### 1 <u>Reviewer #1</u>

- 2 The authors contribute with their study to an ongoing and substantial discussion of the effect of 3 biochar on the hydraulic properties of soils and the potential of biochar to bind and retain nitrate and 4 ammonium in soils. While this is an important discussion for the application of biochar in agricultural 5 soils, the submitted manuscript is not well structured and, much more importantly, it is not clearly 6 providing a novel approach or understanding for the ongoing scientific discussion. Furthermore, the 7 manuscript is not transparent to follow the methodological approach. It is not clear why the column 8 retention experiment was only performed for the HSL and the described effect of additional nitrate 9 leaching with biochar is not supported by shown data. The fairly short discussion is by far not 10 complete. Many aspects contradicting the here reported findings are not considered (please see 11 specific comments). This results also in a lack of new mechanistic understanding and the link to the 12 agricultural soils. For example, the authors are not considering the effect of the two agricultural soils 13 on the nutrient mobility or bring their findings in context of potential field applications. I highly 14 recommend the authors to consider a critical discussion of their findings, developing supported 15 mechanistic understanding from these experiments, improve the transparency of the experimental 16 approach and improve the overall manuscript structure. Given these aspects, I decided to reject the 17 current manuscript for publication in SOIL. 18 19 Response: We greatly appreciate the time and effort that went into this extensive and constructive 20 review. We will address the reviewers concerns by restructuring the manuscript, providing more 21 comprehensive information in the materials and methods section, making linkages between these 22 experiments and our corresponding field trials clearer, and highlighting the novelty of this work through 23 a more nuanced, critical, and lengthy discussion section, as detailed below. Furthermore, we have 24 performed an additional experiment to answer the reviewer's questions about the effect of pH and the 25 mechanistic underpinnings behind observed results. The point of zero charge (PZC) for each biochar is 26 now included, as described below. 27 28 Specific comments: 29 30 Abstract and introduction: 31 32 Line 9-10: specify "saturated hydraulic conductivity (Ksat)" 33 34 Response: We corrected this in the manuscript. 35 36 Line 44-46: Provide reference for this statement • 37 38 Response: We have included a reference to Clough and Condron (2010) and Peiris et al. (2018), as 39 cited in the bibliography at the end of this response. 40 41 • Line 65: What is the mechanism for the high values found in Yin et al (2018). Please provide more 42 details 43 44 Response: The mechanism cited in Yin et al. (2018) is the "abundant surface functional groups" that 45 develop at low pyrolysis temperatures. Following our statement on lines 66-74, there is a well-cited 46 review of mechanisms which details the relationship between pyrolysis temperature and biochar
- 47 characteristics. To make the relationship between this statement and the Yin paper more clear, we

51 "Lower temperatures have been correlated with higher cation exchange capacity (CEC) (Gai et 52 al., 2014a), higher O/C ratios (Yang et al., 2017), and more abundant surface functional groups 53 (Yin et al., 2018)." 54 55 We have also revised the original statement to exclude specific adsorption values, as follows: 56 57 "While most reported Q<sub>max</sub> values are less than 20 mg NH<sub>4</sub><sup>+</sup>-N g<sup>-1</sup> (Zhang et al., 2020), higher 58 values have been observed (Yin et al., 2018, Gao et al., 2015)." 59 60 This allows for discussion of the range and inconsistencies found within the literature, without 61 overburdening the reader with specific values and mechanisms for each of the 15 cited papers, 62 immediately prior to a 9-line discussion and summary of mechanisms. Furthermore, this revised 63 sentence matches the format provided for the discussion of nitrate sorption on line 55. 64 65 Line 96-102: Too detailed method description for an introduction. Please shorten to avoid ٠ 66 repetition. 67 68 Response: We have removed 7 lines, to develop the paragraph below: 69 70 "In this project, biochar characterization, sorption, and soil column experiments were carried 71 out using biochars of diverse feedstocks and production temperatures, in order to determine to 72 what degree these biochars: 1) chemically bind nitrate and ammonium; 2) physically alter the 73 soil to influence saturated hydraulic conductivity; or 3) influence nutrient leaching, through 74 either chemical or physical means. This information was used to determine the parameters that 75 may optimize hydrologic and nutrient retention benefits in two agricultural soils, and to 76 investigate the combination of chemical and physical mechanisms by which these benefits are 77 delivered. Our results are expected to inform the process of biochar production or modification 78 for the above-mentioned specific purposes, as well as improve predictions on biochar behaviour 79 in specific agricultural conditions. 80 81 **Material and Methods:** 82 Line 106-108: What are the production durations of the selected chars 83 84 Response: As the biochars are commercially available, many of the production details are 85 proprietary and were not disclosed. However, we can amend the paragraph to state the individual 86 producers, as below. This would allow for other scientists to repeat experiments with these 87 biochars, and to contact the companies for more information if desired. It also emphasizes that 88 individual production details were beyond the control of the authors. 89 90 "Seven biochars were obtained from the following feedstocks and produced at the following 91 temperatures: almond shell at 500 °C (AS500, produced by Karr Group Co.), almond shell and 92 800 °C (AS800, Premier Mushroom and Community Power Co), coconut shell at 650 °C (CS650,

made two corrections. On line 69, we added Yin et al. (2018) to the discussion of studies which find

higher adsorption values at lower temperatures, to state:

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92 Solo C (Assoc, Fremer Musmoon and Community Fower Co), coconditional at 050 °C (CS050
 93 Cool Planet), softwood at 500 °C (SW500, Karr Group Co.), softwood at 650 °C (SW650, Cool
 94 Planet), and softwood at 800 °C (SW800, Pacific Biochar), and an additional softwood biochar

95 96 97		produced at 500 °C and inoculated with a proprietary microbial formula (SW500-I, Karr Group Co.)."
98 99	•	Line 107-108: Please provide details on the char with inoculated microbial formula
100 101 102 103		Response: As stated above, the microbial formula is proprietary and was not disclosed to authors. That fact has now been made clear in the above text. Additionally, as this product is commercially available, the experiment can be reproduced by other researchers by purchasing this material.
103 104 105	•	Line 113: What is the duration of the individual temperature steps?
106 107 108		The sentence has now been revised to contain the requested information as well as the reference for this method, as below:
109 110 111 112		"and moisture, volatile, and ash content were measured as a percent of total dry weight through sequential shifts in furnace temperature (briefly, 2 h at 105 °C, 6 m at 950 °C, and 6 h at 750 °C, respectively) (ASTM D 1762-84, 2011)."
113 114 115	•	Line: 122: The authors can avoid to mention a private company because they followed the standardized protocol/ Line 123: Provide ISO number here
116 117 118		Response: The company name has been removed, and the ISO number has been included, as follows:
119 120 121 122		"Specific surface area was determined from CO₂ adsorption isotherms according to the Brunauer, Emmet, Teller (BET) method ISO 9277:2010 (International Organization for Standardization (ISO), 2010)."
122 123 124	•	Line 124-128: Not clear if the authors used finally the DRIFT or FTIR. Please clarify.
125 126 127 128		Response: DRIFT (diffuse reflectance infrared Fourier transform) is a specific sampling method of FTIR (Fourier transform infrared) spectroscopy; DRIFT was used as the FTIR sampling method. We have edited the FTIR method to be explicitly clear. The text now reads:
129 130 131 132		"Fourier transform infrared (FTIR) spectra of AS500, AS800, and SW500 biochars were collected using the diffuse reflectance infrared Fourier transform (DRIFT; PIKE Technologies EasiDiff) sampling mode with air dried samples diluted to 3% with potassium bromide."
133 134 135	•	Line: 137-138: Not clear to what field trials they authors are referring here. Were the soils taken from long-term field trials locations?
136 137 138		Response: We believe the below paragraph makes clear that the soils were taken from field trials. However, we have modified the sentence (added details in bold) to provide more detail:
139 140 141 142		"Hanford sandy loam (HSL) and Yolo silt loam (YSiL) soils were chosen for continuity between laboratory experiments and ongoing <b>3-year</b> field trials <b>utilizing the same biochars and soils</b> . Collectively, these soils represent over 260,000 hectares of arable land in California and offer textural distinctions within a range of soils commonly farmed in the Central Valley of California

143 (Soil Survey Staff, 2014). Soils were located via Web Soil Survey 144 (http://websoilsurvey.sc.egov.usda.gov/) and collected from the top 30 cm in fallowed agricultural fields in Parlier, California (HSL) and Davis, California (YSiL)." 145 146 147 Line 147: What was the core volume? 148 149 Response: This information has been added to line 176 in Methods section 2.4 Column experiments, 150 as follows below (in bold): 151 152 "To investigate the influence of biochar on saturated hydraulic conductivity (K<sub>sat</sub>), constant head 153 column experiments were performed in five replicates using the 5 station Chameleon Kit 154 (Soilmoisture Equipment Corporation (SEC) 2816GX). SEC tempe cells, each with a volume of 155 **136.4 cm<sup>3</sup>** were packed with soils amended with 0 and 2% (w/w) AS500, AS800, or SW500 biochars..." 156 157 Line 165: The authors should include more information about the tested models in the 158 159 supplement. Which fitting parameter were considered to evaluate the goodness of fit and avoid 160 over parameterization (e.g. AICc) 161 162 Response: Our simple linear models did not have random effects or interactions, and are therefore 163 not at danger of being overfit. We have made our statistical approach clearer by rephrasing (new content in bold): 164 165 166 "All data were analysed with linear models (Im(response variable ~ biochar)) and one-way analysis of variance (ANOVA) in the stats and Tidyverse packages in R (R Core Team, 2020; 167 168 Wickham et al., 2019). When more than one soil type was tested (as in K<sub>sat</sub> measurements), 169 separate models were built for each soil type to determine the effect of biochar within soil 170 types. For analysis of results, all effects with p-values < 0.05 were considered significant. P-171 values were generated using the emmeans package in R (Lenth, 2019) and corrected for 172 multiple comparisons using Tukey's honestly significant difference (HSD) method. Plots were 173 generated in R using the ggplot2 package (Wickham, 2016) and visualized as the mean plus or 174 minus the standard error of the means." 175 176 Line 176-177: Was the soil and biochar homogeneous mixed? How was this ensured? 177 178 Response: Yes, soils and biochars were thoroughly and homogenously mixed through a combination 179 of stirring and shaking within a sealed container for a minimum of 120 seconds. The following sentence has been added to line 178: 180 181 182 "Soils and biochars were thoroughly and homogenously mixed prior to being added to tempe cells." 183 184 185 Line 177: What would be the typical application rate on the agricultural soils used in this study? 186 187 Response: The biochar community has yet to reach consensus on recommended application rates, 188 and therefore there is no typical or standard rate used in agricultural soils. One meta-analysis concluded that the greatest agronomic benefits were observed in studies utilizing 100 t ha<sup>-1</sup> (Jeffery 189 190 et al., 2011). More recently, Oladele (2019) developed a soil quality index using data from a three-

year field trial, which concluded that a biochar application rate of 6-12 t ha<sup>-1</sup> was optimal, though 191 192 results were constrained to acidic alfisols (USDA Soil Taxonomy) (Oladele, 2019). Pandit et al. (2018) 193 conducted an economic analysis which included payments for C sequestration, to determine an 194 optimal rate of 15 t ha<sup>-1</sup> (Pandit et al., 2018). Guo (2020) made even more specific recommendations 195 based on the results of a literature review and from greenhouse trials, concluding that biochar 196 should be applied at a concentration of 2–5% by weight for wood- and crop residue-derived 197 biochars, and 1-3% for manure-derived biochars (Guo, 2020). Our rate of 2% falls within the 198 recommendations contained within Guo (2020) and Jeffery (2011). If incorporated to a depth of 12 199 inches, assuming a bulk density of 1.33 g cm<sup>-3</sup>, this is an application rate of 81.2 t ha<sup>-1</sup>. This rate was 200 chosen as the result of the studies herein mentioned, and as described in the text, is "the midrange of those represented in similar experiments (Blanco-Canqui, 2017)." The paper cited here is a 201 202 literature review that contains data from 28 experiments on biochar's effect on  $K_{sat}$ .

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- Line 181: Why did the authors not include both soils here? Please provide a clear argument since
   this is substantial for the whole discussion of the manuscript.

206 207 We agree that the study would have benefited from leaching data from both the YSiL and the HSL 208 soils. However, column experiments were performed without the aid of autosamplers or mechanization of any kind. As shown in Figure 3, the K<sub>sat</sub> for the unamended HSL soil columns was 209 210 1.2 cm s<sup>-1</sup>. To manually collect 20 pore volumes of leachate, 15 hours of active maintenance was 211 required per treatment, for a total of 4 treatments. The YSiL  $K_{sat}$  was 0.044 cm s<sup>-1</sup>, or a 96% 212 reduction in flow rate from the HSL. Therefore, we considered it unfeasible for someone to stay in 213 lab for the time required to collect 20 pore volumes at this speed. After attempting it for two 214 treatments, we decided to proceed with the HSL data, as it was logistically possible and would 215 provide more valuable information. To make this clear to readers, we will include the following 216 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<sup>-1</sup>) 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: Large parts of the result section describes the biochar and soil. The author should
 consider to include the characterizations in the material and method section. The result section
 should focus on the actual findings regarding the sorption and Ksat effect of the biochar on the
 soils.

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Response: As one of our objectives was to "determine the soil and biochar parameters which may optimize hydrologic and nutrient retention benefits in two agricultural soils," we do not agree that this information is extraneous or takes away from the results that follow. This is especially true given how important IR and microCT data was for interpreting those results. However, we have shortened this section by moving *Table 2: Functional group assignments corresponding to organic biomass* to supplementary information.

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- Line 196: Please specify "carbon, hydrogen contents and leachable DOC"

- Response: We are not sure why this is different than the phrase already included ("decreased
  carbon, hydrogen, and DOC") as the word "contents" is implied when discussing biochar
  constituents, and "leachable" is both implied from the OC having been dissolved (D), and explicit
  from the description of DOC methodology.
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# Line 196-197: Please avoid interpretation of the data and comparison to the litterateur in the result section. This is part of the discussion.

Response: We have addressed this in the manuscript by moving any interpretation and comparison
to the literature to the discussion section. This will further shorten the biochar characterization
results by two lines.

- Line 203-204: This aspect should be considered in the discussion and clearly mentioned in the
   material and methods. The oxidation state of the biochar will also influence the surface reactivity,
   which may, in fact, explain the here observed findings.
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Response: We agree that the oxygen content (interpreted from "oxidation state" in reviewer
content) of the biochar will influence surface reactivity and explain results. As such, we covered this
extensively in the discussion section beginning on line 317:

- 257 258 While it is typical for biochars produced at high temperatures to have low O/C ratios and low 259 CEC (Hassan et al., 2020), AS800 had the largest O/C ratio at 0.56 (presumably due to postpyrolysis oxidation), and the second highest CEC at 52.75 cmolc kg<sup>-1</sup>. These properties, as well as 260 261 the IR band at 1405 cm<sup>-1</sup> (COO<sup>-</sup>), likely explain the high ammonium retention, as they indicate 262 increased exchange sites and oxygen-containing functional groups which can react with 263 ammonium. The relationship between these biochar properties and ammonium binding capacity was also demonstrated with SW800, which had the highest CEC at 60.83 cmolc kg<sup>-1</sup>, the second 264 265 highest O/C ratio at 0.27, and the second highest ammonium binding capacity. These observations are consistent with those of other studies (Gai et al., 2014; Yang et al., 2017). 266
- As the specific details of biochar production methodology were proprietary, this is not a "method" but a hypothesis to explain an observed result. As such, it cannot be included in the methods section. However, we have made this more clear by removing the line about post-pyrolysis oxidation from the results section and including it strictly in the discussion section.
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273 • Line 211: include "1410 and 1418 cm<sup>-1</sup>"

- Response: We will correct this by adding "cm<sup>-1</sup>" in the manuscript, and thank the reviewer for this
   attention to detail.
- Line 213-215: As mentioned above these differences in biochar production should be clearly
   presented in the material and method section and also critically discussed in the discussion
- 280281 Response: We agree, and will move this section into the materials and methods.
- Line 237: Soil texture expressed as mass per mass (g/g) is a content and not a concentration.
   Furthermore, avoid digits for these values.
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- 286 We agree that percent soil texture should be reported as content and have made this change.
- Table 3: Correct the number of digits for texture. Also, pH is commonly measured with on digit
   precision.
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- 291 Response: We have made these changes as recommended.
- Section 3.3: Provide the data for the nitrate leaching. What is the order of magnitude if the nitrate
   release? This data needs to be shown.
- 295 Response: This data has been added to the supplementary information document.
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Figure 2: Please show the fitted isotherms

298 Response: We initially visualized Freundlich and Langmuir models for each biochar in figure 2. 299 However, due to the high number of biochars included in this study, the figure became cluttered 300 and difficult to read. While we acknowledge that fitted isotherms are one appropriate way to display 301 sorption data, there is a rich literature base which shows Ce vs Qe, or % adsorbed vs quantity in 302 solution, without model fits, but rather provides R<sup>2</sup> values for models instead (Gai et al., 2014; Wang et al., 2015; Yao et al., 2012, to name just a few). Due to the relatively low R<sup>2</sup> values we discuss, we 303 304 believe simply visualizing Ce vs Qe for each rep of each treatment is a more descriptive and 305 quantitative way of viewing this data, with model R<sup>2</sup> values in a table provided directly following the 306 figure.

- Line 268-369: Please specify this statement and clearly indicate to which the p values correspond
   to.
- 311 Response: We have edited the statement as follows:
- 313 "There was a main effect of biochar (p = 0.001) and soil texture (p < 0.001), as well as a</li>
  314 significant interaction between biochar and soil texture (p = 0.006), on saturated hydraulic
  315 conductivity."
- Line: 285: "HSL at pore volume 14.3" corresponds this to the controls?
- 319 Response: We have edited the statement to say: "HSL (control) at pore volume 14.3"
- Discussion: This discussion is not complete and is not discussion available contradicting literature.
   A few suggestions can be found below. However, I recommend an extensive literature review to
   develop a structured and complete discussion.
- We agree that the manuscript could be improved by a lengthier, more nuanced, and more detailed
  discussion, and thank the reviewer for this suggestion. However, we believe that this manuscript
  already includes an extensive literature review, covering most of the articles the reviewer
  suggested. We do not believe we need *more* literature, but, as the reviewer stated, a *better structured* literature review. Currently, we have included a lengthy discussion of the contradictory
  literature 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 relate all findings to our results, as described extensively throughout this document.
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- Line **315**: t is mentioned already that this char might be oxidized, the authors should clearly indicate this in the sections before. This initial "bias" effect needs more critical discussion here.
- Response: We have revised the information about potential post-pyrolysis oxidation as described in
  this document on page 5, regarding the comment about line 21.
- The hole paragraph provides no mechanist discussion. It is just comparing the findings with the
   literature. Please improve the discussion here and connect the different sportive capacities with
   the properties of of the chars.
- Response: We respectfully disagree that this paragraph does not include mechanistic discussion, as
   we clearly delineate the relationship between biochar properties (high O/C, CEC, and oxygen containing function groups) and their demonstrated ability to retain positively charged ammonium
   ions, as copy/pasted below:
- 349 350 "AS800 had the largest O/C ratio at 0.56 (presumably due to post-pyrolysis oxidation), and the 351 second highest CEC at 52.75 cmolc kg<sup>-1</sup>. These properties, as well as the IR band at 1405 cm<sup>-1</sup> 352 (COO<sup>-</sup>), likely explain the high ammonium retention, as they indicate increased exchange sites 353 and oxygen-containing functional groups which can react with ammonium. The relationship 354 between these biochar properties and ammonium binding capacity was also demonstrated with 355 SW800, which had the highest CEC at 60.83 cmolc kg<sup>-1</sup>, the second highest O/C ratio at 0.27, and 356 the second highest ammonium binding capacity. These observations are consistent with those of other studies (Gai et al., 2014; Yang et al., 2017). No clear trends between surface area and 357 358 ammonium retention emerged in this study."
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# Line 318-320: Figure 2 shows actually no clear differences between SW800 and the other chars. What is the explanation? In fact, only AS800 shows the previous mentioned large binding capacities of ammonium.

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364 Response: Figure 2 visibly demonstrates that SW800 has a higher binding capacity than all biochars (except AS800) at initial ammonium concentrations of 50, 100, and 200 mg L<sup>-1</sup>. The reviewer is correct in 365 366 their statement that this effect is less clear at the higher concentrations of 400 and 600 mg L<sup>-1</sup>. 367 Furthermore, authors of this manuscript never claimed any biochar to have a large binding capacity, but 368 rather stated: "all biochars exhibited the capacity to remove ammonium from solution (Fig. 2), though K<sub>f</sub> 369 values were low (Table 4)" and "The ability of all seven biochars to retain ammonium, and within the 370 demonstrated ranges, is consistent with other published studies (Zhang et al., 2020). AS800 exhibited 371 substantially higher ammonium binding capacity than the other biochars tested." These statements are 372 in agreement with those the reviewer made in this comment. 373

- 374• Line 324-329: The whole paragraph misses to bring the findings of this study in context of studies with
- 375 contradicting results which is actually in some of the already cited papers. But there is certainly more
- 376 literature on this effects and higher nitrate binding capacities are reported. Only Zhang et al (2020) is
- cited here to support the findings of this study, which is by far not complete. Here are a few
   suggestions also providing contradictory findings (and literature within):

- Kameyama, K., Miyamoto, T., Iwata, Y., and Shiono, T.: Influences of feedstock and pyrolysis
   temperature on the nitrate adsorption of biochar, Soil Science and Plant Nutrition, 62, 180–184,
   https://doi.org/10.1080/00380768.2015.1136553, 2016.
- Cao, H., Ning, L., Xun, M., Feng, F., Li, P., Yue, S., Song, J., Zhang, W., and Yang, H.: Biochar can
   increase nitrogen use efficiency of Malus hupehensis by modulating nitrate reduction of soil and
   root, Applied Soil Ecology, 135, 25–32, https://doi.org/10.1016/j.apsoil.2018.11.002, 2019.
- Yang, J., Li, H., Zhang, D., Wu, M., and Pan, B.: Limited role of biochars in nitrogen fixation through nitrate adsorption, Science of The Total Environment, 592, 758–765, https://doi.org/10.1016/j.scitotenv.2016.10.182, 2017.
- Aghoghovwia, M. P., Hardie, A. G., and Rozanov, A. B.: Characterisation, adsorption and desorption of ammonium and nitrate of biochar derived from different feedstocks, Environmental Technology, 1–14, https://doi.org/10.1080/09593330.2020.1804466, 2020.
- Hagemann, N., Kammann, C. I., Schmidt, H.-P., Kappler, A., and Behrens, S.: Nitrate capture and slow
   release in biochar amended compost and soil, PLoS ONE, 12, e0171214,
   https://doi.org/10.1371/journal.page.0171214.2017
- 393 https://doi.org/10.1371/journal.pone.0171214, 2017.
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395 Response: We agree that there are many studies which report results contradictory to our own, and as 396 the reviewer mentioned, many were cited in this paper. Zhang et al (2020) was cited as the only source 397 for the statement on line 324 because, as explicitly stated, this study is a literature review which 398 calculated mean nitrate sorption for a range of biochars across the literature. However, we have revised 399 this statement to include more of the sources already cited, as well as those the reviewer has offered, to 400 make our knowledge of the literature base more explicit. Furthermore, our introduction section 401 currently includes 11 sources to support the discussion of contradictory nitrate sorption. To present a 402 clearer argument and provide a better manuscript structure, we will reorganize the material aiming for a 403 shorter introduction and a lengthier discussion section, in which each of our results are directly linked

- 404 with the studies that found similar or contradictory sorption.
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Section 4.2: Similar to the paragraph before, this section misses a critical discussion of the findings.
The authors need to include a more mechanistic explanation of the ammonium and nitrate retention
in soils. Actually, the soil effect (e.g. texture and pH) is not included at all. All these observations are
also based on the experiment of the HSL. This need to be critically discussed. The effect may change
drastically with different soils. Please follow also here the above mentioned literature, which is only a
short list of literature on this topic.

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Response: As stated in the previous response, we have reorganized the manuscript to include the
extensive discussion that is currently in place on lines 45-74 of the introduction section, in the discussion
section instead. This discussion includes detailed descriptions of mechanisms from contradictory results
in the literature:

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418 "Due to the deprotonation of surface functional groups at agronomic soil pHs, biochar is typically 419 negatively charged..... Electrostatic repulsion between nitrate and biochar has indeed been regularly 420 cited as the reason behind little to no nitrate removal in batch sorption experiments... Higher Q<sub>max</sub> 421 values for biochar and ammonium are to be expected, as ammonium exists in the cationic form in 422 aqueous environments and would more readily adsorb to negatively charged biochar surfaces..... 423 Multiple authors have observed that sorption capacity decreases with increasing production 424 temperature (Gai et al., 2014; Gao et al., 2015; Yin et al., 2018). Lower temperatures have been 425 correlated with higher cation exchange capacity (CEC) (Gai et al., 2014), and higher O/C ratios (Yang

- 426 et al., 2017). These properties may contribute to biochars with the ability to remove ammonium
- from solution, as they provide a greater number of exchange sites and oxygen-containing functional
- groups which can react with ammonium (Yang et al., 2017). The reverse trend has also been
- 429 observed, however, with authors noting that an increase in production temperature resulted in
- higher ammonium Q<sub>max</sub> values (Chandra et al., 2020; Zeng et al., 2013; Zheng et al., 2013). These
- authors point towards the higher specific surface area (SA) of biochar at higher production
- 432 temperatures as a critical parameter to predicting ammonium adsorption."
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434 To further address the effect of soils not tested in this experiment, we have included a critical discussion 435 of the impact of soil texture as demonstrated in other experiments, and explicitly state that our results 436 are constrained to a sandy loam, and may not be observed in other contexts. To address the pH effect of 437 various soils, we have conducted one additional experiment to learn the point of zero charge (PZC) of 438 the three biochars in question. We have included this data, as well as the appropriate methods 439 description and citation of sources. Briefly, we found that the PZC was 6.8 for AS800, 3.2 for AS500, and 440 3.9 for SW500. As most agricultural soils have a pH well above 4, the behavior of AS500 and SW500 are 441 not likely to change as the result of agricultural soil pH, as thereactive functional groups on soil organic 442 matter and minerals will remain deprotonated and able to bind to ammonium more strongly than 443 nitrate. The higher PZC of AS800 was to be expected, as it has a higher ash content, and higher metal-444 oxide content as demonstrated through IR peaks at ~1000 to 700 cm<sup>-1</sup>, consistent with metal oxide 445 vibrations (Parikh et al., 2014). That the pH of AS800 is closer to the soil pH of those tested in this study 446 (7.3), however, indicates that AS800 may be strongly effected by soil pH, and able to bind even more 447 ammonium at lower pHs. We will expand our mechanistic discussion to include this information and 448 citation of the effect of soil pH on the electrostatic affinity between biochar and nitrate and ammonium. 449

# The authors also miss to bring their findings in context of the applicability under field conditions and unsaturated soil conditions.

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Response: We agree that the link between this study and our ongoing field trials 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:

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  - 4.4 Implications for field conditions

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

466 (http://rice.ucanr.edu/About\_California\_Rice/). Data from these trials may help growers in
467 these regions and soil textures determine if biochar can increase water and nutrient retention in
468 their systems.

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470 Recent meta-analyses have concluded that biochar substantially increased soil water content at
471 field capacity and permanent wilting point, in the field and lab, in coarse textured soils only
472 (Blanco-Canqui, 2017; Razzaghi et al., 2020). Despite these observed trends, benefits have also
473 been observed in fine textured soils, including reduced crop water stress, increased yield (Kerré

474 et al., 2017; Nawaz et al., 2019), and reduced crop loss during deficit irrigation (Madari et al., 475 2017). Other authors have reported little to no effect, or transient effects, of biochar on soil 476 water dynamics in both fine and coarse textured soils (Jones et al., 2012; McDonald et al., 2019; 477 Nelissen et al., 2015). However, results from our experiments cannot be extrapolated to dryland 478 agriculture or in soils that experience wet-dry cycles, as unsaturated hydraulic conductivity was 479 not measured. In order to determine how these biochars may behave in unsaturated conditions, 480 three-year processing tomato field trials are currently underway in these same soil textures, in 481 which soil-water dynamics are being measured.

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483• Section 4.3: This section also misses some aspects which need to be discussed in this context. Only
one application rate of biochar was used, it is not discussed if this rate is representative for these soils
and its acricultural use. Furthermore, it is known that also the application rate and particle size has an
effect on the Ksat depending in the soil texture as discussed in the below listed literature.

- Obia, A., Mulder, J., Hale, S. E., Nurida, N. L., and Cornelissen, G.: The potential of biochar in improving drainage, aeration and maize yields in heavy clay soils, PLoS ONE, 13, e0196794, https://doi.org/10.1371/journal.pone.0196794, 2018.
- Herath, H. M. S. K., Camps-Arbestain, M., and Hedley, M.: Effect of biochar on soil physical properties in two contrasting soils: An Alfisol and an Andisol, 209–210, 188–197, https://doi.org/10.1016/j.geoderma.2013.06.016, 2013.
- Barnes, R. T., Gallagher, M. E., Masiello, C. A., Liu, Z., and Dugan, B.: Biochar-induced changes in soil
   hydraulic conductivity and dissolved nutrient fluxes constrained by laboratory experiments, 9,
   https://doi.org/10.1371/journal.pone.0108340, 2014.
- 496

497 Response: We agree that application rate and particle size are important determinants of nutrient 498 retention and hydraulic conductivity in biochar-amended soils, and will include these and other citations 499 in a brief discussion of this. However, as described on page 4 of this document (in response to the 500 comment about line 177), there is no current "representative" biochar amendment rates for particular uses or soil types. The chosen rate is representative of recommendations that exist in the literature (see 501 502 page 4), and is the midrange from experiments of similar design (See tables in literature review from 503 Blanco-Canqui, 2017). This study measured several responses (K<sub>sat</sub> in two soils, nitrate and ammonium 504 leaching (quantity and timing) in one soil, and nitrate and ammonium sorption, using 7 biochars in which 505 we tested the effect of feedstock and production temperature). The effect of application rate was 506 outside the purview of this study, given the extensive work already involved in the experimental design. 507 Furthermore, we did not test the effect of particle size by creating biochars of different sizes, because 508 we sought to use commercially available materials so that experiments could be repeated. This is, in 509 part, in response to a literature review which critiqued biochar studies which use only small-batch lab-510 created biochars (Zhang et al., 2016). Nevertheless, we included a discussion of particle size in lines 353-511 359 when describing hydraulic conductivity. As stated previously, we will lengthen the discussion around 512 these topics by moving citations from the introduction and by making the link between our results and 513 current literature more explicit. 514 515• Line 353-354: What was the relative particle size distribution. These characteristics are not presented.

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518

517 Response: Mean and median particle sizes for all biochars are provided in Table 1.

# 519• Line 354-355: How can the authors provide prove of this statement?

- 521 This statement is a hypothesis backed by evidence from the literature, but cannot be proved within the
- 522 context of our study. As stated, this statement could be further explored and supported through future
- 523 research: "Additional research and quantitative analysis at the micron and sub-micron scale is required
- to assess the influence of biochar on soil porosity and pore architecture."
- 525

## 526• Line 374-376: This has not been discussed so far. But the field applications of this experiment need to

# 527 be included in the critical discussion. The intention of this study was, according to the title, to consider

agricultural soils. Furthermore, how can the authors draw a conclusion for flooded agricultural

- 529 systems when they did not include soils from such systems?
- 530

Response: As described on line 435 of this document (in response to section 4.3), we will add another
 section to the discussion entitled "4.4 Implications for field conditions".

533

## 534 Summary

535 We again thank the reviewer for these detailed and helpful comments, which we believe will strengthen

- the manuscript, broaden its impact, and increase interest from readers of SOIL. To address the
- 537 reviewer's primary concerns, we have restructured the discussion which was previously split between
- the introduction and discussion sections, clarified many details of the materials and methods, and better
- 539 linked these experiments to production-scale agriculture.
- 540

541 Though the reviewer critiqued the lack of discussion and mechanistic investigation, we believe the error 542 is not in a *lack* but in a *non-ideal placement*. We have moved the already cited sources and descriptions 543 from the introduction, and better connected them to our own results in the discussion section. As the

- reviewer described, the current structure of the manuscript is not as strong as it could be. We have
- rearranged according to the reviewer's suggestions as described extensively above. Furthermore, we
- added data from our additional experiment on PZC, literature sources the reviewer provided as well as
- 547 others not provided, and better connected these results to our ongoing and critical field trials. While we
- 548 appreciate the reviewer's suggestions, we respectfully do not believe the comments provided are
- 549 grounds for rejection, as there are no issues with experimental design, results, or importance of the

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- 550 work pursued. We believe we can swiftly implement the provided suggestions for a better structured
- and more transparent manuscript, that will be of great impact.
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