Reviewer #2

Response: We thank the reviewer for their thoughtful and in-depth analysis of our manuscript, and appreciate the time and effort that went into this review. We have addressed the reviewer's comments by restructuring the manuscript to shorten the introduction and lengthen the discussion. Those changes make our knowledge of the literature more explicit, and better situate our specific results within the ongoing work in this field. We have also made significant edits to the materials and methods section which clarify many details that were previously opaque. Finally, we have performed an additional experiment at the reviewer's suggestion, to include point of zero charge (PZC) data for the biochars included in the column studies. As there was overlap in the suggestions from each reviewer, some of our responses can also be found in the document submitted in response to reviewer #1. Details of our edits are included below.

Application of biochar to bind nutrients in soil and alter hydraulic properties of the soil is an important and relevant topic for large scale application of biochar in agricultural fields. The authors of this current paper have tried to add more insights into the existing literature in this context. Overall, after a first glance through, the reader can follow the main message of the paper. However, I have a few main points of concern regarding the manuscript:

- **The title of the paper states "inhibits nutrient leaching" – the data for nitrate does not necessarily show this.**

  Response: We agree that ammonium is retained to a much larger extent, and has greater potential for leaching mitigation in biochar-amended soils. However, nitrate leaching was also inhibited, though to a lesser and more transient extent. While this result is minor in magnitude, it may have great significance for fertilizer use efficiency in cropping systems, especially where biochars can be engineered to have high surface area and low CEC, as described in this study. To address the reviewer's concerns, and more accurately depict the work contained within this manuscript, we have changed the title to "Biochar alters hydraulic conductivity and **impacts** nutrient retention in two agricultural soils."

- **There lacks a sense of novelty in the experimental approach of the manuscript. Experimental details are missing especially for the column studies.**

  Response: Details have been extensively updated, as described below in response to reviewer's specific comments. Regarding the novelty of this work, we agree that we have not made this clear enough in the original manuscript. In the next iteration, we have explicitly stated that this study is novel for the following reasons:

  1) It includes a robust experimental matrix with 7 commercially available biochars included in the sorption experiments (and, based on those results, 3 biochars in 2 soils for K_{sat} data, and then 3 biochars in a sandy soil for leaching data, where results are most important given the potential for sandy soils to leach N). As stated many times throughout the literature, the use of commercially available materials (as opposed to laboratory-produced biochar) is essential for replicability of results, and for the potential for these materials to be used in real world cropping systems;

  2) The experimental approach allows for chemical and physical retention mechanisms to be distinguished: Even where biochar displayed no chemical affinity for nitrate,

nitrate was retained in leaching studies, where it was linked to high surface area and low CEC. This suggests a physical entrapment, as elucidated in-text with appropriate citations. While many studies investigate nitrate/ammonium chemisorption or leaching, rarely are both explored given the extensive labor involved in experimental setup and maintenance. Data from our study will be critical for biochar producers to design materials that improve soil water or nutrient retention dynamics, or for land managers to predict how biochars may behave in specific agricultural conditions.

3) This study utilizes the same biochars and soils as those in 3-year field trials. Results from these lab scale experiments can be used to interpret those obtained from field trials, and help provide both fine resolution mechanistic investigation, and effects from real-world agricultural systems.

A more mechanistic insight would have been interesting. Key factors which would have been critical for achieving this and making a more impactful statement are (i) measurement of point of zero charge (for supporting any statements using electrostatic repulsion or attraction) (ii) measurements of anions and cations released during column nutrient leaching tests (iii) use of non-reactive tracers such as "deuterated water" could have been an interesting approach to understand movement of water through columns, etc.

- **The term "physical and chemical interactions/affinity" is used very lightly and often in the manuscript without providing concrete proof for these interactions.**
- **An in-depth literature study in the discussion would have provided readers with more confidence in the conclusions that the authors wished to make.**
- **The entire sense of "timing of release of nitrate" and its importance needs to have been brought to light. Is it sufficient for nitrate to be captured physically for a short duration and then released?**
- **The entire discussion in Section 4.3 is underwhelming.**

Response: At the reviewer's suggestion we have included PZC measurements, and extended the discussion of likely and potential mechanisms by including a more extensive literature review in the discussion, which was previously confined to the introduction. We thank the reviewer for their comments, as they have led to a better structured manuscript which will be of greater impact and interest to readers of SOIL. We have addressed the remaining issues in detail in response to specific comments below.

Abstract and Introduction

- **Line 47-48 – this is not always true. There are some biochars which have a PZC of 7.5 or higher and then they might be positively charged.**

Response: We agree that biochars are not always negatively charged, and have changed the statement to include more extensive discussion and citations, as below:

"Biochar surfaces range in their protonation state when added to the soil, as a function of soil pH and their point of zero charge (PZC). While PZCs between 7 and 10 have been observed (Lu et al., 2013; Uchimiya et al., 2011), the high number of oxygen-containing (primarily carboxyl) functional groups typically lead to PZCs between 1.5 and 5 (Peiris et

> al., 2019; Uchimiya et al., 2011; Wang et al., 2020). Due to these PZCs, the deprotonation of biochar surface functional groups occurs, leading to a net negative charge within most agronomic soils (pH ~5-7.5)."

Furthermore, we conducted an additional experiment at the reviewer's suggestion to measure the point of zero charge (PZC) of the three biochars used in our column studies. We have included this data, as well as the appropriate methods description and citation of sources. Briefly, we found that the PZC was 6.8 for AS800, 3.2 for AS500, and 3.9 for SW500. As most agricultural soils have a pH well above 4, including those tested in our study, AS500 and SW500 would be expected to be negatively charged. The higher PZC of AS800 was to be expected, as it has a higher ash content, and higher metal-oxide content as demonstrated through IR peaks at ~1000 to 700 cm^{-1}, consistent with metal oxide vibrations (Parikh et al., 2014). This PZC is lower than the pH of the soil it was added to, and was likely negatively charged.

- **Line 85 – Suggestion is to introduce what is saturated hydraulic conductivity out here itself.**

Response: The line currently reads: "biochar has largely been shown to decrease the ability of a saturated soil to transmit water (saturated hydraulic conductivity (K_{sat}))." This statement both introduces the definition of hydraulic conductivity and the abbreviation it is referred to throughout the rest of the manuscript. If the reviewer is suggesting something different, it is unfortunately not clear to us.

- **Line 91 – how is the biochar "physically altering the soil to influence Ksat?"**

Response: Lines 80-89 directly prior to this statement provide a detailed discussion of how biochar can physically alter soil structure through decreased bulk density, increased porosity, and changes in mean pore size, and therefore influence water movement through the soil (below). However, to make our meaning more clear, we will delete the word "physically" from the sentence on line 91.

> "In addition to chemical and microbial mechanisms, biochar may retain N through physical means (Clough and Condron, 2010). One study determined that biochar decreased soil bulk density by 3 to 31%, and increased porosity by 14 to 64% (Blanco-Canqui, 2017). Biochar can also alter mean pore size and pore architecture, thereby influencing tortuosity and the residence time of water and nutrients within the soil profile (Lim et al., 2016; Quin et al., 2014). The impact of biochar on hydraulic conductivity largely appears dependent on soil texture, which highly influences pore structure. While exceptions have been observed, biochar has largely been shown to decrease the ability of a saturated soil to transmit water (saturated hydraulic conductivity (K_{sat})) in coarse textured soils and increase K_{sat} in finer soils (Blanco-Canqui, 2017). The impact of biochar on these soil physical properties may influence nitrate retention through a mechanism known as "nitrate capture," in which nitrate molecules become physically entrapped within biochar pores (Haider et al., 2016), potentially leading to increased residence time in crop rooting zones and a greater opportunity for plant uptake (Haider et al., 2020; Kameyama et al., 2012; Kammann et al., 2015)."

Materials and methods

- **Line 105 – From which four commercial companies?**

Response: This information has now been included, as follows:

> "Seven biochars were obtained from the following feedstocks and produced at the following temperatures: almond shell at 500 °C (AS500, produced by Karr Group Co.), almond shell and 800 °C (AS800, Premier Mushroom and Community Power Co), coconut shell at 650 °C (CS650, Cool Planet), softwood at 500 °C (SW500, Karr Group Co.), softwood at 650 °C (SW650, Cool Planet), and softwood at 800 °C (SW800, Pacific Biochar), and an additional softwood biochar produced at 500 °C and inoculated with a proprietary microbial formula (SW500-I, Karr Group Co.)."

- **Line 107 – What is the inoculated microbial formula?**

Response: As the biochars are commercially available, many of the production details—including the microbial formula—are proprietary and were not disclosed. However, now that we have included the company names at the reviewers suggestion, other scientists can repeat experiments with these biochars, working with the producers if desired.

- **Line 137 – Do not see the need to specify ongoing field trials if there is no connection with the current paper.**

Response: The connection between these experiments and ongoing field trials is critical to the novelty and importance of this study, as we are using the same soils and biochars to investigate agronomically relevant responses at multiple scales. However, we agree that the connection was not made clear enough, as description of the field trials is currently contained only in the methods section 2.2. In the next iteration of this manuscript, we have included an additional final paragraph in the discussion section, as detailed below:

> "4.4 Implications for field conditions
>
> It is difficult to extrapolate results from these laboratory-scale investigations to field-scale, production agriculture, as real-world conditions will have additional variables in climate, soil-water, and soil-plant dynamics. However, the results of this study suggest these biochars may increase the residence time of water in sandy soils and increase drainage in fine textured soils during irrigation or flooding events, or when soils are otherwise saturated. Results may be particularly relevant for flooded agricultural systems such as rice, where ammonium is the primary source of N and water retention is a key parameter for success (Minami, 1995). Indeed, 95% of California rice production occurs in the Sacramento Valley, where both the YSiL and HSL soils are common (http://rice.ucanr.edu/About_California_Rice/). Data from these trials may help growers in these regions and soil textures determine if biochar can increase water and nutrient retention in their systems.
>
> Recent meta-analyses have concluded that biochar substantially increased soil water content at field capacity and permanent wilting point, in the field and lab, in coarse textured soils only (Blanco-Canqui, 2017; Razzaghi et al., 2020). Despite these observed

> trends, benefits have also been observed in fine textured soils, including reduced crop water stress, increased yield (Kerré et al., 2017; Nawaz et al., 2019), and reduced crop loss during deficit irrigation (Madari et al., 2017). Other authors have reported little to no effect, or transient effects, of biochar on soil water dynamics in both fine and coarse textured soils (Jones et al., 2012; McDonald et al., 2019; Nelissen et al., 2015). However, results from our experiments can only be conservatively extrapolated to dryland agriculture or in soils that experience wet-dry cycles, as unsaturated hydraulic conductivity was not measured. In order to determine how these biochars may behave in unsaturated conditions, current three-year processing tomato field trials are currently underway in these same soil textures, in which soil-water dynamics are being measured."

- **Line 156 – It makes more sense to present electrolyte concentrations on a mM or M basis, to normalize it. Why is this test done with NaCl and the column tests with CaCl2?**

  Response: We have changed the concentrations to mM at the reviewer's suggestion. Monovalent electrolyte solutions are commonly used in sorption studies to avoid cation bridging which would confound sorption results. However, Na is a known dispersing agent when added to soils, and so $CaCl_2$ was used in column tests rather than NaCl to prevent dispersal and the creation of preferential flow paths. We have added a statement about this in the materials and methods section to make this reasoning transparent.

- **Line 165 – Which are the "multiple equations"?**

  Response: We have edited this statement to say "Langmuir, Freundlich, and Langmuir-Freundlich equations were tested to model the adsorption isotherms, with the Freundlich equation (Eq. (2)) demonstrating the best fit based on r^2 values."

- **Line 175 – How were the columns packed?**

  A citation for the packing has been added to increase replicability:

  > "Columns were prepared using the dry packing method according to Gibert et al. (2014)."

- **Was the biochar homogeneously mixed with the soils?**

  Response: Yes, soils and biochars were thoroughly and homogenously mixed through a combination of stirring and shaking within a sealed container for a minimum of 120 seconds. The following sentence has been added:

  > "Soils and biochars were thoroughly and homogenously mixed prior to being added to tempe cells."

- **How was existence of preferential flow ruled out? Any tracer?**

We acknowledge that the use of a tracer would have been beneficial to our mechanistic interpretation of results, and thank the reviewer for this suggestion. Even without a tracer, however, there was no evidence of preferential flow in any of the five replicates for any of the treatments. Error bars were very small for both nutrient concentrations across pore volumes in the breakthrough curves, as well in the hydraulic conductivity measurements as measured by data loggers.

- **What was the flow rate and the pore volume?**

Response: As stated on line 179, each column was gravity-fed a solution at a constant pressure head of 34 cm. The "flow rate" is therefore the K_{sat} itself, provided in the results section. Soil porosity was provided in Table 3. Additionally, we have now edited the methods section to provide core volume, as below in bold:

> "To investigate the influence of biochar on saturated hydraulic conductivity (K_{sat}), constant head column experiments were performed in five replicates using the 5 station Chameleon Kit (Soilmoisture Equipment Corporation (SEC) 2816GX). SEC tempe cells**, each with a volume of 136.4 cm^3** were packed with soils amended with 0 and 2% (w/w) AS500, AS800, or SW500 biochars…"

- **Lines 175-184 – Why was ksat measured for 2 soils, whereas sorption for only 1?**

Response: We agree that the study would have benefited from leaching data from both the YSiL and the HSL soils. However, column experiments were performed without the aid of autosamplers or mechanization of any kind. As shown in Figure 3, the K_{sat} for the unamended HSL soil columns was 1.2 cm s^{-1} · To manually collect 20 pore volumes of leachate, 15 hours of active maintenance was required per treatment, for a total of 4 treatments. The YSiL K_{sat} was 0.044 cm s^{-1}, or a 96% reduction in flow rate from the HSL. It was not feasible for someone to stay in lab for the time required to collect 20 pore volumes at this speed. After attempting it for two treatments, we decided to proceed with the HSL data, as it was logistically possible and would provide more valuable information. To make this clear to readers, we will include the following statement (new content in bold):

> "Columns were also used to investigate the nutrient retention and leaching in HSL amended with 0 and 2% biochar. Preliminary trials with the YSiL demonstrated that leaching rates were very low (~0.044 cm^{-1}) creating logistical challenges for conducting these experiments. Additionally, the impact of nitrate leaching is much more pronounced in more coarsely textured soils and thus leaching experiments were conducted only in HSL columns"

Results

- **Line 196 – increased pyrolysis temperature usually increases carbonization.**

We agree that increased temperature often results in higher carbon content; however, this is dependent on the feedstock and production parameters, especially atmospheric oxygen content. As these materials were obtained from commercial sources, we do not have specific information regarding oxygen levels. The higher ash content in the almond shell biochars was expected, due to the high cation content of almond shell feedstocks (Aktas et al., 2015) which are concentrated at higher temperatures. The impact of pyrolysis temperature on the ash content of softwood biochars is less pronounced.

- **Line 268 – what do you mean by "main effect"? p values correspondence not clear.**

Response: We have edited the statement as follows:

> "There was a significant effect of biochar ($p = 0.001$) and soil texture ($p < 0.001$), as well as a significant interaction between biochar and soil texture ($p = 0.006$), on saturated hydraulic conductivity."

- **Figure 4- It is very hard to discern the data and the decrease in leaching of NO3 from the control to HSL+SW500. Please consider to reduce the y axis from 100 mg/L to something smaller (4(a)) to make the graph better accessible (in regards to the data in the text) for the readers.**

Response: We agree that the data is difficult to read in the one instance the reviewer indicates, however, the y axis cannot be reduced, as the initial nitrate flush in pore volumes 0-10 neared 100 mg L^{-1}. As is, the figure shows the reader that a) HSL had very high but easily leached levels of nitrate, and b) there was not much difference in nitrate leaching in soils with or without biochar. This information is highly descriptive and necessary to the study. To provide a more detailed snapshot of the data the reviewer is interested in, figure 5 was included so that exact nitrate quantities could be obtained across pore volumes 15, 20, and 25. Together, these two figures provide both an overview and a more fine-grained resolution of nutrient leaching in these columns.

Discussion: In general, the discussion is not sufficient, and needs better structuring, with more references.

Response: Our manuscript includes an extensive literature review with many references. We do not believe we need *more* literature, but, as the reviewer stated, a *better structured* literature review would be beneficial. Currently, we have included a lengthy discussion in the introduction. We did not include these same references in the discussion so as to avoid repetition, but agree that this context is important for our specific results. In the revised version, we have moved some of the extensive discussion from the introduction into the discussion, and we have related all findings to our results, as described below

- **Line 324-329 –This explanation is a bit underwhelming. A more mechanistic approach to this would have been to also measure cations and anions in solution – if nitrate is bound to positively charged components in the ash, one should see some anions being released. PZC measurements would have been crucial in the experimental design, since a lot of the reasoning is based on "electrostatic repulsion".**

Response: As described in line 68 of this document, we have now included PZC measurements which substantiate the discussion of electrostatic repulsion and affinity.

- **Line 340-342 – A tracer study using "deuterated water" or something similar would have been a more mechanistic way to explain the movement of water through biochar packed columns.**

  Response: We acknowledge that the use of a tracer would have improved our mechanistic interpretation of results, and thank the reviewer for this suggestion. In future work we will consider this approach.

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