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EDITED BY

Oladele Ogunseitan,
University of California, Irvine, United States

REVIEWED BY

Prabhakar Sharma,
Nagaland University, India
Jie Wang,
China Agricultural University, China

*CORRESPONDENCE

James V. Cizdziel,
✉ cizdziel@olemiss.edu

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Removal of microplastics from agricultural runoff using biochar: a column feasibility study

Boluwatife S. Olubusoye¹, James V. Cizdziel^{1*}, Kendall Wontor¹,
Edward Heinen¹, Tony Grandberry¹, Erin R. Bennett² and
Matthew T. Moore³

¹Department of Chemistry and Biochemistry, University of Mississippi, Oxford, MS, United States, ²School of the Environment, Trent University, Peterborough, ON, Canada, ³Water Quality and Ecology Research Unit, U.S. Department of Agriculture, Agricultural Research Service, Oxford, MS, United States

Plastics are extensively used in agriculture, but their weathering and degradation generates microplastics (MPs) that can be carried by runoff into water bodies where they can accumulate and impact wildlife. Due to its physicochemical properties, biochar has shown promise in mitigating contaminants in agricultural runoff. However, few studies have examined its effectiveness at removing MPs. In this study, we assessed MP pollution (>30 µm) in runoff from a farm in the Mississippi Delta and examined the effectiveness of biochar (pinewood and sugarcane) to remove MPs from aqueous solutions. Using micro-Fourier Transform Infrared spectroscopy (µ-FTIR), we observed an average of 237 MPs/L (range 27–609) in the runoff, with most particles identified as polyethylene, polyamide, polyvinyl chloride, polyurethane, acrylonitrile butadiene styrene, and polyarylamide. Biochar columns effectively removed MPs from runoff samples with reductions ranging from 86.6% to 92.6%. MPs of different sizes, shapes, and types were stained with Nile red dye (to facilitate observation by fluorescence) and quantified their downward progress with multiple column volumes of water and wet/dry cycles. Smaller MPs penetrated the columns further, but ≥90% of MPs were retained in the ~20 cm columns regardless of their shape, size, and type. We attribute these results to physical entrapment, hydrophobic behaviors, and electrostatic interactions. Overall, this proof-of-concept work suggests biochar may serve as a cost-effective approach to remove MPs from runoff, and that subsequent field studies are warranted.

KEYWORDS

microplastics, biochar, agricultural runoff, plasticulture, microplastic removal, column study, FTIR microscopy, fluorescence

1 Introduction

Microplastics (MPs) consist of a suite of synthetic polymers <5 mm in size with varying chemical makeup, shapes, densities, additives, and other characteristics (Thompson et al., 2004; Arthur et al., 2009; Zhang et al., 2018; Padervand et al., 2020). These environmental pollutants, which stems in part from the degradation of plastic litter by natural physical, chemical, and biological processes, can have deleterious effects on certain organisms (Galgani et al., 2013; Cauwenberghe et al., 2015; Mukherjee et al., 2022). MPs pose a

critical challenge as they are widespread, persistent, and can bioaccumulate in wildlife, and, potentially, in humans (Mukherjee et al., 2022).

Agricultural production is a prominent source of MPs, as plastics are extensively used in farming for soil moisture retention, weed control, temperature regulation, and irrigation piping (Horton et al., 2017; Jansen et al., 2019; Isari et al., 2021). Notably, plastic mulching has been widely employed for over half a century, resulting in the accumulation of MPs in soils worldwide (Li et al., 2020). The MPs themselves can alter soil biophysical properties, including bulk density, water-holding capacity, and soil microbial interactions with water-stable aggregates (Tang, 2020). Studies have demonstrated the uptake and accumulation of MPs in crop tissue cultures, suggesting the potential transfer of MPs to humans through the food chain (Li et al., 2019). MPs may serve as sources and/or sinks for pesticides in agricultural fields via adsorption of compounds (Wang et al., 2020a). For example, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and heavy metals are known to adhere to MPs due to various surface interactions, including electrostatic attraction and surface complexation with functional groups like carboxyl groups (Sharma et al., 2024). Furthermore, the practice of biosolids fertilization often introduces MPs, particularly fibers, into soils, leading to increased MP incidence in farmland runoff (Gao et al., 2022; Schell et al., 2022). Additionally, evidence suggests that areas where agricultural plastics such as greenhouse covers, plastic film, and silage film are commonly used tend to have higher levels of MP pollution (Piehl et al., 2018; Jin et al., 2022). These tiny, nearly invisible plastics can also infiltrate soil potentially affecting groundwater systems and human drinking water sources (Re, 2019; Sharma and Sharma, 2024). Runoff from agricultural fields, whether due to rainfall or irrigation, plays a crucial role in the migration of MPs from terrestrial to aquatic systems (Watts et al., 2014; Wang et al., 2020b; Ajith et al., 2021; Mukherjee et al., 2022). Thus, cost-effective solutions are needed to effectively remove MPs from agricultural runoff.

Biochar is obtained by carbonizing biomass in the absence of oxygen (Xiang et al., 2020; Jagadeesh and Sundaram, 2022). Biochar production involves a variety of thermochemical processes, including gasification and pyrolysis (Ambaye et al., 2020). Biochar typically possesses high porosity, large surface area-to-volume ratio, and active surface functional groups. Thus, it serves as an effective adsorbent for pollutant removal from aquatic systems (Lee et al., 2013; Abhishek et al., 2022; Jagadeesh and Sundaram, 2022; Sinha et al., 2022). Applying biochar to soil is an emergent practice and potentially cost-effective method to replenish nutrients, increase agricultural yields, remove contaminants, and sequester carbon (Kuppusamy et al., 2016; McCalla et al., 2022; Dong et al., 2023). Biochar has also been used to remove pollutants, including heavy metals, persistent organic compounds, and, most recently, MPs, from aquatic systems (Wang et al., 2020b; Siipola et al., 2020; Wang et al., 2021a; Magid et al., 2021; Dong et al., 2023; Sharma and Sharma, 2024). Biochar also shows potential in removing MPs in wastewater systems (Wang et al., 2020b; Hsieh et al., 2022).

Removal of MPs by biochar is based on adsorption to-and physical entrapment in-the biochar matrix by various mechanisms, including electrostatic attraction and surface complexation with functional groups like carboxyl groups

(Beckingham and Ghosh, 2017; Ye et al., 2020; Wang et al., 2021a; Li et al., 2021; Kumar et al., 2023). Others have highlighted the significance of biochar pyrolyzing temperature, electrostatic interactions, hydrophobicity, specific surface area, pore-filling, and hydrogen bonding in the adsorption process (Magid et al., 2021). Due to the hydrophobic nature of many MPs, they are attracted to the adsorptive sites of biochar in the aqueous media (Beckingham and Ghosh, 2017; Wang et al., 2021a; Kumar et al., 2023). Although considerable knowledge has been gained regarding the adsorption of various chemicals on biochar (Gwenzi et al., 2017; Dai et al., 2019), research on the potential use of biochar in removing MPs is still in the early stages of development (Wang et al., 2020b). Others have recently shown that geomedia (e.g., a mixture of sand and compost materials) in bioretention systems can effectively remove MPs from stormwater runoff (Wolfand et al., 2023).

In this study, we collected and characterized MP pollution in runoff from a farm in the Mississippi Delta, an alluvial region in northwestern Mississippi, using micro-Fourier Transform Infrared (μ -FTIR) spectroscopy. We then passed runoff samples through two types of biochar in glass columns in the laboratory to quantify MP removal efficiency. Additionally, we examined the downward penetration of MPs in the biochar columns based on their size, shape, and type using fluorescent-labeled MPs. This study was not intended to provide a detailed analysis of the MP-biochar sorption mechanisms nor to capture all the effects of environmental conditions on those processes. Instead, the goal was to assess the extent to which MPs are retained in the biochar columns, where high retention rates and minimal penetration suggest that larger field studies are warranted. To our knowledge, this is the first study focused on characterizing MPs in agricultural runoff in the Mississippi Delta. By shedding light on this relatively unexplored aspect of MP pollution, we hope to lay the groundwork for larger-scale field studies aimed at developing effective management strategies for mitigating MP pollution in agricultural settings.

2 Materials and methods

2.1 Collection of agricultural runoff and determination of MPs by μ -FTIR

Triplicate samples of agricultural runoff were collected at two sites from a farm near Beasley Lake in the Mississippi Delta (Figure 1). The farm, like others in the region, typically rotates crops, primarily soybean, corn, and cotton, depending on economics and other factors. The samples were collected after a rain event on 12 May 2023 produced significant runoff. The nearest NOAA weather station (<10 km away) recorded 4.2 cm of rainfall on the day. Samples were collected directly into one quart (0.95 L) glass jars and transported to the University of Mississippi in a cooler on ice and stored in a refrigerator at $\sim 4^{\circ}\text{C}$ until analysis.

To quantify and characterize MPs in the runoff, we used the “one pot” method, where sample preparation steps occur in the same jar that the sample was collected in to minimize contamination and losses (Scircle et al., 2020), combined with μ -FTIR analyses for MP identification. Briefly, to isolate MPs, samples underwent digestion with Fenton’s reagent (to remove natural organic matter without

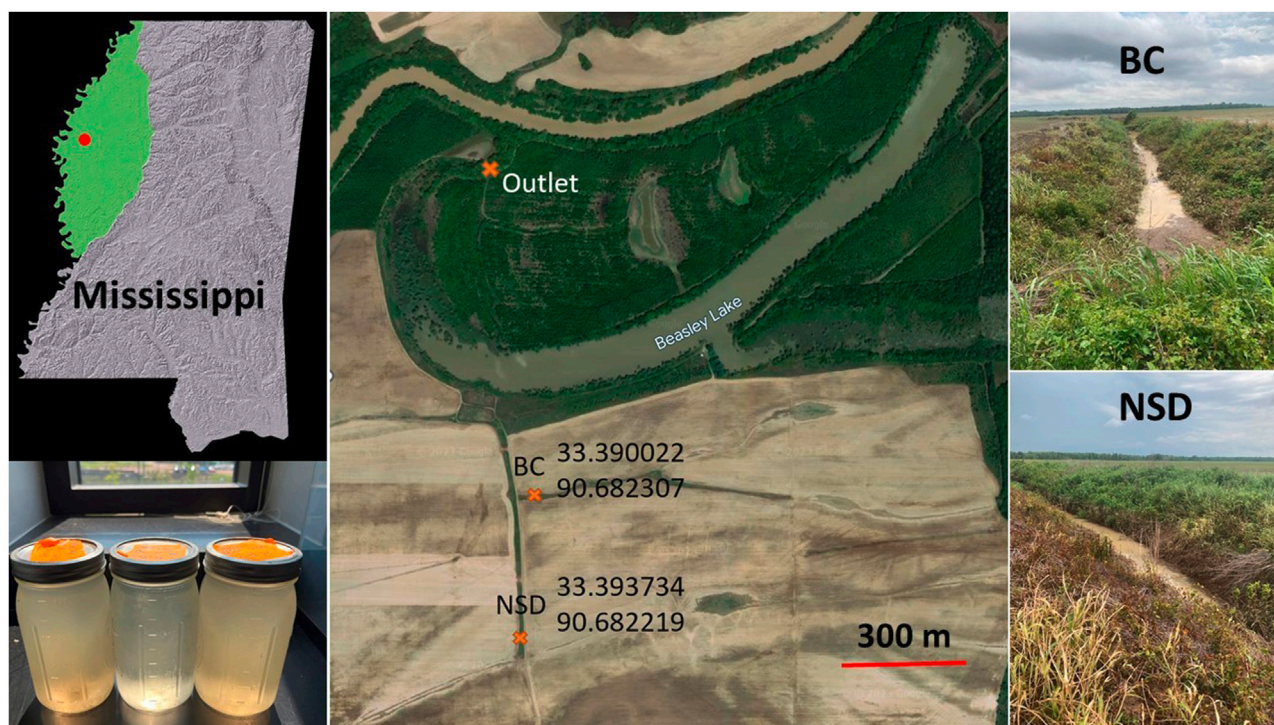


FIGURE 1
Map showing the location of Beasley Lake in the Mississippi Delta (upper left), runoff sampling locations (BC and NSD) with decimal GPS coordinates (center), and photos of the runoff in ditches (right) and samples in glass Mason jars (lower left).

damaging the plastics), followed by density separation using ZnCl_2 (1.6 g/cm^3) (to remove inorganic particles). The MPs were collected off the top layer of solution with a glass pipette before being filtered onto a $10 \text{ mm} \times 10 \text{ mm}$ silicon filter ($0.2 \mu\text{m}$ pores). Silicon filters were used as they are transparent in the mid-IR range. Spectra in this region correspond to the vibrational fingerprint of molecules in the sample and thus are commonly used for identifying chemical composition.

Particles on the filter were analyzed by $\mu\text{-FTIR}$ using a Bruker LUMOS II equipped with a liquid nitrogen-cooled MCT detector (Bruker Corp., Billerica, MA, United States). An optical image with $8 \times$ magnification was taken of the silicon filter to select particles for spectral analysis. Transmission spectra were then collected in point mode. Both sample and background scans were collected between 4000 and 650 cm^{-1} with 4 cm^{-1} resolution and 16 co-added scans. The background was collected from an area of the silicon filter without particles. Data was processed using OPUS 8.7.4 software. Particle chemical compositions were identified by comparing their spectrum to a series of polymer spectral libraries using the program's Cluster ID function. These libraries include Bruker's polymer libraries as well as FLOPP and FLOPP-e, free databases of FTIR spectra of virgin polymers and polymers sourced from the environment (De Frond et al., 2021). Only particles with a Hit Quality Index (HQI) of >200 were assigned to a polymer type. Plastic polymers that did not fall into one of these categories were classified as "other plastics," while particles identified as other materials were classified as non-plastic and excluded from further analysis.

Because we used a Monel screen with $\sim 30 \mu\text{m}$ openings in the sample preparation process, we do not include any particles smaller than $30 \mu\text{m}$ in our results. To avoid plastic contamination during sample preparation, cotton laboratory coats dyed bright orange were worn, nitrile gloves were used, and all work was performed in a clean room. Glassware was thoroughly rinsed with milliQ water and heated at 450°C for 4 h before use, and samples were covered or sealed with aluminum foil until analysis.

2.2 Column study: Biochar and MPs

Sugarcane and pinewood biochar were pyrolyzed at temperatures of 500°C and 900°C , respectively. Bulk density of the sugarcane and pinewood biochars (when gently packed into the columns described below) were 0.2 g/cm^3 and 0.4 g/cm^3 , respectively. A portion of the biochar was gently dry-sieved to assess particle size distribution. Particles of sugarcane biochar (formed at 500°C) and pinewood biochar (formed at 900°C) were also examined by field-emission scanning electron microscopy (SEM) (JSM-7200FLV, JEOL Ltd., Japan). Biochar particle size distributions and SEM images are presented in Section 3.1.

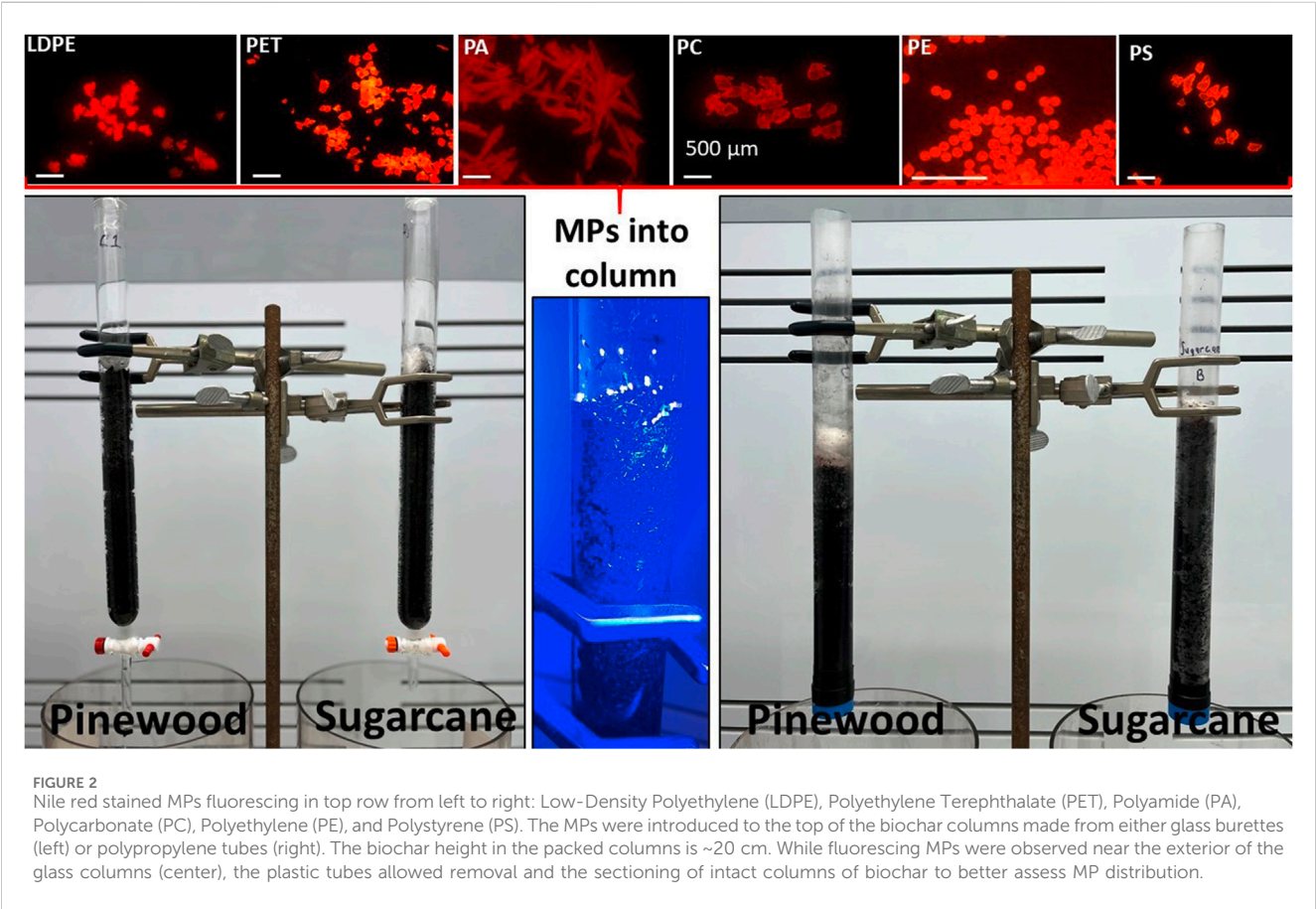
Characteristics of MPs used in the column study are provided in Table 1. The MPs include pristine polyethylene beads (Aldrich Chemical Co., St. Louis, MO) along with MPs generated from weathered plastic debris found on Sardis Lake Dam located in north-central Mississippi. The latter MPs were produced through cryogenic grinding using a cryo mill (Spex CertiPrep, Metuchen,

TABLE 1 Characteristics of Nile-red stained microplastics used in this study. All microplastics (MPs) stemmed from environmentally weathered plastic, except the PE beads, which were purchased (see text for details). MPs in the size ranges reported were obtained after cryomilling of naturally weathered plastics.

Polymer	Shape	Size (μm)	Density (g/cm ³)
Polyethylene (PE)	Beads	40–48	0.91–0.96
Low-Density Polyethylene (LDPE)	Fragments	45–125	1.32
Polyethylene Terephthalate (PET)		45–250	1.38
High-density Polyethylene (HDPE)		125–250	0.93–0.97
Polycarbonate (PC)		250–500	1.20–1.22
Polyamide (PA)		250–500	1.03–1.14
Polystyrene (PS)		250–500	1.04–1.09
Polyvinyl chloride (PVC)	Films	500–1,000	0.91–0.94

TABLE 2 Overview of column study with experimental conditions.

Study phase	Polymer tested	Column	Height of biochar (cm)	Biochar (g)
I	50 mg each of LDPE, PET, PA, PC, PE, PS	Glass	25	50
II	50 mg each of LDPE, PET, PA, PC, PE, PS	Polypropylene	20	30
III	30 pieces each of LDPE, PA, PC, PE	Polypropylene	20	30
IV	Agricultural runoff	Polypropylene	20	30



NJ). Together the material represents three different shapes and seven different types of MPs commonly found in the environment.

To facilitate observation and recovery of MPs, we stained them with Nile red dye which makes them fluoresce brightly under certain wavelengths of light (e.g., 420–510 nm) (Gao et al., 2022). Briefly, 10 mL of Nile red solution (10 µg/mL in methanol) were added to glass vials containing the different types of MPs. The mixture was diluted to 40 mL with Milli-Q water and vials were heated to 70°C for 3 h. After staining, MPs were recovered by filtration, washed with DI water, and dried.

2.3 Column study: Design and approach

The column study was conducted in four phases (Table 2). In phase I, we used 25-mm diameter glass burettes adding ~50 g of biochar (filling ~30 cm of the column) and topping it with ~50 mg of Nile red stained MPs (Figure 2, left side). We then passed three column volumes of filtered (0.45 µm) water (~1.2 L) through the columns. Although we observed little penetration (<3 cm) of MPs into either the pinewood or sugarcane columns (see Section 2.5 for fluorescence method), the glass burette only allowed for detection of MPs at the exterior (just inside the glass) and there was no way to remove the biochar from the column without disturbing the distribution of MPs.

In phase II, we used 22-mm diameter polypropylene tubes as columns (Figure 2, right side) because the biochar could be pushed out intact and subsequently divided into 1-cm sections using a metal spatula to carefully inspect each individual section for MPs. To prepare the plastic columns, we sealed one end of the tube with a plastic end cap and punctured it to give a 1–2 mm diameter hole. Glass wool was placed at the bottom of the tubes and 30 g of sugarcane and pinewood biochar were added. Columns (~30 cm in height) were gently tapped a few times to settle the biochar resulting in a ~20 cm packed biochar height in column. To prevent MPs from floating on the water added to the column, a glass-wool plug was added to cover the biochar after the MPs were introduced. Specifically, we added 50 mg of each type of Nile red-stained MPs to the top of each column (pinewood and sugarcane). We then passed 400 mL (~1 column volume) of filtered water through the column vertically (gravity-fed) at 1–2 mL/min (gravity fed). Columns were allowed to dry for ~24 h and the process was repeated nine times (10 wet-dry cycles). Biochar was then carefully pushed out of the tube with a wooden stick matching the inside diameter of the tube and divided into 1-cm fractions. Each fraction was spread-out on weighing paper and allowed to air-dry before a visual inspection by fluorescence and stereomicroscopy. Representative samples of pinewood and sugarcane were also analyzed by SEM.

In phase III, we repeated the phase II experiment, but this time added exactly 30 MPs of a single polymer to four separate pinewood biochar columns, one column each for PE beads, PA fragments, PC fragments, and LDPE films (Table 1). Using an exact number of MPs in individual columns allowed us to quantify individual MP distributions and assess recoveries.

In phase IV, we passed 1.9 L of agricultural runoff from both BC and NSD sites through pinewood biochar columns (0.95 L through each column, four columns in total). Pinewood biochar was selected for this phase due to its discernible presence of pores and surface

features when compared to sugarcane biochar, as evidenced by SEM images (Section 3.2). This choice was made based on the superior structural characteristics of pinewood biochar, which are conducive to enhanced adsorption properties and efficacy in pollutant removal applications. We then analyzed the column effluent using µ-FTIR and compared the results to the sample collected from the same location but analyzed directly (without passing through biochar). This approach tested whether the biochar column retained MPs in agriculture runoff itself (rather than laboratory spiked MPs). The collection of runoff and the µ-FTIR method was detailed earlier.

2.4 Observation of MPs in column fractions by fluorescence and microscopy

Columns spiked with Nile-red stained MPs were examined using a Crime-lite® 82S (Foster + Freeman United States Inc., Ashburn, VA) operated in the 420–510 nm range. Laser safety glasses were used to block light from entering the Crime-lite operator's eyes. For the recovery experiments, intensely fluorescing particles were counted in each 1-cm column fraction after the biochar was spread on weighing paper and allowed to air-dry. In addition, samples were visually inspected and further examined with a Stemi 508 Stereomicroscope equipped with an AxioCam 105 color digital camera (Carl Zeiss, Jena, Germany).

3 Results and discussion

3.1 Occurrence and characteristics of MPs in the agricultural runoff

Abundances of MPs in runoff from the farm ($n = 2$) ranged from 27–609 particles/L, with an average of 237 particles/L. These concentrations fall into the wide range reported for agricultural runoff in the literature (Cao et al., 2021). Most MPs were fragments (95.7%), followed by films (2.7%), and fibers (1.6%). While these MP morphologies are commonly encountered in agricultural samples, their relative distribution can vary depending on their sources (Zhang et al., 2020; Choi et al., 2021; Schell et al., 2022). Potential sources include the degradation of larger plastics (e.g., sheeting), application of sewage sludge abundant in fibers, and wind transport and atmospheric deposition from sources off site (Cai et al., 2017; Allen et al., 2019; Leonard et al., 2024). We found polyethylene (PE) as the dominant type of MP measured at the BC sample site, followed by polyarylamide (PARA), PA (nylon), and PVC (poly vinyl chloride) at 21%, 20%, 19%, and 11% respectively (Figure 3A). These plastics are used in agriculture for variety of purposes, including mulching and irrigation polypipe. At our study site, we observed remnants of PE plastic sheeting. PE is also the most used plastic worldwide and accounts for about a third of the total plastic market (Geyer et al., 2017). Other polymer types were also measured, albeit in low concentrations. At the NSD site, acrylonitrile butadiene styrene (ABS, 32%) was the dominant type of MP, followed by PU (21%), PE (18%) and PS (10%), respectively (Figure 3B). The different distribution of MP types in runoff collected at two different sites in the same agricultural field shows the potential for heterogeneity of MPs in field samples.

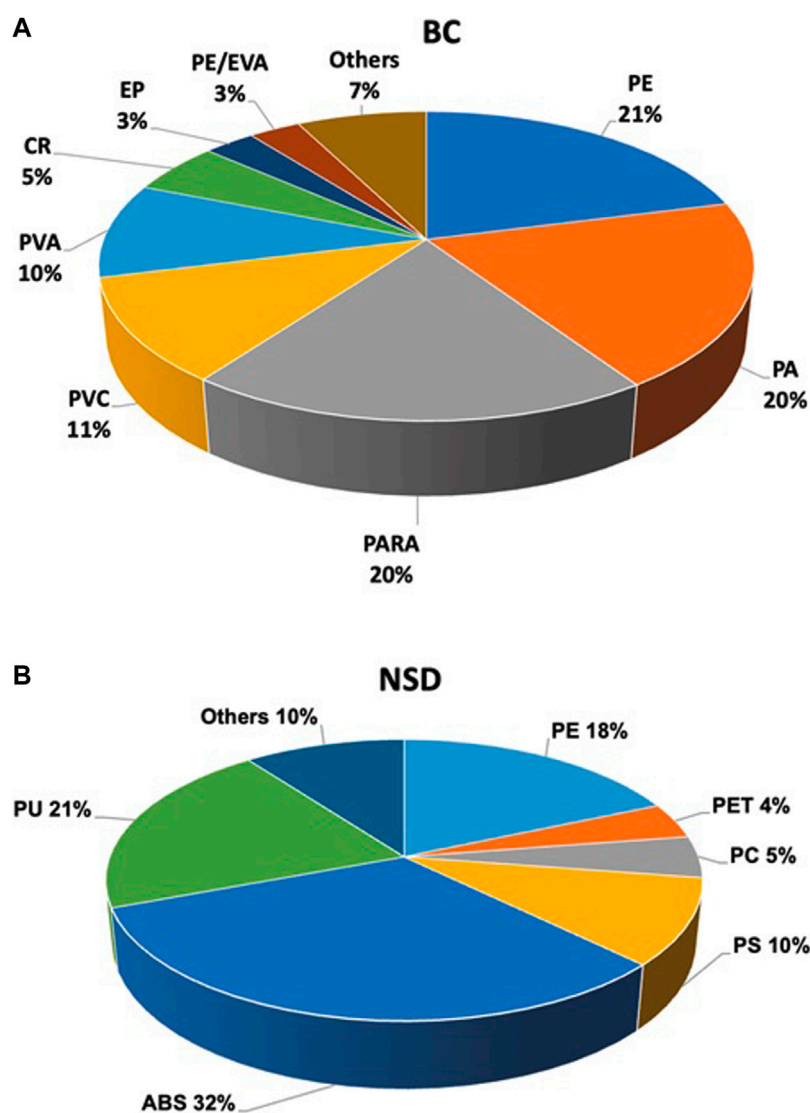


FIGURE 3
Distribution (%) of microplastics by type in BC (A) and NSD (B) sample sites ($n = 2$ per site) in agricultural runoff at a farm in the Mississippi Delta. Acronyms not previously defined: CR, crumb rubber; EVA, ethylene vinyl acetate; PVA, polyvinyl alcohol; EP, ethylene propylene rubber; PU, polyurethane; PS, polystyrene.

However, for the purposes of this study, the presence and abundance of MPs in the runoff, regardless of their type, indicate suitability for both the column study and for future fieldwork evaluating methods for mitigating MP pollution from agriculture.

3.2 Biochar characteristics

Approximately 70% of the pinewood biochar was between 250 and 1,000 μm , with most of the remaining biochar mass being >1 mm (Figure 4). In contrast, only ~35% of the sugarcane biochar fell between 250 and 1,000 μm with a greater percentage in both the fines and larger particle fractions.

Both biochars exhibit a rough surface with pores ~10 μm or less, with pinewood biochar showing more surface features (Figure 5). This is likely due the pinewood's 400°C higher pyrolysis temperature

given that increasing pyrolysis temperature increases biochar surface area and surface features that, in turn, provide more trapping capabilities for particles like MPs (Hsieh et al., 2022).

3.3 Effectiveness of biochar columns at trapping MPs

In phase II, we compared the depth of MP penetration into sugarcane and pinewood biochar columns by examining column fractions using microscopy (Figure 6). MPs penetrated deeper into the sugarcane biochar with particles detected in the seventh fraction (up to 7 cm deep), whereas MPs were unable to progress beyond the third fraction (up to 3 cm deep) in the pinewood biochar. This disparity may be attributed to the different biochar particle size distributions and how that affects column packing. Alternatively,

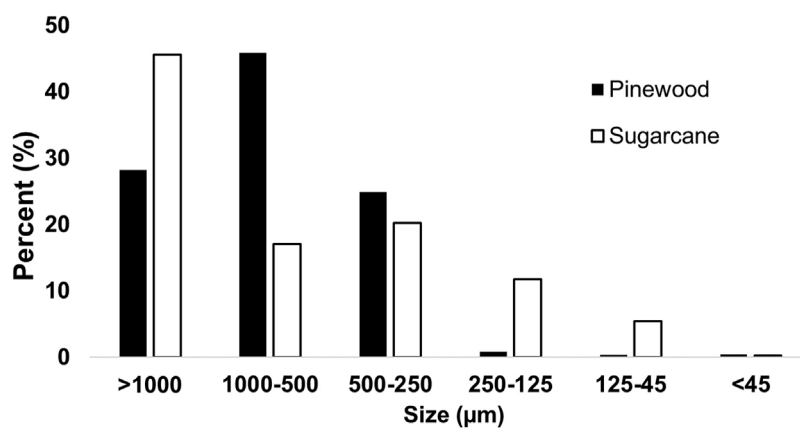


FIGURE 4
Particle size distribution (percent by mass) of pinewood and sugarcane biochar.

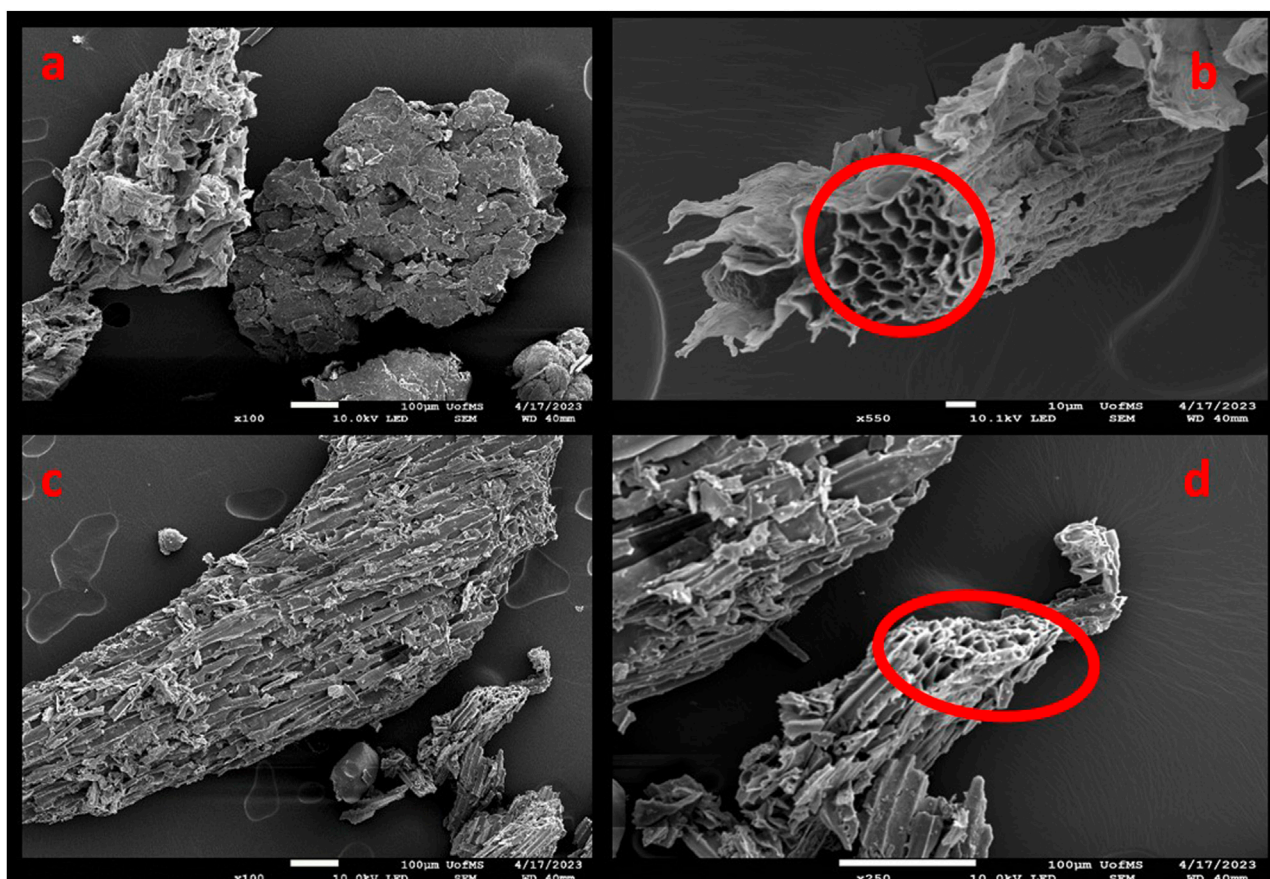


FIGURE 5
SEM images of sugarcane biochar (A,B) and pinewood biochar (C,D) showing rough surface features and pores (circled in red). Images at 100 × magnification (A,C), 250 × magnification (D), and 550 × magnification (B).

these disparities may be due to different pyrolysis temperatures used to produce biochars and how higher temperatures increase surface area and surface features in biochar, or both. The pinewood biochar, generated at 900°C, had more surface features that promote effective trapping, entanglement, or adsorption of MPs in aqueous media

compared to the sugarcane biochar formed at 500°C. In a batch sorption experiment, Magid et al. (2021) observed significant adsorption of PS nanoplastics by corncob biomass pyrolyzed at high temperatures. They noted that oxidized corncob biochar displayed notably higher adsorption, exceeding 90%. This was

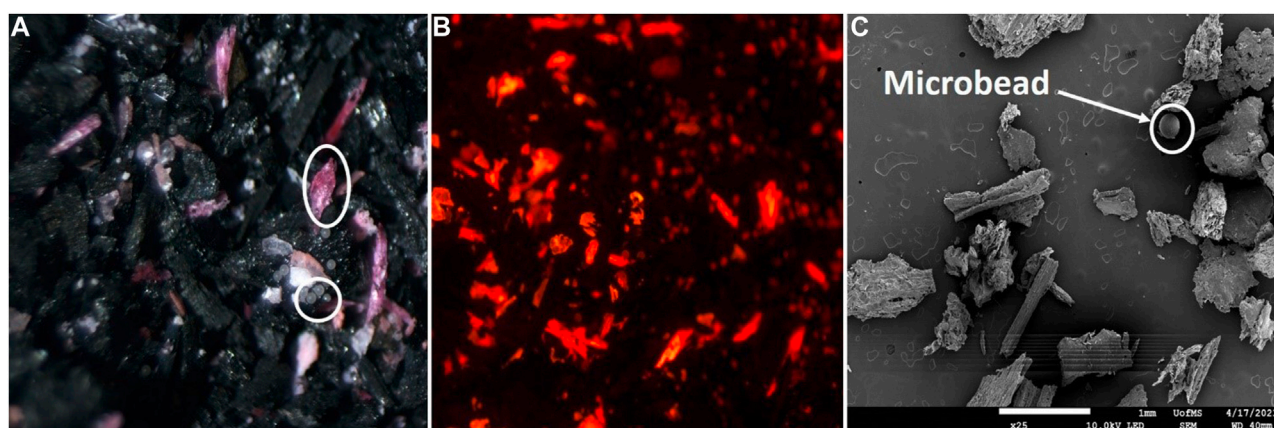
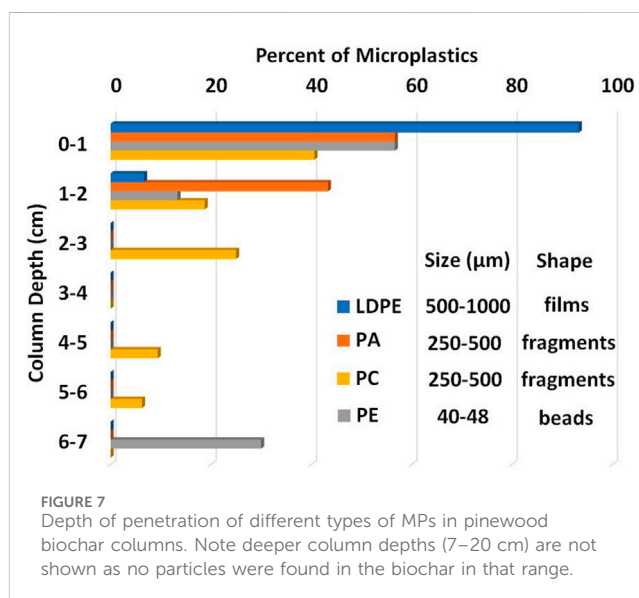


FIGURE 6
Representative microscopy images of Pinewood biochar column fraction containing microplastics (LDPE, PA, PET, PC, PS, PE, PVC): optical (A), fluorescence (B), and SEM (C). All images are from the same Pinewood biochar column fraction.

attributed to the presence of hydroxyl groups, which facilitated PS adsorption compared to biochar derived solely from corncob. Furthermore, the adsorption capacity of oxidized corncob biochar for PS increased with pyrolysis temperature. This phenomenon was attributed to various factors, including electrostatic interactions, hydrophobicity, specific surface area, pore-filling, and hydrogen bonding (Magid et al., 2021; Kumar et al., 2023). Similarly, Ganie et al. (2021) reported that biochar prepared at a pyrolysis temperature of 750°C exhibited increased surface area and pore abundance, resulting in drastically higher removal of nanoplastics (>99%) compared to biochar pyrolyzed at 550°C and 350°C, which showed comparatively lower nanoplastics sorption. Research has documented that the pyrolysis temperature used for biochar production significantly influences the aggregation of biochar colloids in aqueous environments (Yang et al., 2019).

The difference between the penetration depth of MPs for the two biochars may also suggest that particles 250–1,000 µm are important in retention as the pinewood biochar had a substantially higher percentage of this “mid-sized” fraction (~70%) compared to the sugarcane biochar (~35%). Further, the sugarcane effluent was darker than the pinewood effluent suggesting that the fine biochar particles (present in greater proportion in the sugarcane) were being washed out of the columns, leaving behind a particle distribution skewed to larger sizes. This, in turn, would increase the size of flow paths for MPs to travel down the column, especially for the sugarcane.

Smaller biochar particles generally have a larger specific surface area, providing more active sites for interaction with MPs. This increased surface area may enhance the adsorption capacity of biochar, allowing it to effectively capture MPs from the water. Additionally, smaller biochar particles can penetrate deeper into the aqueous environment, reaching MP sources present throughout the water column. This phenomenon has also been observed in other studies with quartz sand particles (Sharma et al., 2014; Mao et al., 2020). However, the surface morphology of biochar is more complex than that of sand, and the shape and pyrolysis temperature of biochar particles also influence their interaction with MPs (Wang et al., 2020b). Irregularly shaped particles and higher pyrolysis



temperatures provide more surface roughness and binding sites compared to spherical or homogeneous particles with low pyrolysis temperatures. In our study, the pinewood biochar is a mixture of both mid-sized and small-sized particles, and its relatively high pyrolysis temperature provides more binding sites for the MPs compared to sugarcane biochar. SEM images show that MPs were trapped or entangled within the pores or rough surface features of the pinewood biochar, which were more prevalent than on the sugarcane biochar. Fine particles (<~250 µm) with low pyrolysis temperatures should be avoided in future experiments as they would likely be lost from filter socks adapted to house biochar in field experiments.

To better understand the factors affecting the retention of MPs in the biochar columns, we individually examined the penetration depth of several types of MPs (PE beads, PA fragments, PC fragments, and LDPE films), each consisting of 30 MPs. This approach allowed us to assess both MP recoveries and the

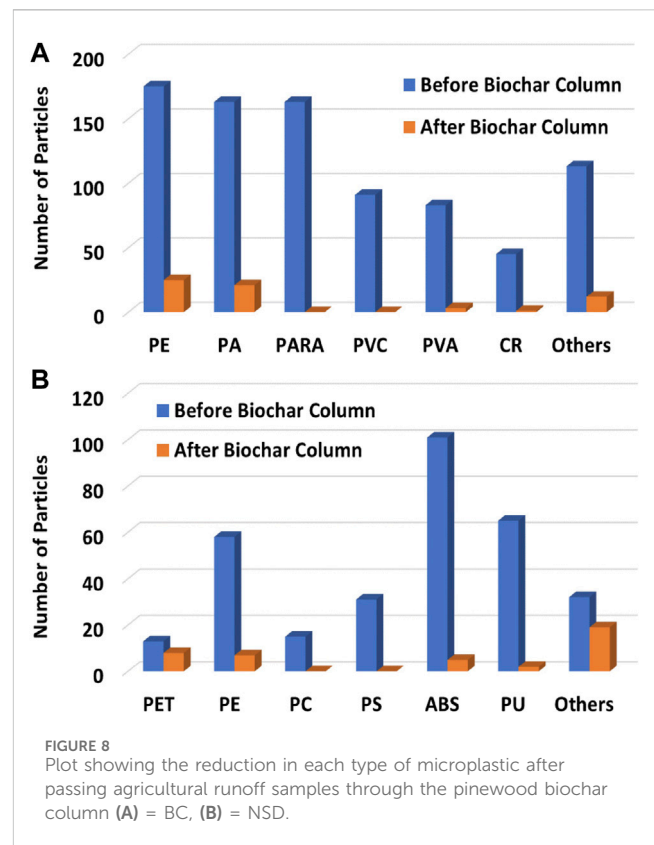
influence of size and shape on their retention and penetration depth. In each case, we observed 100% recoveries for the spiked MPs.

We observed that the smaller MPs, such as PE beads, exhibited the greatest potential for movement. Additionally, we noted that MP migration depth increased with a greater number of wet-dry cycles. However, most of the particles were found within the upper 7 cm of the columns (Figure 7). This finding aligns with previous research suggesting enhanced vertical migration for smaller-sized MPs, particularly those with spherical shapes, and with increased wet-dry cycles (Kurlanda-Witek et al., 2015; O'Connor et al., 2019). Others have also reported that wet-dry cycles can significantly affect soil behavior and deposited colloids. Consequently, soils can absorb water, leading to swelling and changes in pore structure (Haque et al., 2017; Sharma, 2023). Kumari et al. (2017) observed that wet-dry cycles can influence the transport of contaminants, fertilizers, or pesticides in soil and groundwater. As wet-dry cycles increase, colloids carrying contaminants might be transported back and forth within the soil profile, potentially altering the distribution of contaminants and their availability for migration (Kumar et al., 2022). Similarly, Sharma (2023) showed in their study that wet-dry cycles can cause biochar colloids to undergo repeated cycles of absorption and desorption. As water is absorbed during wet cycles, biochar colloids might be transported deeper into the sediment. During dry cycles, the biochar colloids can become concentrated closer to the sediment surface, leading to redistribution, which can impact nutrient transport, contaminant migration, and soil fertility (Kumar et al., 2022; Sharma, 2023). This highlights the significance of size and shape in determining the penetration depth of MPs in pinewood biochar columns. These findings underscore the importance of considering such factors in the design and implementation of strategies aimed at mitigating MP pollution in agricultural runoff.

A few MPs, however, did break through the biochar columns. Three particles of LDPE were found in the effluent, but interestingly their particle sizes were smaller ($<500\text{ }\mu\text{m}$) than those introduced to the column, suggesting possible breakdown during the experiment. In this case, the LDPE particles were films which can be more fragile compared to fragments and beads. For the other columns, there were three fragments of PC, two fragments of PA, and one PE bead in the effluent. It is possible the wet-dry cycles contributed to the enhanced migration by opening pathways. Regardless, the biochar showed $\geq 90\%$ recovery rate of MPs from the aqueous solutions.

3.4 Effectiveness of biochar columns at removing MPs from agricultural runoff

Four samples of agricultural runoff were analyzed for MPs (two from each site, BC and NSD). Duplicate samples (from the same location) were passed through separate columns made of pinewood biochar. The BC samples averaged 416 MPs/L, but after passing duplicate samples through the column, an average of only 31 MPs were recovered, a reduction of 92.6%. Similarly, NSD samples averaged 157 MPs/L, but duplicates run through the column yielded an average of only 21 MPs, a reduction of 86.6%. Columns were effective for all types of MPs in the runoff (Figure 8). These findings suggest biochar used to remove contaminants from agricultural runoff may also be effective at



removing MPs. Thus, subsequent field studies on the subject are prudent.

3.5 Study limitations

While this study provides valuable insights into the potential of biochar as a cost-effective adsorbent for removing MPs from agricultural runoff, there are some limitations that should be acknowledged. First, the laboratory-based setup may not fully replicate real-world conditions, potentially leading to discrepancies between observed and actual MP removal efficiencies. Second, the study focused solely on the characterization and removal of MPs using biochar columns, neglecting other potential factors influencing MP transport and fate in agricultural environments. Also, the sample size and scope of the study were relatively small, limiting the generalizability of the findings to broader agricultural settings. Finally, the study did not explore the long-term effectiveness of biochar in mitigating MP pollution, nor did it consider potential secondary impacts of biochar application on soil health and ecosystem functioning. Addressing these limitations through larger-scale field studies with more diverse experimental conditions will be crucial for obtaining a comprehensive understanding of the efficacy and feasibility of biochar-based interventions for mitigating MP pollution in agricultural runoff from agricultural fields, where plastic is used extensively in agricultural practices, now referred to as plasticulture. Such studies could include, for example, biochar placed in filter socks situated at locations that funnel runoff.

4 Conclusion

This study examined the potential of biochar, an economical carbonaceous material, to capture MPs in agricultural runoff. For the first time, MPs were quantified and characterized in runoff from a farm in the Mississippi Delta. PE was the predominant type of MP, with PA, ABS, PU, PARA, PVC, PS, PVA, PC, PET, CR and PE/EVA, also detected. Most of the MPs were fragments, followed by films and fibers. Passing the runoff through a biochar columns in the laboratory removed between 86% and 92% of the MPs. Using fluorescence-labeled MPs we observed that smaller MPs penetrate more deeply into the columns and that MPs migrated further into sugarcane biochar compared to pinewood biochar, a difference attributed to the biochar's surface characteristics and particle size distribution. By demonstrating the effectiveness of biochar, a readily available material, in capturing MPs from runoff, this study offers a promising solution for mitigating MP contamination in agricultural environments. The quantification and characterization of MPs in runoff from a farm in the Mississippi Delta provides valuable insights into the prevalence and composition of MP pollution in this agricultural setting. The identification of PE as the predominant type of MP, along with the detection of various other plastic types, underscores the diverse sources contributing to MP pollution in agricultural runoff. Overall, these findings underscore the potential of biochar to be a cost-effective adsorbent for the removal of MPs from agricultural runoff. Future research and implementation efforts should focus on scaling up biochar-based remediation techniques and integrating them into agricultural practices to effectively reduce MP contamination and safeguard environmental and human health.

Data availability statement

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Author contributions

BO: Conceptualization, Investigation, Methodology, Writing–original draft, Writing–review and editing. JC: Conceptualization, Investigation, Methodology, Project administration, Supervision, Writing–original draft, Writing–review and editing. KW: Methodology, Writing–review and editing. EH: Data curation, Writing–review and editing. TG: Investigation, Writing–review and editing. EB: Conceptualization, Data curation,

Writing–review and editing. MM: Conceptualization, Data curation, Writing–review and editing.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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