013) a second sampling was carried out (T_1). Soil samples were obtained by taking five randomly distributed soil cores to a depth of 25 cm with a Split-Tube sampler (5 cm diameter) from each mini-plot. Afterwards, samples were dried at 40°C and sieved ≤~~-~~2 mm. Zinc concentrations at T_0 and T_1 were used to calculate a correction factor F_Z, which determines the recovery-rate of incubated biochars in the field study

2.3 Batch sorption experiments

Soil-~~bio~~char mixtures used solely in the laboratory were produced by mixing 0.5 g of ~~bio~~char with 10 g soil in order to roughly double the soil's C content. Two soils were used for the char-soil mixtures: a silt loam (Blagodatskaya et al., 2014) from a cropland site at the Thünen-Institute in Braunschweig, Germany (52°17'N, 10°26'E, 80 m a.s.l.) and a sandy loam from a cropland site of the University of Göttingen (Reinshof), Germany (51°28'N, 9°58’E, 205 m a.s.l.). The soil was dried at 105°C to inhibit any microbial activity and sieved ≤ 2 mm. The pH-value of soils and ~~bio~~chars was measured in 0.01M $CaCl_2$ with a ratio of 1:5 (volume soil / volume solution). Carbon and N contents were determined using dry combustion with an elemental analyzer (LECO TrueMac CN LECO Corp., St. Joseph (MI), USA). Soil texture was determined by the combined sieve and pipette method.

Preliminary sorption kinetic experiments were conducted to determine the sorption equilibrium by shaking the batches for 4, 8, 12, 24, and 48 h at 9 rpm in an overhead shaker. Based on the results of the kinetic experiments, shaking time for the determination of the sorption isotherms was set to 24h. An amount of 10.5 g of soil only (control) and soil-~~bio~~char mixtures were added to 40 mL of a nutrient solution in a 50 mL plastic centrifuge tube. Six concentration levels of a nutrient solution containing several nutrients that were chosen in order to mimic a “typical” agricultural soil solution were used (Table 3). In addition, the pH-value of the solution was adjusted to 6 by adding HCl. Triplicates were measured for each concentration level. ~~Cation exchange capacity (CEC) and~~ The pH ~~were~~ was measured immediately after shaking in the ~~bio~~char/soil-solution mixtures. Thereafter, suspensions were centrifuged at 4500 rpm for 30 min. The supernatant was aspirated with a syringe and filtered through 0.45 µm membrane filters (CHROMAFIL PET-45/25 disposable syringe filters, Macherey-Nagel). The ion-concentrations of the filtrates were analyzed using ion chromatography (IC) (METROHM 761) for anions (NO_3^-, PO_4^{3-}) and inductively coupled plasma chromatography (ICP) (ICS-90 Dionex / Thermo Fisher Scientific) for cations (NH_4^+). Moreover, contents of Ca^{2+}, Mg^{2+}, K^+, and SO_4^{2-} were also determined and fitted isotherms can be found in Table S1. The potential CEC of separate soil-char mixtures was determined after ISO 13536.

Kommentar [MG6]: REFEREE #1, Comment 3 - Reply: We did not measure CEC immediately after shaking the mixtures. We made separate char-soil mixtures for determining CEC. CEC was measured as potential CEC with the standard method after ISO 13536:1995. We corrected our writing and added this to the materials & method-section (revised manuscript page 8, line 6-7).

Soil-~~bio~~char mixtures from the field experiment were used directly in the batch sorption experiments (NO_3^-, NH_4^+, PO_4^{3-}), which were carried out as described above. To calculate the ~~bio~~char adsorption effect relative to the control we used the following equations:

Relative adsorption of the control:

$$Q_{Ctrl} = \left(1 - \left(\frac{IC\ (Ctrl)}{IC\ (Blind)}\right)\right) \times 100 \qquad \text{(Eq. 1)}$$

Relative adsorption of the ~~bio~~char treatment to control:

$$Q_{\cancel{B}Char} = \left(1-\left(\frac{IC\ (\cancel{B}Char)}{IC\ (Ctrl)}\right)\right)\times F_Z \times 100 \qquad \text{(Eq. 2)}$$

Whereby F_Z was only used to calculate relative adsorption for field incubated ~~bio~~chars. IC is the equilibrium ion content of the nutrient solution after shaking for blinds (IC_{Blind}), control (IC_{Ctrl}) or soil- ~~bio~~char mixtures ($IC_{\cancel{B}Char}$).

2.4 Statistical Analyses

Adsorption data were fit to Freundlich and linear adsorption isotherms:

Freundlich isotherm: $Q_e = K_F \cdot IC^{1/n}$ (Eq. 3)

Linear isotherm: $Q_e = a \cdot IC + Y_0$ (Eq. 4)

Q_e is the amount of ion adsorbed, while IC is the concentration in the solution after 24 h equilibration. A positive Q_e indicates adsorption of ions in the nutrient solution on an adsorbent and a negative Q_e desorption from adsorbent to the nutrient solution.

Logarithmized equilibrium-concentration and log adsorbed amount was used to calculate the Freundlich sorption partitioning coefficients (K_F) and the Freundlich exponents (1/n) following nonlinear fitting. For linear isotherm, Y_0 is the intercept.

The Akaike information criterion (AIC) was used to select the best fitting isothermal model. Significance of treatment effects on shape of isotherms was tested using two procedures:

(i) If, for two treatments, the same model type resulted in the best fit, their difference was tested with a likelihood-ratio test. It was tested whether fitting the model to the data separately resulted in a better fit than fitting the model to the combined data. If the separately fitted model resulted in a better fit than the combined model, treatments were different with their corresponding p-value. This test could only be conducted if it was numerically possible to fit the model to the combined data.

(ii) Generalized additive models (GAM, R package *gam*, (Hastie, 2013)), including and excluding treatment as a predictor, were fitted and compared using analysis of deviance with a χ^2 statistics.

All p-values were adjusted for multiple testing using the procedure of Benjamini and Hochberg (1995). All statistical analyses were conducted using R 3.1.1 (RCoreTeam, 2014). The results of the statistical analyses can be found in the supplement (Table S1, S3, S5, S7 &

S8). Significant differences between washed an unwashed chars were tested with the unpaired t-test.

3 Results

3.1 ~~Biochars Chars p~~Physico-chemical properties of the chars

The pH values ~~for~~ of the ~~used~~ hydrochars were acidic ranging from 3.8 to 6.2~~,~~ and 4.2 to 5.7~~,~~ for Hydro200 (hydrochars produced at 200°C) and Hydro250 (hydrochars produced at 250°C), respectively (Table 1). The pH-values of Pyro750 (pyrochars produced at 750°C) were alkaline~~, ranging from pH~~ (8.7 to 9.8). The ash content increased with increasing carbonization temperature and was highest for pyrochars from woodchips (24.6 %). Generally, ~~the~~ woodchips had the highest C concentration (48.6% C) as a raw material, but after carbonization, Pyro750 from *Miscanthus* had the highest C concentrations (Lab: 76.9% C; Field: 81.8% C). The highest amounts of total N and P were found in Hydro200 and Hydro250 from digestates. After carbonization, highest SSA was observed for pyrochars and decreased in the order Pyro750 > Hydro200 > Hydro250 (Table 1). Pyro750 showed the highest pore volume, followed by Hydro200 and Hydro250. In general, Pyro750 showed smaller average pore size than Hydro200 and 250 by a factor of 10.

3.2 Influence of soil, feedstock and carbonization type on nutrient sorption (Laboratory experiments)

Figures 1, 2, and 3 show the relative change of ion concentrations of the ~~bio~~char treatments from the three feedstocks (triangles = *Miscanthus*, circles = digestates, squares = woodchips) to the control (0% line) at all applied nutrient concentration levels. Positive values correspond to adsorption and negative values to leaching.

3.2.1 Sorption of nitrate

The pure sandy loam (control in Table 3) showed neither NO_3^- sorption nor release (all data points are around 0%). In contrast, the pure silty loam tended to a high NO_3^- release of around 60%: ~~(while the N concentration in batch solution (C_{Blind}) was: 5.19 mg N L^{-1}, the; N concentration in batch solution with control soil (C_{Ctrl}) was: 8.22 mg N L^{-1})~~ at the lowest

Kommentar [MG7]: **REFEREE #1, Comment 4 – Reply:** We hope that we have understood your comment correctly by assuming that you were referring to the effects of washing, which was indeed missing in the material & methods part. Besides the statistical procedures for the adsorption experiments, we tested for differences between unwashed and washed chars with the unpaired t-test. We added this fact in the material & methods part. We write (revised manuscript page 9, line 18-19).

Kommentar [MG8]: **REFEREE #1, Comment 7– Reply:** We rewrote the entire results-section and shortened it considerably (from 2.476 words to 1.982 words) in order to make it more easily and fluently readable

Kommentar [MG9]: **REFEREE #1, Comment 5– Reply:** We add a short repetition of the definitions for the used terms in the beginning of the result section (revised manuscript page 9, line 24-26).

concentration level of the nutrient solution (Table 3). This release decreased to 5% with increasing concentrations of the nutrient solution.

Mixing soil with Pyro750 significantly reduced NO_3^- leaching, independent of the soil and feedstock used (Figure 1A, B). The relative amount of adsorbed NO_3^- in pyrochar amended soils was higher in sandy loam than in silty loam. At the lowest concentration level of the nutrient solution~~ (5 mg N L^{-1})~~, application of Pyro750 raised NO_3^- adsorption between 2-15% (silty loam) and 7-30% (sandy loam) compared to the respective control soil (Figure 1A, B). The relative adsorption on Pyro750 decreased with increasing nutrient solution concentration to 5-12%. For both soil types, the fitted isotherms for Pyro750 were significantly different from the control ($p \leq 0.01$) and to both Hydro200 and Hydro250 ($p \leq 0.01$). Further, isotherms of NO_3^-adsorption by Pyro750 mixed with sandy loam were significantly different to those of silt loam ($p \leq 0.01$). Further, ~~T~~the effects of nutrient retention in Pyro750 mixtures compared to the control soil depended on the carbonized feedstock ($p \leq 0.01$; Figure 1A, B). ~~For Pyro750, a~~Adsorption increased in the order digestates (3-8%)< *Miscanthus* (10-14%) ≤~~<~~ woodchips (10-15%) in both soil types depending on the nutrient solution concentration. ~~Values for digestates ranged from 8% (N concentration in batch solution with control soil (IC$_{Ctrl}$): 5.23 mg N L^{-1}; N concentration in batch solution with soil biochar mixtures (IC$_{BChar}$): 5.08 mg N L^{-1}) and decreased to 3% with increasing NO_3^--N concentration level (sandy loam) or remains at the same 3-5% level (silty loam). For Pyro750 from *Miscanthus*, relative NO_3^- adsorption was higher with 14% (IC$_{Ctrl}$: 5.23 mg N L^{-1}; IC$_{BChar}$: 4.78 mg N L^{-1}) for low NO_3^--N concentrations and 10% at high NO_3^--N concentrations (IC$_{Ctrl}$: 60 mg N L^{-1}; IC$_{BChar}$: 55.13 mg N L^{-1}). For Pyro750 from woodchips, the relative adsorption was highest and ranged from 15% (IC$_{Ctrl}$: 5.23 mg N L^{-1}; IC$_{BChar}$: 4.10 mg N L^{-1}) and decreased to 10% with increasing NO_3^--N concentration level.~~Addition of hydrochar to the soils had no effect on NO_3^- adsorption irrespective of the used carbonization temperature, feedstock or soil type (Figure 1C, D).

~~After addition of hydrochars (both, Hydro200 and Hydro250), significant effects on NO_3^- retention were observed neither in the sandy loam nor in the silty loam (Figure 1C, D;). Fitted isotherms showed no differences between Hydro200 and Hydro250 and the control soil but significant differences between both control soils ($p \leq 0.01$). Hydrochars from the three carbonized feedstocks showed no significant differences in their relative NO_3^- adsorption (Figure 1C, D) or fitted isotherms.~~

~~In summary, the relative amount of adsorbed NO_3^- in pyrochar amended soils was higher in sandy loam than in silty loam and adsorption increased in the order digestates < *Miscanthus* < woodchips in both soil types.~~ ~~Addition of hydrochar had no effect on NO_3^- adsorption irrespective of the used carbonization temperature, feedstock or soil type.~~

3.2.2 Sorption of ammonium

The NH_4^+ sorption in the ~~control~~ soils without char was around 3-4 times higher ~~in~~ for the silty loam than ~~in~~ the sandy loam (Table 3). The silty loam a~~b~~dsorbed~~Values were~~ around 55% ~~(IC_{Blind}: 4.68 mg N L^{-1}; IC_{Ctrl}: 2.16 mg N L^{-1})~~ at the first concentration level, and adsorption decreased to 32% with increasing nutrient concentrations, while the sandy loam adsorbed around 15% at all concentration levels.

Comparison of fitted isotherms of both soils mixed with Pyro750 showed significant differences between sandy loam and silty loam ($p \leq 0.01$). The effect of feedstock on relative NH_4^+ adsorption was soil-dependent and significant for both soils (Figure 2A, B; $p \leq 0.05$). ~~Addition of pyrochars to the~~While NH_4^+ adsorption was enhanced by the application of pyrochar in the sandy loam, pyrochar addition to the silty loam showed no effect or even led to leaching. Further, the effect of the feedstock differed between the two soils investigated: When added to sandy loam, pyrochar application increased the adsorption relative to control. ~~between~~ Depending on the nutrient solution concentration,~~T~~ the relative adsorption increased in the order ~~0 % (Pyro750 from~~ *Miscanthus* (0%) < woodchips (2-8%) and digestate (7-17%) ~~(Pyro750 from digestates) (IC_{Ctrl}: 3.85 mg N L^{-1}; IC_{BChar}: 3.15 mg N L^{-1}) at the first concentration level~~ ($p \leq 0.01$; Figure 2A). ~~This effect decreased with increasing ion concentration level. The fitted isotherms for Pyro750 mostly showed significant differences to control soil ($p \leq 0.01$). For the silty loam, addition of pyrochars did not raise relative NH_4^+ adsorption but led to leaching compared to the control.~~ For the silty loam, the ~~order for reduction of~~effect of pyrochar addition on the relative NH_4^+ adsorption was: woodchips (0%) < *Miscanthus* (0-20%) < digestates (up to -45% at the first two NH_4 concentration levels; Figure 2B) only at the first three nutrient concentration levels.~~Comparison of fitted isotherms of both soils mixed with Pyro750 showed significant differences between sandy loam and silty loam ($p \leq 0.01$). The effect of feedstock on relative NH_4^+ adsorption was soil-dependent and significant for both soils (Figure 2A, B; $p \leq 0.05$). Pyro750 from digestates caused the strongest increase of relative NH_4^+ adsorption when mixed with sandy loam (17-17% from lowest to highest nutrient solution concentration level). Pyro750 from woodchips raised NH_4^+~~

Kommentar [MG10]: REFEREE #1, Comment 6– Reply: We switched the values from lowest to highest (2-8 %) and completed the values with the addition 'depending on the nutrient solution concentration' (revised manuscript page 11, line 14).

~~adsorption by only 8-2-8%. Pyro750 from *Miscanthus* showed no effect. When Pyro750 from digestates was added to silty loam, the highest reduction of relative NH_4^+ adsorption through leaching was observed for the first two NH_4 concentration levels (level P1: -45% (IC_{Ctrl}: 2.16 mg N L^{-1}; IC_{BChar}: 3.15 mg N L^{-1})) (Figure 2B). For silty loam amended with Pyro750 from *Miscanthus*, relative NH_4^+ adsorption was reduced by 20% (IC_{Ctrl}: 2.16 mg N L^{-1}; IC_{BChar}: 2.62 mg N L^{-1}) at the first concentration level and decreased to 0% at highest level.~~

Application of hydrochars to either soil type ~~had only marginal~~ showed no consistent effects. These ranged from leaching to adsorption with relative values between +10 and -20%, respectively (Figure 2C, D). In general, NH_4^+ adsorption by the control soil was significantly different to that in the soil amended with hydrochars ($p \leq 0.01$) for both sandy loam and silty loam. For Hydro200, NH_4^+ adsorption was close to zero when compared to the control at all concentration levels. A significant relative adsorption effect was observed for only some concentration points (Figure 2C). Hydro250 showed both NH_4^+ release at the lowest concentration level and little adsorption of NH_4^+ at the higher concentration levels reaching up to about 10 % (Figure 2D). The fitted isotherms for Pyro750 are significantly different from those for hydrochars and pure soil (depending on soil type), but there ~~are~~ were no differences between Hydro200 and Hydro250. For hydrochars, no effect of feedstock on NH_4^+ adsorption was observed except for lower adsorption of Hydro200 from digestates compared to *Miscanthus* and woodchips ($p \leq 0.01$,).

~~In summary, only pyrochars enhanced NH_4^+ adsorption (and only as a mixture with sandy loam), but hydrochars had either no effect or led to NH_4^+ release. The effect of pyrochar feedstock on NH_4^+ adsorption was soil-dependent. Relative NH_4^+ adsorption increased in the following order for pyrochars in the sandy loam: *Miscanthus* < woodchips < digestates. For the silty loam, the order for reduction of relative NH_4^+ adsorption was: woodchips < *Miscanthus* < digestates only at the first three nutrient concentration levels.~~

3.2.3 Sorption of phosphorous

The sandy loam leached PO_4^{3-} at the lowest concentration level ~~(IC_{Blind}: 1.25 mg P L^{-1}; IC_{Ctrl}: 2.29 mg P L^{-1})~~, but this changed to 65 % adsorption at higher levels ~~(IC_{Blind}: 14.07 mg P L^{-1}; IC_{Ctrl}: 4.88 mg P L^{-1})~~, while the silt loam adsorbed up to 80 % ~~PO_4^{3-}~~ at all PO_4^{3-} concentration levels (~~up to 80 %;~~ Figure 3A, B).

Kommentar [MG11]: REFEREE #1, **Comment 7– Reply:** We rewrote the entire results-section and shortened it considerably (from 2.476 words to 1.982 words) in order to make it more easily and fluently readable

Only pyrochars enhanced PO_4^{3-} adsorption. ~~Addition of pyrochars had significant effects on PO_4^{3-} adsorption (~~T~~t~~he fitted isotherms for pyrochars ~~are~~ were significantly different ~~to~~ from the respective control soil ~~used~~ ($p \leq 0.01$)), but this effect strongly depended on feedstock material (digestates (only leaching) < *Miscanthus* < woodchips) and soil (silty loam < sandy loam). ~~Comparison of fitted isotherms showed significant differences between carbonized feedstocks for~~ For Pyro750, there were significant ($p \leq 0.01$) differences between feedstocks:~~.~~ Pyro750 from *Miscanthus* mixed with the sandy loam resulted in a relative PO_4^{3-} adsorption of 20-30% (Figure 3A) ~~(IC_{Ctrl}: 2.29 mg P L^{-1}; IC_{BChar}: 1.82 mg P L^{-1})~~ but 20% less adsorption (leaching) when mixed with the silty loam (Figure 3B). Woodchip pyrochar was most effective in adsorbing PO_4^{3-} (15-40% for the silty loam and 60-70% for the sandy loam) during all nutrient solution concentrations. However, pyrochar from digestates showed strong leaching in both sandy and silty loam (Figure 3A, B). ~~Addition of~~Adding Pyro750 from digestates enriched the nutrient solution by up to 1000% (sandy loam~~; IC_{Ctrl}: 1.25 mg P L^{-1}; IC_{BChar}: 24.87 mg P L^{-1}~~) and 1300% (silty loam)~~; IC_{Ctrl}: 1.25 mg P L^{-1}; IC_{BChar}: 14.47 mg P L^{-1})~~ at the lowest PO_4^{3-}-P concentration level, and ~~decreased~~ still by~~to~~ 100% at the highest PO_4^{3-}-P concentration. ~~Overall, a~~Although relative PO_4^{3-} adsorption was higher in the sandy loam than in the silty loam after addition of Pyro750, these differences were not significant.

The addition of hydrochar (both Hydro200 and Hydro250) to soil ~~led~~ mainly led to leaching of PO_4^{3-} from ~~bio~~chars or had no consistent effect (Figure 3C, D). Fitted isotherms showed significant differences between Hydro200 and Pyro750 ($p \leq 0.01$) but no differences to control or Hydro250. The adsorption of the soil was lowered by maximum values of around 40% for the sandy loam and 60% for the silty loam due to PO_4^{3-} leaching. Values depended on the feedstock used ~~and PO_4^{3-} adsorption was significantly different in both~~ and soil types ($p \leq 0.01$). Again, the effect of feedstock (or any effect at all) was less pronounced for hydrochars than pyrochars: Hydrochars from digestates tended to reduce the relative PO_4^{3-} adsorption by leaching. Mixing soil with Hydro200 and Hydro250 from *Miscanthus* and woodchips resulted in no effect on PO_4^{3-} adsorption (Figure 3C). For both soil types, differences between Hydro200 from digestates to *Miscanthus* and to woodchips were significant ($p \leq 0.01$). For Hydro250 only digestates to *Miscanthus* and to woodchips were significantly different ($p \leq 0.01$) in the sandy loam.

~~In summary, only pyrochars enhanced PO_4^{3-} adsorption (especially as a mixture with the sandy loam), but hydrochars had either no effect or led to PO_4^{3-} release. The effect of pyrochar feedstock on PO_4^{3-} adsorption was soil-dependent. Relative PO_4^{3-} adsorption increased in the following series for pyrochars in the sandy loam: digestates (only leaching) < *Miscanthus* < woodchips. For the silty loam, series for relative PO_4^{3-} sorption was: digestates (only leaching) < *Miscanthus* (little leaching) < woodchips.~~

3.3 The effect of ~~bio~~char ageing on nutrient sorption (Field experiment)

At all three experimental sites NO_3^- was leached from pure soil with no ~~bio~~char addition (control; data not shown). However, leaching was less pronounced at T_1 than T_0 ($p<0.01$). Amending the soils with ~~bio~~char led to adsorption of NO_3^- for both pyrochar and hydrochar at all experimental sites (Figure 4A-C). However, adsorption was higher for pyrochars than hydrochars ($p \leq 0.01$,). Pyrochar reduced NO_3^- leaching up to 58% relative to the control soil at the lowest nutrient solution concentration while hydrochar reduced leaching up to 25% (Figure 4A-C). After 7 months of ageing in the field (T_1), adsorption by pyrochars decreased by 60 to 80% often ending up with no nutrient retention relative to control ($p<0.01$; Figure 4A-C). Slight differences were observed between the three investigated sites but they were not significant. The effect of hydrochar addition diminished in a similar way after seven months: relative adsorption decreased by 10 to 100%, ending up with no nutrient retention at Bortfeld (Figure 4A) or even nutrient leaching (site Querenhorst and site Volkmarsdorf, Figure 4B-C), as compared to the non-amended control soil. In four of our six cases, sorption effects of both pyrochar and hydrochar were found to be significantly different for the aged biochar-soil mixture as compared to fresh biochars mixed into soils.

Highest adsorption of NH_4^+ was observed for fresh ~~bio~~chars (T_0) and adsorption was higher for pyrochar than for hydrochar at two sites (Bortfeld & Volkmarsdorf, $p \leq 0.01$,), but was similar at the third site (Querenhorst) (Figure 4D-F). For soils amended with fresh pyrochar, adsorption of NH_4^+ was up to 40% higher than observed for the control soil. After seven months, NH_4^+ adsorption of pyrochar-soil mixtures was significantly lower at all experimental sites than right after the ~~bio~~char application ($p<0.01$). Little relative NH_4^+ adsorption was found for fresh hydrochar and for aged hydrochar in the field. The relatively low adsorption capacity of hydrochars sometimes even changes to NH_4^+ ~~-~~leaching.

The effect of pyrochar ageing on PO_4^{3-} adoption was different from the other nutrients: Ageing increased the PO_4^{3-} retention capacity of pyrochar soil mixtures at all three sites from leaching or no effect (T_0) to adsorption (T_1) (Figure 4G-I). The effect of hydrochar on PO_4^{3-} was minor. Hydrochar was a source for PO_4^{3-} in most soils with no consistent changes due to char ageing.

~~The effect of pyrochar ageing on PO_4^{3-} adoption was different from the other nutrients: Ageing increased the PO_4^{3-} retention capacity of pyrochar soil mixtures at all three sites (Figure 4G-I). The effect of hydrochar on PO_4^{3-} was minor. Hydrochar was a source for PO_4^{3-} in most soils with no consistent changes due to biochar ageing.~~

3.4 Effects of ~~bio~~char preparation (washing)

Washing was carried out in order to reduce initial leaching effects from ~~bio~~chars, i.e., it was assumed that nutrients and salts were removed from the surface of the chars by washing. Figure 5 shows relative changes of ion concentration to control (0% line; IC_{Blind}: 20.23 mg N L^{-1}; IC_{Ctrl}: 23.37 mg N L^{-1}) at nutrient concentration level P3 (Table 3). Positive values indicate higher, and negative values indicate lower~~,~~ removal of ions from nutrient solution compared to control due to adsorption or leaching, respectively. Washing of both Hydro200 and Hydro250, increased pH of the nutrient solution by 0.1 to 0.2 pH-units and for Pyro750, pH was decreased by 0.2 to 0.4 pH-units due to washing. The sorption behavior of both~~,~~ pyrochars and hydrochars significantly changed due to washing (Figure 5). Washing increased the potential NO_3^- adsorption of pyrochars by 3-4% ($p \leq 0.05$; Figure 5A). For hydrochars, a similar effect was only observed for Hydro200 from digestates, turning the soil-hydrochar mixture from a NO_3^- source (leaching) into a sink (absorption) ($p \leq 0.05$). In the case of NH_4^+, a decrease in net leaching was observed for all treatments (Figure 5B). For most hydrochars, washing even turned soil-hydrochar mixtures from NH_4^+ sources (leaching) into net sinks (adsorption (Figure 5B). Strongest reductions in leaching were observed for Pyro750 (-37%) and Hydro200 from digestates (-35%). Washing effects on PO_4^{3-} sorption were inconsistent. Pyro750 showed increased PO_4^{3-} leaching (digestates), decreased adsorption (wood chips) and leaching instead of sorption (*Miscanthus*) (Figure 5C). In the case of Hydro200 from digestates, PO_4^{3-} leaching was reduced by up to -950%. For all other hydrochar mixtures, washing reduced both PO_4^{3-} leaching and sorption close to zero. Overall, washing seemed to be an effective measure to reduce the ion leaching of those ions that were adsorbed to the surface of fresh ~~bio~~chars.

4 Discussion

4.1 Char-induced effects on nutrient sorption: effects of carbonization process and feedstock material (laboratory experiments)

Pyrochars and hydrochars showed general differences in their sorption behavior. In most cases, pyrochars ~~could~~ removed NO_3^-, NH_4^+, and PO_4^{3-} from soil solution. This is in line with previous studies (Hale et al., 2013; Sarkhot et al., 2013; Yao et al., 2012). Hydrochars showed marginal or no sorptive effect on NO_3^-, NH_4^+, and PO_4^{3-}. Similar to our findings, Yao et al. (2012) found no sorptive effect of hydrochar from peanut hulls on NO_3^-, NH_4^+, and PO_4^{3-}. Previous studies indicate that increasing carbonization temperature results in higher SSA of the produced char (Cantrell et al., 2012), which in turn leads to higher NO_3^- adsorption (Hale et al., 2013; Lehmann, 2009; Yao et al., 2012). However, Akaike information criterion (AIC) was used to select the best fitting isothermal model. For NO_3^- sorption on pyrochars, AIC prefers the fitted linear model rather than the Freundlich isotherm, which indicates a non-saturated surface of ~~bio~~chars at increasing ion concentration of the nutrient solution. This contradicts previous studies which prefer Freundlich or Langmuir (Hale et al., 2013; Mizuta et al., 2004). In most cases, hydrochars showed no sorptive effect but partly, in particular for hydrochars from digestates, PO_4^{3-} release into aqueous solution was observed. This finding is corroborated by Yao et al. (2012) who also found 4% PO_4^{3-} leaching into aqueous solution ~~by~~ in sandy soil mixed with~~a~~ hydrochar ~~(~~from peanut hull~~) – sandy soil mixture~~. The digestate feedstock~~s~~ and ~~the~~ digestate~~s~~ carbonized to pyrochar and hydrochar contained 10 times more phosphorous (2.51%, Table 1) than the ~~bio~~chars produced from the other two feedstock materials, which explains the high PO_4^{3-} leaching.

Besides carbonization process, the feedstock material had a marked influence on the sorption behavior, which is in accordance with findings from other studies: while NO_3^- sorption was observed for pyrochar from Monterey Pine (Knowles et al., 2011), sugarcane bagasse and bamboo (Mizuta et al., 2004; Yao et al., 2012), pyrochar from pure washed cacao shell and corn cob without soil led to NO_3^- release (Hale et al., 2013). This implies strong adsorption capacity variations with carbonized feedstock. The three carbonized feedstocks we tested (*Miscanthus*, digestates, and woodchips) for pyrochars showed high correlations between NO_3^- adsorption and logarithmized SSA ($R^2 = 0.57$; $p \leq 0.05$ for amended loamy soil / 0.64; $p \leq 0.01$ amended sandy soil), and average pore size ($R^2 = 0.64$ for amended loamy soil / 0.72 for amended sandy soil; both $p \leq 0.01$). We also found strong correlations between H:C (indicates carbonization temperature) and NO_3^- adsorption ($R^2 = 0.65$ / 0.75 for amended loamy and sandy soil respectively; both $p \leq 0.01$). The NH_4^+ sorption is strongly nonlinear with increasing solution concentration (Freundlich coefficient $n = 1.1 – 1.5$), which indicates a limited number of cation exchange sites of ~~bio~~char (Hale et al., 2013). For all pyrochars, irrespective of feedstock, pore volume ($R^2 = 0.52$, $p \leq 0.01$), and ash content ($R^2 = 0.66$, $p \leq 0.01$) correlated with NH_4^+ adsorption. No saturation was found for PO_4^{3-}, with increasing solution concentration, especially evident for pyrochars from *Miscanthus* and also from woodchips for our used concentration range (2.5 – 15 mg P L^{-1}). This indicates that pyrochars could remove more PO_4^{3-} at higher solution concentrations, which is supported by Sarkhot et al. (2013), who tested 2 g pyrolysed hardwood ~~bio~~chars (without soil) in 40 mL nutrient solution at higher solution concentrations in comparison to ours (up to 50 mg P L^{-1}).

Generally, nutrient retention potential of ~~bio~~char is a result of cation or anion exchange combined with the large surface area, internal porosity and polar and nonpolar surface sites of functional groups (Hale et al., 2013; Laird et al., 2010; Lehmann, 2009). Additionally, Keiluweit and Kleber (2009) reviewed cyclic aromatic π-systems which showed specific π-electron donor-acceptor (EDA) interactions (i.e., cation-π; hydrogen-π; π-π EDA; and polar-π-interaction*)* with bonding energies between 4 and 167 kJ mol^{-1} to nutrients. Thus, ~~bio~~chars' surface charge is assumed to be negative, resulting in low anion exchange capacity and repellence of NO_3^- and PO_4^{3-} (Hale et al., 2013; Mukherjee et al., 2011). However, our results and results from previous studies showed anion adsorption the processes of which are not yet fully understood. Chun et al. (2004) and Chen et al. (2008) disproved the ability of PO_4^{3-} ions to bind with negatively charged ~~bio~~char surface functional groups like hydroxyls, carbonyls, carboxyls and phenolics. However, Sarkhot et al. (2013) proposed the exchange of surface hydroxyl groups on biochar with PO_4^{3-} inducing a pH controlled anion sorption capacity. Another mechanism is the ability of PO_4^{3-} ions to form bridge bonds using the residual charge of electrostatically attracted or ligand-bonded multivalent cations (Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}) (Mukherjee et al., 2011). We could not directly verify this assumption in our study because Ca^{2+} and Mg^{2+} were strongly leached (see supplemental; Table S1), but we suspect residual charge of electrostatically attracted cations to bind PO_4^{3-} in the double layer sheet. Klasson et al. (2014) showed that pore blocking ash-content could be reduced by washing ~~bio~~chars with rainwater, thereby micropore volume, total pore volume, and SSA increased. Hale et al. (2013) suggests enhanced PO_4^{3-} sorption due to increasing availability of binding sites on ~~bio~~char's surface after washing. However, in our lab-experiment we did not find increasing

PO_4^{3-} adsorption due to washing for any type of ~~bio~~char. We assume that primary bonding agents for PO_4^{3-} (Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}) are leached out, which results in no adsorption to the ~~bio~~char surface. Secondly, PO_4^{3-} compounds from the ~~bio~~char matrix itself are rinsed.

4.2 Soil induced effect on nutrient sorption (laboratory experiments)

Our results show that pyrochars could remove NO_3^- and PO_4^{3-} from soil solution when added to different soils (sandy and silty loam). NH_4^+ was retained only in the sandy loam which confirms the findings of Yao et al. (2012), who also mixed pyrochars to a sandy soil. For pyrochars mixed with loamy soil, we found reduced sorption capacity for NO_3^-, NH_4^+, and PO_4^{3-} , which is corroborated by Hale et al. (2011) who reported a reduction in the sorption capacity of ~~bio~~chars mixed with a fine-loamy soil. Hydrochars showed little (silty loam) or no (sandy loam) sorptive effect on NO_3^-, NH_4^+, and PO_4^{3-}.

The adsorption capacity of ~~bio~~chars for nutrients interacts with the amended soil type. Generally, soil's adsorption capacity for NO_3^-, NH_4^+, and PO_4^{3-} is determined by pH, CEC, AEC, SSA, organic matter content, and soil texture. Hale et al. (2011) suggest a decreased reduction in the sorption capacity of ~~bio~~chars caused by blocking of sorption sites by ~~dissolved organic carbon (~~DOC~~)~~, which could leach out from soil and may adsorb to ~~bio~~chars. The solubility of DOC can be increased by increasing negative charge on the DOC due to a raised pH through ~~bio~~char application to soils (Alling et al., 2014). In our study, application of pyrochars led to a stronger rise in pH in the silty loam than in the sandy loam (Table S2). According to Hale et al. (2011), this could have induced higher DOC solubility in the sandy loam and the leached DOC was adsorbed by pyrochars resulting in blocked binding sites. Further, the soils tested in this study differed strongly in their texture and CEC. The silty loam contained higher amounts of multi-layer clay minerals, which led to higher adsorption competition between ~~bio~~char and clay mineral surfaces. Ersahin et al. (2006) report SSA between 46.5 and 90.38 as well as 20.60 and 61.95 m^2 g^{-1} for silty loams and loamy sands, respectively. The pyrochars we tested had SSAs between 210 and 448 m^2 g^{-1}, which are considerably higher than the SSA of the used soils. The difference in SSA between pyrochar and soil was larger for the sandy loam than the silty loam. This resulted in stronger adsorption potential for ions from sandy loam or nutrient solution to the pyrochars. However, the larger SSA of the silty loam enhanced the adsorption competition for ions between loamy sand and pyrochars. In addition, ions from the nutrient solution are more attracted to the silty loam than to the sandy loam or to the pyrochars. Furthermore, soil-bound ions such as NO_3^-, K^+, Mg^{2+}, Ca^{2+} were leached from the silty loam and were directly adsorbed by pyrochars, suggesting that this direct adsorption may result in occupied binding sites on the pyrochars, which led to no or less adsorption of NO$_3^-$, NH$_4^+$ and PO$_4^{3-}$ from the nutrient solution.

4.3 Effect of ~~bio~~char ageing on nutrient sorption (field- & laboratory experiment)

The ability of both pyrochar and hydrochar to adsorb NO$_3^-$ and NH$_4^+$ from soil solution was stronger for fresh ~~bio~~char as compared to aged ~~bio~~char (i.e., after seven months field incubation). This was an unexpected behavior and often lead to a complete loss of the ~~bio~~char's nutrient retention capacity and has rarely been studied to date. Since the overall adsorption capacity of hydrochar observed in our study was small, the ageing effect was also less ~~important~~ pronounced compared to pyrochars. For hydrochars, other studies reported the physical structure and chemical properties result in a lower recalcitrance towards microbial degradation compared to pyrochars (Bargmann et al., 2014a; Hale et al., 2011; Steinbeiss et al., 2009). –Explanations for the decreasing nitrogen adsorption capacity of pyrochar may include: a) binding sites of both types of ~~bio~~char may be blocked with organic matter or mineral particles such as clay, b) binding sites of pyrochar may be reduced by microbial degradation changing the char's surface properties, which in turn leads to a diminished number of negatively charged binding sites (Cheng et al., 2008; Cheng et al., 2006; Glaser et al., 2000). But for our study, we could not explain decreasing adsorption with these mechanisms.

Such a trend of decreasing adsorption capacity over time was also reported by Bargmann et al. (2014b) who incubated 2% and 4% hydrochars from beet-root chips with a loamy soil for 8 weeks in the laboratory. A diminished number of negatively charged binding sites may result in higher leaching of positively charged ions (such as NH$_4^+$, Ca^{2+}, Mg^{2+}, K$^+$). In our experiment, the adsorption-rate of NH$_4^+$ was reduced over time and Ca^{2+} as well as Mg^{2+} showed higher leaching after seven months (Table S5). The ~~bio~~chars used in the field experiment had not been pretreated by washing. The increased adsorption capacity of ~~bio~~char for PO$_4^{3-}$ may thus be partly a result of initially bound PO$_4^{3-}$ that was leached from fresh ~~bio~~chars (T$_0$), and was leached less after seven months (T$_1$). However, in our laboratory experiment, washing did not reduce PO$_4^{3-}$leaching but increased the adsorption ~~capacity in the laboratory study~~. Phosphate adsorption on ~~bio~~char depends strongly on pH. For our used ~~bio~~chars, effect on pH in the nutrient solution was lower for washed than unwashed ~~bio~~chars.

5 Conclusion

The nutrient retention potential of ~~bio~~chars (i.e., nitrate, ammonium, and phosphate) differs strongly with nutrient, ~~bio~~char type (hydrochar vs. pyrochar), and type of carbonized feedstock, as well as amended soil type. Among nine different types of ~~bio~~chars tested in a laboratory batch experiment, only pyrochars showed the ability to effectively retain nitrate, ammonium, and phosphate. Moreover, the nutrient retention effect ~~was~~ seems to be of very limited duration. After seven months in the field, around 60 to 80% of the adsorption capacity of pyrochar~~s~~ was lost. Underlying mechanisms are poorly understood, but our results cast doubt on the efficiency of ~~bio~~char application to minimize the problems of nutrient leaching from agricultural soils to the groundwater and adjacent ecosystems.

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Table 1

General properties of feedstock materials and ~~bio~~chars used in the laboratory study (“Lab”) and field incubation (“Field”). Data for chars used in the laboratory only derived from Eibisch et al., 2013 & 2015; n.d. = not determined.

Experiment	Feedstock	Char type	°C	pH ($CaCl_2$)	Ash content [%]	C [%]	N [%]	S [%]	O:C	H:C	P [%]	Ca [%]	Mg [%]	Na [%]	K [%]	SSA [m^2 g^{-1}]	Pore volume [cm^3 g^{-1}]	Average pore size [Å]
Lab	Digestates	raw	-	-	11.9	41.9	1.57	0.28	0.87	0.14	1.28	0.87	0.66	0.05	2.88	8.6	0.03	61
		Hydrochar	200	6.2	10.3	53.8	2.59	0.30	0.46	0.10	1.23	1.39	0.48	0.03	0.98	13	0.09	192
		Hydrochar	250	5.7	13.6	61.8	2.98	0.22	0.29	0.08	1.56	1.60	0.85	0.03	1.41	2.8	0.02	167
		Pyrochar	750	9.8	46.0	69.7	<1.0	0.18	0.17	0.04	2.51	2.91	1.12	0.24	8.10	448	0.28	12
	Miscanthus	raw	-	-	2.9	45.6	<1.0	0.07	0.86	0.13	0.09	0.22	0.07	0.01	0.53	1.0	0.01	154
		Hydrochar	200	4.6	3.9	58.0	<1.0	0.07	0.46	0.10	0.13	0.30	0.05	0.02	0.27	5.2	0.05	180
		Hydrochar	250	4.2	4.5	69.0	<1.0	0.07	0.27	0.08	0.17	0.30	0.06	0.01	0.30	5.8	0.05	179
		Pyrochar	750	9.0	15.0	76.9	<1.0	0.12	0.10	0.02	0.41	1.14	0.30	0.18	2.12	279	0.19	14
	Woodchips	raw	-	-	4.2	48.6	<1.0	0.05	0.71	0.12	0.07	0.62	0.07	0.02	0.27	1.6	0.02	206
		Hydrochar	200	4.6	5.0	59.7	1.07	0.06	0.40	0.10	0.08	0.90	0.07	0.02	0.25	10	0.09	180
		Hydrochar	250	4.8	5.4	67.7	1.22	0.06	0.27	0.08	0.11	0.59	0.06	0.03	0.21	3.5	0.04	207
		Pyrochar	750	8.7	24.6	68.4	<1.0	0.13	0.10	0.02	0.35	3.43	0.29	0.12	0.87	210	0.17	17
Field-	Miscanthus	raw	-	-	2.9	46.3	<1.0	<0.1	0.28	0.13	0.09	0.11	0.09	0.01	0.52	n.d.	n.d.	n.d.
		Hydrochar	200	3.8	3.9	63.8	<1.0	<0.1	0.15	0.08	0.13	0.11	0.13	0.21	0.13	n.d.	n.d.	n.d.
		Pyrochar	750	9.0	15.0	81.8	<1.0	0.10	0.09	0.01	0.39	0.35	0.39	0.03	1.50	n.d.	n.d.	n.d.

Table 2

General properties of the soils used for the lab and field study.

Experiment		Site	Soil type	Soil texture class	sand [%]	silt [%]	clay [%]	C_{org} [%]	N_{tot} [%]	C/N	pH ($CaCl_2$)	CEC [$cmol_c$ kg^{-1}]
Lab	1	Goettingen	haplic Luvisol	Sandy loam	61.5	32.8	5.8	1.23	0.10	12.3	5.6	4.0
	2	Braunschweig	haplic Cambisol	Silty loam	15.4	67.6	17.0	1.27	0.12	10.6	5.6	10.8
Field	1	Bortfeld	loamic Cambisol	Sandy loam	57.0	37.1	5.9	0.93	0.13	7.3	6.4	n.a.
	2	Querenhorst	arenic Planosol	Loamy sand	74.7	18.0	7.3	1.13	0.13	8.8	6.8	n.a.
	3	Volkmarsdorf	cambic Planosol	Sandy loam	67.1	21.7	11.2	1.16	0.12	9.9	6.5	n.a.

Table 3

Ion concentrations of the nutrient solution and relative sorption rates of the two control soils (soil without application of ~~bio~~char) at the six applied concentration levels.

	Ion	P1	P2	P3	P4	P5	P6
Nutrient solution	NO_3^--N [mg L^{-1}]	5	10	20	30	40	60
	NH_4^+-N [mg L^{-1}]	5	10	20	30	40	60
	PO_4^{3-}-P [mg L^{-1}]	1.25	2.5	5	7.5	10	15
Sandy loam	NO_3^--N [%]	-6	0.1	3	0	0.1	0
	NH_4^+-N [%]	15	15	16	15	16	11
	PO_4^{3-}-P [%]	-78	6	50	59	57	65
Silty loam	NO_3^--N [%]	-58	-28	-16	-8	-9	-5
	NH_4^+-N [%]	54	52	49	39	36	33
	PO_4^{3-}-P [%]	10	45	75	73	69	81

Figure 1

Mean NO_3^--N removal rates in soil-char composites relative to the control [%] (the respective soil with no char added) for pyrochars (Pyro750)(A-B) and hydrochars derived at 200°C (Hydro200) and 250°C (Hydro250)(C-D) from *Miscanthus* (M), woodchips (W), and digestates (D) mixed with the sandy and silty loam soil at the six nutrient-solution levels (n=3).

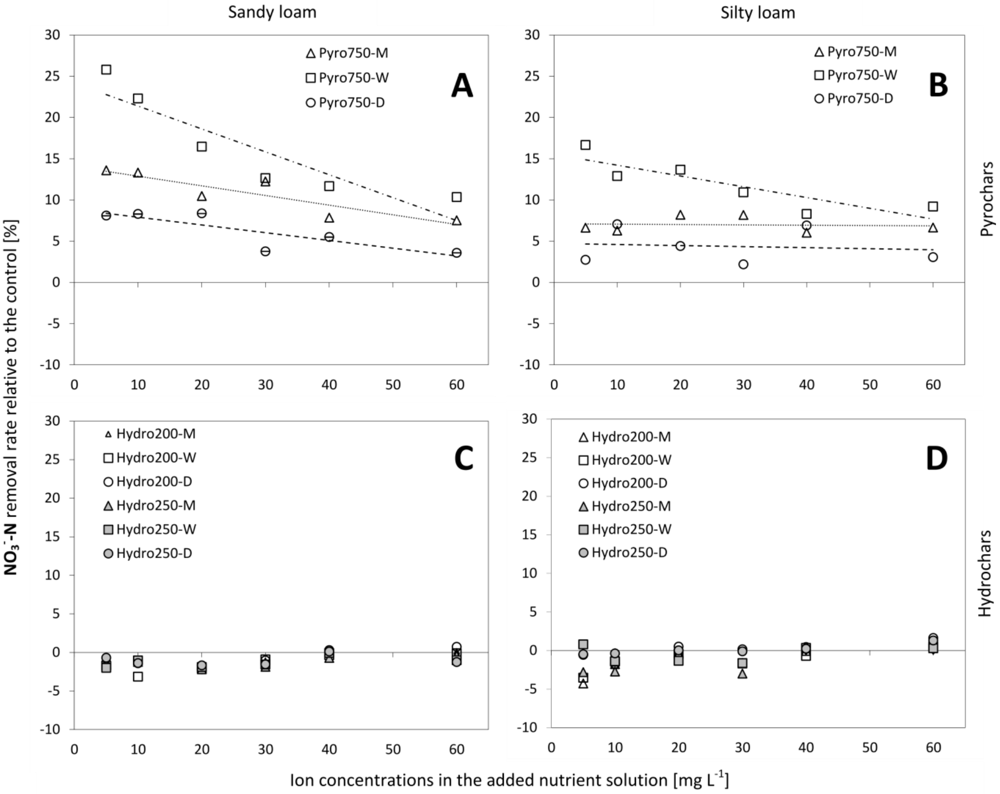


Figure 2

Mean NH_4^+-N removal rates in soil-char composites relative to the control [%] (the respective soil with no char added) for pyrochars (Pyro750)(A-B) and hydrochars derived at 200°C (Hydro200) and 250°C (Hydro250)(C-D) from *Miscanthus* (M), woodchips (W), and digestates (D) mixed with the sandy and silty loam soil at the six nutrient-solution levels (n=3).

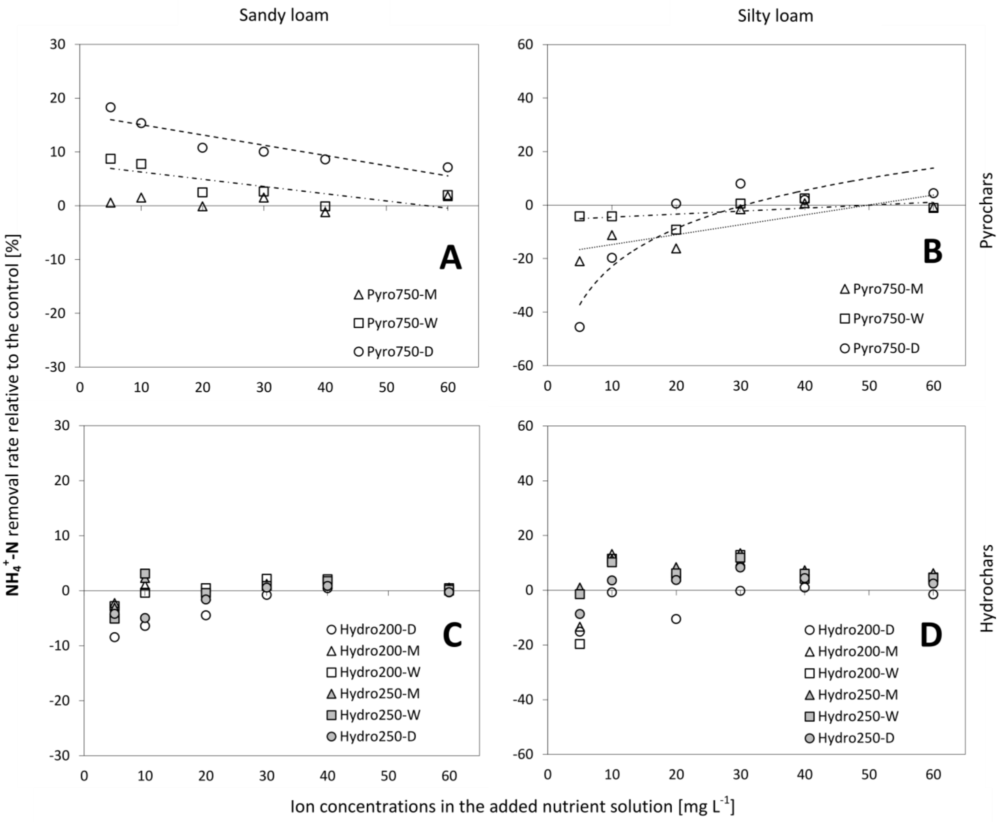


Figure 3

Mean PO_4^{3-}-P removal rates in soil-char composites relative to the control [%] (the respective soil with no char added) for pyrochars (Pyro750)(A-B) and hydrochars derived at 200°C (Hydro200) and 250°C (Hydro250)(C-D) from *Miscanthus* (M), woodchips (W), and digestates (D) mixed with the sandy and silty loam soil at the six nutrient-solution levels (n=3).

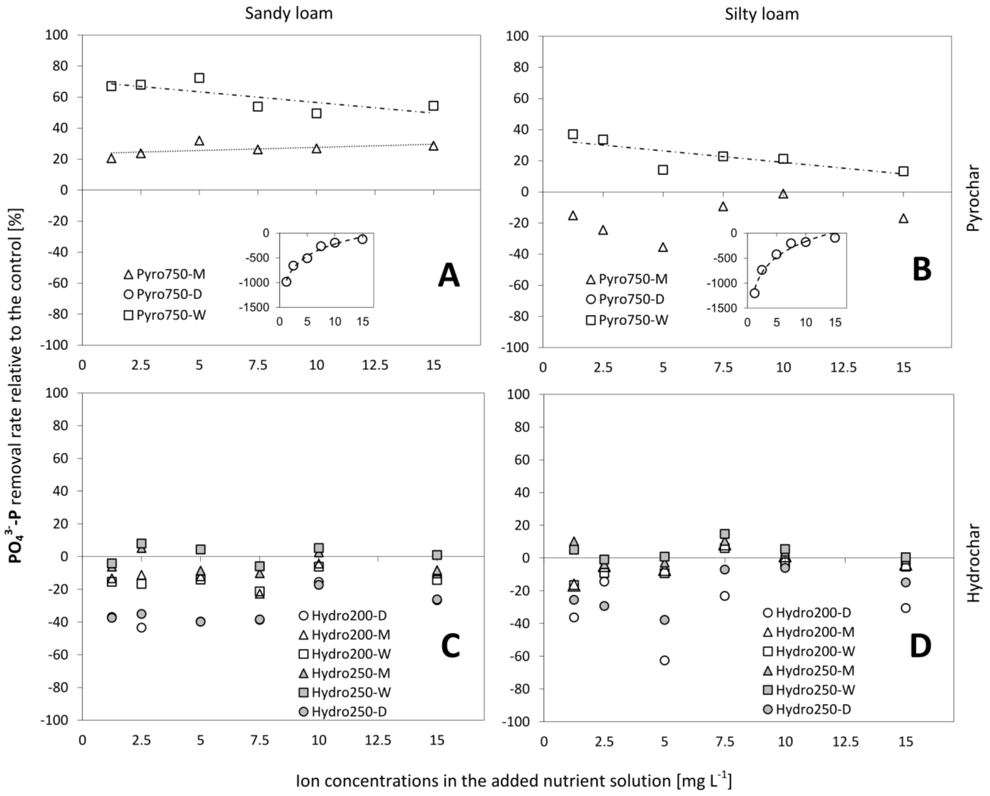


Figure 4

Mean NO_3^--N (A-C), NH_4^+-N (D-F), and PO_4^{3-}-P (G-I) removal rate relative to the control for fresh (T_0) and degraded (T_1) pyrochars and hydrochars and relative removal rate of control to blind nutrient solution of the field experiment (For all Treatments n=3). Test statistics can be found in Table S5, S7, and S8.

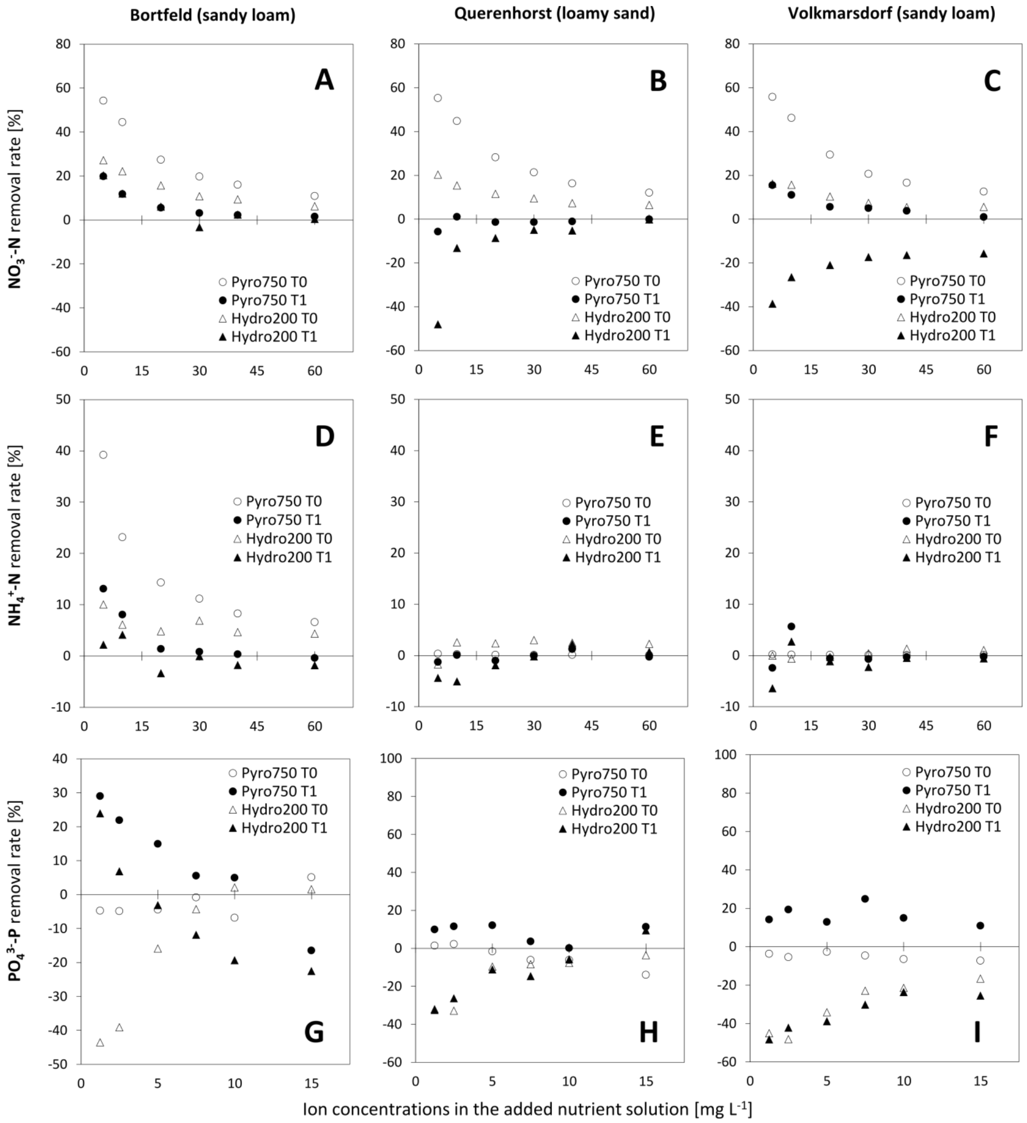
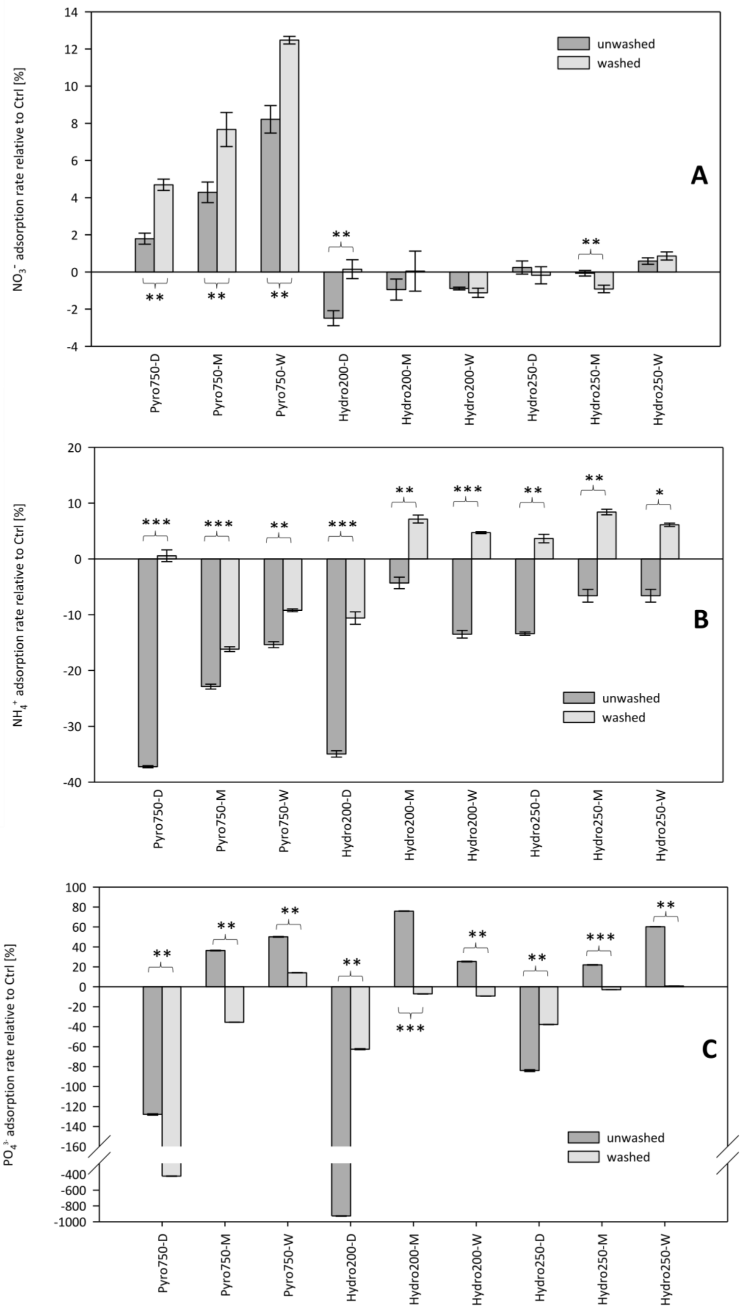


Figure 5

(A) NO_3^-, (B) NH_4^+, and (C) PO_4^{3-} removal rates in soil-char composites relative to the control (silt loam without char) for washed and unwashed pyrochars (Pyro750) and hydrochars derived at 200°C (Hydro200) and 250°C (Hydro250) from *Miscanthus* (M), woodchips (W), and digestates (D). Significant differences between washed and unwashed ~~bio~~chars were tested with the unpaired t-test. P-values are indicating by *** <0.01; ** <0.05; * <0.1 (for each treatment n=3, means ± SE).



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