Author's response

We have made the suggested changes and thank the editor for their input and expertise. Specific details of our changes are outlined below.

Topical editor comments:

Most reviewer comments were addressed to a satisfactory degree, I have a few minor remarks before I can advise for final publication:

- Please explicitly address the concerns about preferential flow and the lack of a tracer in your experiments in the main manuscript.

  Response: We have added text to the end of the results section beginning on line 330: "Evaluation of data revealed no evidence of preferential flow in any replicate in any of the columns, which were carefully prepared according to the dry packing method in Gibert et al. (2014). This is demonstrated in the small error bars in figures of nutrient concentrations across pore volumes, as well as in hydraulic conductivity measurements taken by data loggers. To further monitor columns for preferential flow, the use of a conservative tracer could be considered in future experiments."

- The BET specific surface area is typically measured via N_2 physisorption, not CO_2. CO_2 physisorption (usually not analyzed via BET but other models) can be used as a complementary method for the characterization of micropores. For biochar which is expected to also contain mesopores and some macropores, N_2 is the agreed on standard method that can be complemented by CO_2 if needed. If you have indeed used CO_2 I suggest to also measure N_2 according to IBI as well as EBC standards. If the gas was actually N_2, please correct this accordingly.

  Response: The use of N_2 to measure surface area via the BET method is a standard approach which has long been used. However, significant drawbacks of this approach arise from the fact that the BET equation was developed to predict surface area of non-porous materials. N_2 cannot access pores < 0.5 nm, while CO_2 can. Additionally, CO_2 permits monolayer coverage and does not have the volume-filling effect which can arise with N_2. This information is presented in Sigmund et al., 2017. In an evaluation of 12 biochars analyzed for surface area using the BET equation and both N_2 and CO_2, results demonstrated numerous artifacts and unreliable results from N_2 isotherms (Maziarka et al., 2021). In that study, CO_2 showed greater efficacy for

detecting micropores with increasing highest temperature treatment (HTT) and, unlike N_2, did not show hysteresis in any sample. The use of CO_2 is routine for determining the surface areas of many carbon-based materials (e.g., activated carbon, biochar, carbon-based superconductors). In an analysis of carbon-based superconductors, CO_2 was shown to reveal the presence of pores in the ~1 nm range, probing pores much smaller than was possible with N_2. Additionally, N_2 isotherms demonstrated pore condensation and type H2 hysteresis (IUPAC classification) (Zhu et al., 2011). We believe that the use of CO_2 to measure surface is a sound approach, and that making comparisons between samples measured with the same methodology is appropriate.

The IBI and EBC standards were developed in 2015 as a means to standardize characterization for biochars. While these criteria have great value, we do not believe that the exclusive use of these methods is required for scientific research. We do not challenge the value of BET measurements with N_2, but do feel that using CO_2 is also commonplace and appropriate. The ideal scenario would be to complement CO_2 data with N_2 measurements, as neither method is perfect. While this is unfortunately not feasible for us to do at this time, we will consider this approach for future experiments.

Editorial support team:

- With the next revision, please re-name your "Figure S2" to "Figure S1".

Response: We have made the suggested change.

References

Sigmund, G., Hüffer, T., Hofmann, T., & Kah, M. (2017). Biochar total surface area and total pore volume determined by N2 and CO2 physisorption are strongly influenced by degassing temperature. *Science of the Total Environment*, *580*. https://doi.org/10.1016/j.scitotenv.2016.12.023

Maziarka, P., Wurzer, C., Arauzo, P. J., Dieguez-Alonso, A., Mašek, O., & Ronsse, F. (2021). Do you BET on routine? The reliability of N2 physisorption for the quantitative assessment of biochar's surface area. *Chemical Engineering Journal*, *418*. https://doi.org/10.1016/j.cej.2021.129234

Zhu, Y., Murali, S., Stoller, M. D., Ganesh, K. J., Cai, W., Ferreira, P. J., Pirkle, A., Wallace, R. M., Cychosz, K. A., Thommes, M., Su, D., Stach, E. A., & Ruoff, R. S. (2011). Carbon-based supercapacitors produced by activation of graphene. *Science*, *332*(6037). https://doi.org/10.1126/science.1200770