Author's response

We have addressed concerns regarding specific surface area measurements in the below text, as well as in the accompanying revised manuscript. We thank the editor for their input and expertise. Specific details of our changes are outlined below.

Topical editor comments:

Unfortunately, the authors have not addressed my concerns regarding specific surface area measurements in relation to the expected pore-size distribution in biochar, the applicability of the BET equation to CO2, as well as the comparability to standardized measurements according to international guidelines (IBI as well as EBC).Further, hysteresis in typical setups cannot be measured with CO2, as only adsorption and no desorption is measured when using CO2, which makes the hysteresis argument beside the point. The ISO norm mentioned is tailored to multilayer-adsorption gases such as nitrogen; CO2 is not mentioned in the cited guideline as far as I can tell. I advise the authors to re-consider their arguments for using CO2 and perhaps re-read the literature cited in their response (including the mentioned paper by this editor).

Author's Response:

We once again thank the editor for their input and expertise on the topic. We have reviewed our surface area data and communicated with the lab manager at Micromeritics, where we had the samples analyzed to clarify the methodology used. We were incorrect to report the surface area was calculated using the BET equation. The CO_2 isotherms at 273 K were used to determine micropore volume and micropore area ($SSA_{\mu p}$) using the non-local density functional theory (NLDFT) model specific for CO_2. The testing done by Micromeritics utilizes elements of ISO9277, such as sample preparation and aspects of the analysis approach; however, the BET method does not apply to CO_2 based measurements and was not used. These methodological nuances were not clear from the data initially returned to us by Micromeritics. We are grateful that the editor has specific expertise in this area, and thank them for their persistence with this aspect of our manuscript, as we can now more accurately report the methods used in our study. In our revised manuscript we specify that our values correspond to $SSA_{\mu p}$, instead of "SA", to make clear our data are specific to micropore surface area.

As the use of both N_2 and CO_2 to determine surface area each has distinct limitations, we agree with the editor that data from both measurements would provide complimentary information and a more quantitative understanding. We fully agree that the use of CO_2 has important limitations, specifically that it does not determine exterior surface area nor macropore surface area. Rather, this approach provides information of pores ranging, approximately, from 0.35 to 1.5 nm (or 3 nm if higher pressure is used). As the surface area

of many biochars is dominated by micropores, this method typically gives $SSA_{\mu p}$ values greater than SA measured via N_2 (e.g., Zeng et al., 2013; Maziarka et al., 2021). BET surface area with N_2 has a long history for surface area measurements and is indeed recommended by the International Biochar Initiative and the European Biochar Certificate for biochar characterization. However, this approach also has limitations, as it cannot access the microporosity of materials with pores < 0.5 um (e.g., Pignatello et al., 2006) (range for N_2: ~2 to 50 nm); it relies on assumptions that may not be true for small pores and materials with very high surface areas (Walton and Snurr, 2007); and pore flexing is limited at 77 K (too cold) and inhibits diffusion into micropores. These points are well stated by the editor in one of their publications (Sigmund et al., 2017).

It is commonly recommended that N_2 and CO_2 measurements both be conducted, to provide complimentary data regarding surface area of materials such as biochar. Although we do not have the BET surface area via N_2, we believe that reporting of the $SSA_{\mu p}$ provides meaningful information and is valuable in making comparisons between biochars and providing information for our study. Although not quantitative, we do have qualitative data regarding macropores as evidenced by X-ray microCT images. For future studies it would be best to have surface area measurements using both N_2 and CO_2 to provide complimentary analysis and "overcome" the limitations of each approach. We have edited our manuscript to reflect this information and hope that the editor will find our efforts satisfactory (new content in red):

Methods

, which are not probed via the CO_2 surface area approach The micropore specific surface area ($SSA_{\mu p}$) was determined from CO_2 adsorption isotherms at 273 K using the Non-Local Density Functional Theory (NLDFT) (Particle Testing Authority, Micromeritics TriStar II Plus 3.0). The micropore specific surface area ($SSA_{\mu p}$) was determined from CO_2 adsorption isotherms at 273 K using the Non-Local Density Functional Theory (NLDFT) (Particle Testing Authority, Micromeritics TriStar II Plus 3.0, NLDFT model mod11.df2). Prior to analysis, samples were degassed with N_2 at 393K for 16 h.

Results

Line 221: Softwood biochars produced at 500 and 800 °C had substantially higher SSAμp than almond shell biochars produced at the same temperatures. It should be noted, however, that SSAμp measured by CO2 adsorption frequently results in higher values than surface area measured by N2, as CO2 can access micropores unavailable to N2 (Maziarka et al., 2021; Zeng et al., 2013). While

results from each method tend to be well correlated and are considered to provide complementary information (Sigmund et al., 2017), neither should not be regarded as providing precise total surface area.

Discussion

Line 438: This is consistent with the increase in soil Ksat after addition of AS800 in YSiL, and the smaller effect of AS800 in HSL compared to AS500 and SW500 (discussed in section 4.3). Future investigation should include measurements of biochar surface area utilizing both CO_2 and N_2 adsorption. While CO_2 is commonly used to probe micropores in carbon-based materials (Maziarka et al., 2021; Sigmund et al., 2017; Zhu et al., 2011), IBI criteria recommends the use of N_2 for biochar analysis (International Biochar Initiative, 2015). Including N_2 measurements would aid in standardization across studies. Furthermore, the differences in results from each method may be descriptive of the relative pore size distribution between each biochar in this study. Differences in pore size distributions, as observed by X-ray microCT, have been demonstrated to have a varying effect on water retention and conductivity in previous studies (Devereux et al., 2013; Quin et al., 2014).

Other minor changes have been made to our manuscript, as indicated in the revised document with changes tracked.

References:

Pignatello, J.J., Kwon, S., Lu, Y., 2006. Effect of natural organic substances on the surface and adsorptive properties of environmental black carbon (char): attenuation of surface activity by humic and fulvic acids. *Environ. Sci. Technol*., **40**(24):7757-7763. [doi:10.1021/es061307m]

Ravikovitch, P.I., Neimark, A.V., 2001. Characterization of nanoporous materials from adsorption and desorption isotherms. *Coll. Surface A*, **187-188**:11-21. [doi:10.1016/S0927-7757(01)00614-8]

Gabriel Sigmund, Thorsten Hüffer, Thilo Hofmann, Melanie Kah. Biochar total surface area and total pore volume determined by N2 and CO2 physisorption are strongly influenced by degassing temperature. 2017. Science of The Total Environment, 580: 770-775, https://doi.org/0.1016/j.scitotenv.2016.12.023.

Walton, K.S., Snurr, R.Q., 2007. Applicability of the BET method for determining surface areas of microporous metal-organic frameworks. *J. Am. Chem. Soc*., **129**(27):8552-8556. [doi:10.1021/ja071174k]