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Physical Disintegration of Biochar: An Overlooked Process

K. A. Spokas,*,[†,‡] J. M. Novak,[§] C. A. Masiello,[∥] M. G. Johnson,[⊥] E. C. Colosky,[‡] J. A. Ippolito,[#] and C. Trigo[‡]

[†]Agriculture Research Service, United States Department of Agriculture, 1991 Upper Buford Circle, 439 Borlaug Hall, St. Paul, Minnesota 55018, United States

[‡]Department of Soil, Water and Climate, University of Minnesota, 1991 Upper Buford Circle, 439 Borlaug Hall, St. Paul, Minnesota 55108, United States

[§]Agriculture Research Service, United States Department of Agriculture, 2611 West Lucas Street, Florence, South Carolina 29501, United States

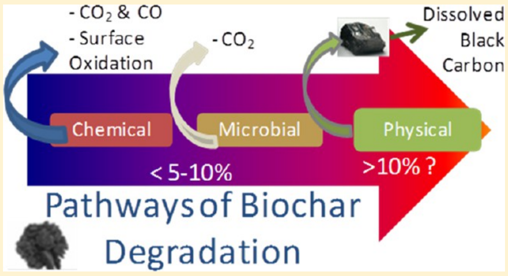
[∥]Departments of Earth Science and Chemistry, Rice University, 6100 Main Street, Houston, Texas 77005, United States

[⊥]United States Environmental Protection Agency, 200 Southwest 35th Street, Corvallis, Oregon 97333, United States

[#]Agriculture Research Service, United States Department of Agriculture, 3793 North 3600 East, Kimberly, Idaho 83341, United States

Ⓢ *Supporting Information*

ABSTRACT: Data collected from both artificially and field (naturally) weathered biochar suggest that a potentially significant pathway of biochar disappearance is through physical breakdown of the biochar structure. Via scanning electron microscopy, we characterized this physical weathering that increased the number of structural fractures and yielded higher numbers of liberated biochar fragments. This was hypothesized to be due to the graphitic sheet expansion accompanying water sorption coupled with comminution. These fragments can be on the microscale and the nanoscale but are still carbon-rich particles with no detectable alteration in the oxygen:carbon ratio from that of the original biochar. However, these particles are now easily dissolved and could be moved by infiltration. There is a need to understand how to produce biochars that are resistant to physical degradation to maximize long-term biochar C sequestration potential within soil systems.



INTRODUCTION

Black carbon (BC) is the continuum of solid residuals resulting from the chemical−thermal conversion of carbon-containing materials and includes soot, char, and charcoal.[1,2] Because of its economic, soil fertility, and archeological importance, BC has been examined over the past century for its susceptibility to microbial and chemical oxidation.[3,4] Biochar is intentionally created BC for soil carbon sequestration and soil fertility improvement.[4] Therefore, biochar is chemically a BC, but not all BC is biochar.

The degradability of BC in soils is a function of its chemical composition, physical incorporation, and host soil microbial community structure,[5−7] but with an overall consensus that BC does represent a carbon pool with increased resistance to microbial degradation.[8,9] Because BC has extrapolated mean residence times from centuries to thousands of years in soils,[6,8] it should be a major constituent of soils. Nevertheless, comparisons of the estimated BC generation rates with the measured soil BC pool require losses of BC to maintain mass balance: this is termed the "black carbon paradox".[1] Some potential solutions to this paradox include transportation of BC with surface runoff,[10−12] explaining surface and hill slope losses.[13] In addition, vertical movement in the soil profile also occurs and will be a function of BC particle size or its protective incorporation into the soil matrix.[14,15] However, BC does not maintain its original physical size following soil incorporation.[16] Physical deterioration has been hypothesized to impact the longevity of BC in soils as well as its potential input into fluvial systems.[12,17] It is our contention that the physical disintegration of BC is an important yet overlooked process in current biochar research, dramatically reducing the longevity of BC in soils.

Physical degradation of biochar occurs via several mechanisms. High-oxygen:carbon (O:C) ratio BC materials (e.g., brown coals) are known to dissolve rapidly upon being exposed to desiccation and rewetting/saturation cycles (i.e., slacking).[18] Sorption of water and water vapor can stress the physical structure of BC because of exothermic graphitic sheet swelling.[19] These mechanisms result in swelling and expansion of the physical biochar structure, which improves the opportunity for further physical weathering.[20] Furthermore, fresh exposures of new biochar surfaces and fissures could accelerate microbial mineralization,[21] abiotic reactions,[22] or surface sorption phenomena.[23] BC typically is thought to be

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Table 1. Summary of Biochar Characteristics and Mass Losses Caused by Physical Dissolution of Various Biochars[a]

			from EDS point analysis		
BC	feedstock	pyrolysis temperature (°C)	C (%)	O (%)	% mass loss
1	switch grass	500			5.7 (1.4)
	original		85.6 (0.9)	12.3 (0.9)	
	24 h rinsed		81.8 (0.1)	12.5 (0.1)	
	fragments		83.1 (0.1)	12.6 (0.2)	
2	poultry litter	350			47.0 (2.1)
	original		47.9 (0.2)	20.6 (0.4)	
	24 h rinsed		80.1 (0.3)	14.8 (0.5)	
	fragments		83.4 (0.5)	10.2 (0.1)	
3	coconut shell (two pyrolysis steps)	500, then 900			1.0 (0.3)
	original		94.7 (0.2)	5.0 (0.2)	
	24 h rinsed		95.8 (0.4)	3.9 (0.2)	
	fragments		96.4 (0.2)	3.2 (0.1)	
4	pine chip	350			16.9 (0.9)
	original		76.4 (0.2)	15.7 (0.1)	
	24 h rinsed		86.7 (0.2)	10.7 (0.3)	
	fragments		85.4 (0.5)	9.8 (0.7)	
5	pine chip/poultry litter (50:50)	350			27.9 (0.9)
	original		53.3 (0.4)	15.9 (0.5)	
	24 h rinsed		78.4 (0.6)	11.0 (0.2)	
	fragments		82.4 (0.5)	12.0 (0.9)	
6	pine chip	700			9.7 (0.3)
	original		84.7 (1.2)	13.5 (0.5)	
	24 h rinsed		90.5 (0.2)	8.4 (0.2)	
	fragments		91.7 (1.0)	7.9 (0.6)	
7	hardwood	500			12.9 (1.6)
	original		86.4 (0.2)	20.4 (0.8)	
	24 h rinsed		92.4 (0.3)	6.3 (0.3)	
	fragments		93.0 (0.5)	5.4 (0.2)	
8	macadamia nut shell	500			18.7 (2.0)
	original		68.4 (1.2)	26.4 (1.8)	
	24 h rinsed		87.4 (3.1)	14.9 (1.2)	
	fragments		89.7 (3.2)	11.4 (4.1)	
	field exposed biochars				
F1	macadamia nut shell	500			24.9 (2.3)
	original		55.4 (2.1)	36.4 (2.8)	
	24 h rinsed		65.7 (1.1)	11.0 (2.1)	
	fragments		75.3 (2.1)	10.2 (1.9)	
F2	hardwood charcoal	550			34.9 (4.5)
	original		92.4 (1.1)	19.4 (1.8)	
	24 h rinsed		95.1 (1.8)	9.6 (1.2)	
	fragments		95.8 (3.1)	10.2 (1.4)	

[a] Processing and characterization of biochars have been outlined previously.[16,45]

mechanically stronger than the original biomass but is subject to structural fracturing at lower strains than the original biomass.[24] Furthermore, with aging (weathering), this mechanical strength is reduced.[20] These structural defects will eventually lead to the formation of fragments, when BC is exposed to additional mechanical stresses.[25] Ultimately, the comminution of BC particles leads to the creation of small liberated fragments, termed dissolved black carbon (DBC).[26]

The fate of DBC is an especially uncertain aspect of global BC cycles. The mobilization of DBC from biochar-amended soils to wetlands and riparian areas could provide a source of DBC to ground and surface waters.[17] It is also possible that DBC production is a major loss process for biochar-amended soils, reducing biochar's climate mitigation potential. However, the converse scenario is at least as plausible: it may be essential to break BC into smaller, more easily extractable fragments to improve the opportunity for these molecular pieces to react with soil minerals, creating stable organo−mineral complexes.[27,28] These complexes are known to increase native soil organic carbon residence times.[29]

Here we present data confirming the physical disintegration of biochar over short time periods (24 h), a result that has implications for this material as a soil carbon sink. Despite its documented recalcitrance to microbial reactions, biochar may be very susceptible to physical deterioration, abrasion, and subsequent transport by fluvial or alluvial processes. We suggest that physical comminution is a previously overlooked loss mechanism of biochar degradation and needs to be understood for the accurate extrapolation of biochar's soil C sequestration potential and the interpretation of charcoal's presence in the archeological and geologic record.[30]

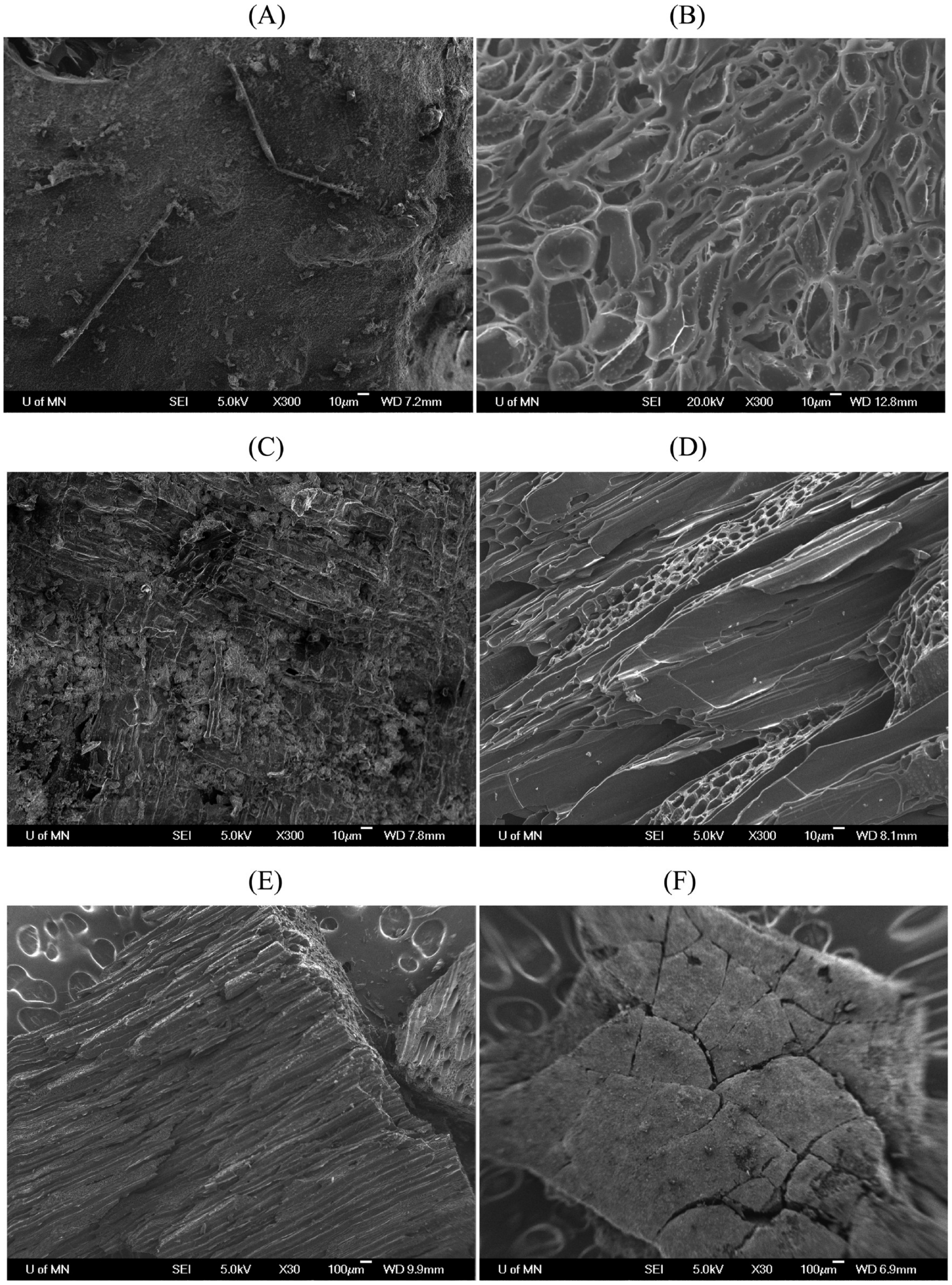

Figure 1. Representative SEM images of the (A) fresh fast pyrolysis macadamia nut biochar (BC 8), (B) rinsed fast pyrolysis macadamia nut biochar (BC 8), (C) fresh slow pyrolysis hardwood biochar (BC 7), (D) rinsed slow pyrolysis hardwood biochar (BC 7), (E) fresh slow pyrolysis hardwood biochar (BC F2), and (F) a 5 year field exposed biochar (BC F2). All images were recorded at a probe current of 5.0 kV, with each pair at identical magnifications, and the scale bar is shown in each panel.

■ MATERIALS AND METHODS

To determine whether biochar physical stability is a control on its carbon residence time, we added various biochars (5 g oven-dried weight) to distilled water [1:20 (w/w)] in triplicate 125 mL polyethylene bottles and placed the bottles in a reciprocating shaker (60 cycle min^{-1}) for 24 h. Even though this artificial weathering does not fully mimic field weathering conditions,[31] this methodology has also been used for estimating water dispersible clays,[32] batch sorption experiments,[33] and water extractable nutrients from biochar.[34] Following this agitation period, the solution was filtered (20–25 μm, Whatman No. 40). The bottle was triple rinsed [20 mL of deionized (DI) water] to remove BC particles, which were also filtered. The solid residue collected on the filter paper was oven-dried (105 °C) for 24 h and weighed to assess the overall biochar mass loss (Table 1). Because of the errors associated with manual rinsing and the difficulty removing adsorbed biochar particles from the polyethylene bottle, this method may not be 100% accurate but has been used to assess the order of magnitude mass loss through physical fragmentation of the various biochars.[35] We also conducted inductively coupled plasma-optical emission spectrometry (ICP-OES) and dissolved carbon (DOC) analyses of the filtrate to evaluate the dissolved content.

We analyzed pre- and postrinsed biochars using scanning electron microscopy–electron dispersion spectroscopy (SEM–

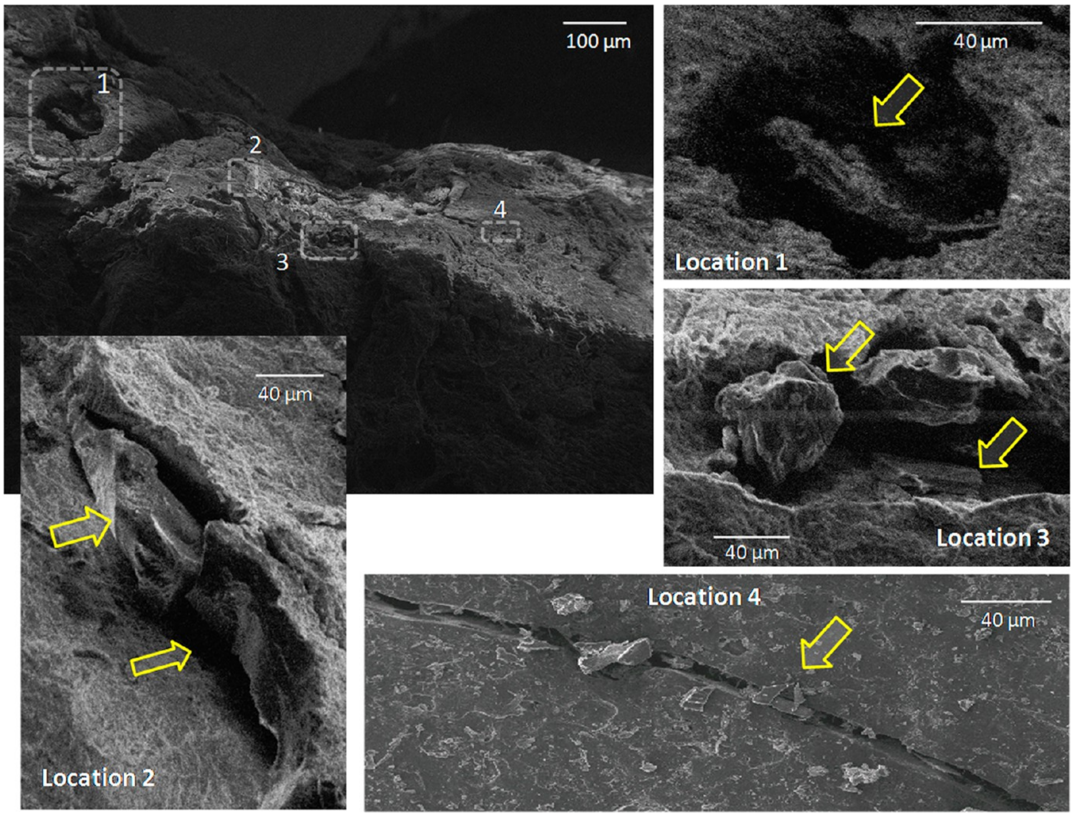

Figure 2. SEM images after a pine chip/poultry litter biochar (BC 5) had been rinsed for 24 h. Location 1 illustrates a local collapse in the BC structure (i.e., sink hole) with an approximately 100 μm liberated BC particle being formed. Location 2 illustrates the expansion of the intrasheet spacing between the graphitic layers resulting in the structural failure (fragment designated by the arrow). Location 3 illustrates the preferential erosion by water of the weaker BC layers, leading to the fragmentation of the top layer as support is removed. Location 4 illustrates a developing fracture in the biochar particle. The original biochar is shown in Figure S5 of the Supporting Information. Arrows highlight the described features.

EDS). These biochars were mounted with a carbon conductive adhesive pad (PELCO Tabs, Ted Pella, Inc., Redding, CA). In addition to the solid biochars, we also analyzed the dissolved residuals in the rinsewater by direct evaporation of 100 μL directly on the aluminum SEM mount. In addition to these artificially laboratory weathered biochars, two biochars were included that had been aged for 5 years in agricultural field plots in Rosemount, MN,[16] and compared to their laboratory stored counterparts (Table 1). These biochars were applied to an agricultural soil [Waukegan silt loam, 1% (w/w)] under continuous corn production, with annual rototilling. Biochar particles located at the soil surface were collected, rinsed with DI water attempting to dislodge the entrapped soil, and then dried at 105 °C for analysis. These biochars were also attached to the SEM mounts by carbon conductive adhesive pads (PELCO Tabs, Ted Pella, Inc.). Because of the conductivity of the charcoal, no surface coatings (i.e., gold or carbon) were used during this SEM imaging. The elemental composition was determined using the point EDS analysis method, averaging a total of 10 different representative particles and locations.[36] Unfortunately, EDS data are a semiquantitative measure of elemental concentration, and relative amounts can be inferred from differences in peak heights.[37]

■ RESULTS AND DISCUSSION

Fresh biochar had various salts and organic oils coating their surfaces (Figure 1). After being rinsed with water for 24 h, these coatings were reduced, revealing further structural details not immediately visible on the "fresh" biochar (Figure 1). A majority of these surface deposits disappeared after being rinsed with water. In many cases, the EDS data indicate a higher carbon content in the postrinsed biochar (Table 1). Some of the deposits were inorganic salts due to the presence of inorganic elements (e.g., K, Cl, Ca, Mg, P, Ca, N, and O) visualized with EDS point data analyses, which was also confirmed in the ICP-OES analysis of the rinse waters (Table S1 of the Supporting Information). From these analyses, we concluded that a majority of these deposits were precipitated surface salts, which upon being shaken with water were removed from the surface. The inorganic elements evaluated contained from 0.1 to 90% of the total mass loss observed from the biochar rinsing (Table S1 of the Supporting Information), which suggests that some of the mass lost from the biochar was DBC (see Figure 3). It is clear that these surface precipitates conceal the actual biochar surfaces and some of these salts are actually precipitated in pores limiting their immediate availability (Figure S1 of the Supporting Information). Thereby, the removal of these surface coatings through dissolution opens additional porosity. However, under field conditions, the release of these surface inorganic salts and organics would vary with climatic conditions and soil hydrology.

In addition, water-rinsed biochars showed some interesting physical surface features, including occasional microscopic erosion features (Figure S2 of the Supporting Information). These features suggest that the water shaking did remove material from the biochar surface leaving these relic erosion structures. In addition, the biochar surfaces had smaller

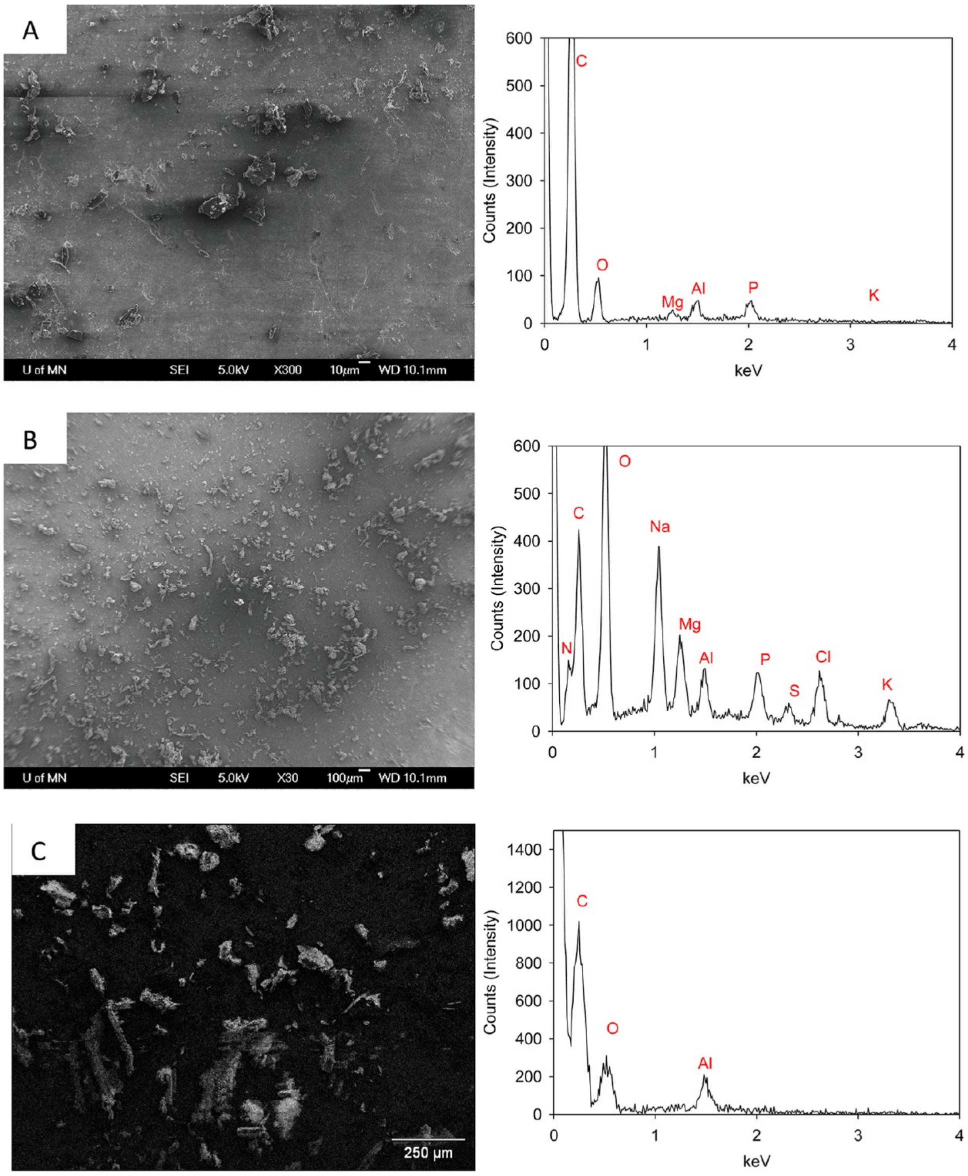

Figure 3. Illustration of observed particles in 100 μL of rinsewater evaporated on a SEM mount for (A) hardwood biochar (BC 7), (B) poultry litter biochar (BC 9), and (C) switchgrass biochar (BC 1). The corresponding spectral scan of the view areas with EDS is shown immediately to the right of each panel. The presence of an Al peak could be due to the SEM mount itself and not conclusive evidence of its presence in the biochar rinsewater (Table S1 of the Supporting Information). There is evidence of a peak for carbon, but its exact amount cannot accurately be determined from this analysis.

micrometer and submicrometer size pieces of biochar that were structurally freed from the biochar particle (Figure S3 of the Supporting Information). The results show water rinsing not only removed the fine biochar particles that are loosely attached to the biochar particle surface [via physical forces (see Figure 1A)] but also modified the surface morphology of the biochar particle itself by removing material by physical force. This exfoliation and structural friability of BC have been noted in other studies with exposure to water, particularly in an alkaline environment.[22] Biochar physical breakdown is more pronounced in lower-temperature biochars (<500 °C), where >50% of mass loss could be attributed to this physical fragmentation process.[35] This increased friability could be responsible for its quicker transport through laboratory columns.[38] Therefore, biochar particle size should not be regarded as a static property.

In addition to these comminution processes, there was also evidence of cracking and fracturing of the biochar surface with water and upon soil exposure (Figure 2 and Figure S3 of the Supporting Information). The SEM images present a suggestion of weaker layers of BC in the biochar matrix that are preferentially broken down during water extraction (Figure 2), analogous to geologic sediment layer and geologic outcrop weathering.[39] More importantly, there are visible fragments from the biochar that have broken off from the parent BC physical structure (Figure S3 of the Supporting Information). These dissociated BC fragments are estimated to range in size from nanoscale to >100 μm as estimated through measurement with the SEM software tools. This fragmentation occurs more readily in sandy textured soils (Figure S4 of the Supporting Information). From our observations, wood and high-lignin feedstocks appear to disintegrate into smaller particles more readily than the corresponding feedstocks with higher cellulose contents (e.g., manures, grasses, and corn stalks). A higher pyrolysis temperature leads to the formation of smaller fragments and, consequentially, lower physical mass loss rates. This temperature dependency has already been noted for archeological reconstructions,[35] and the biochar particle size dependency agrees with observations of biochar particle movement in a laboratory column[38] and field studies.[11]

Despite being dislodged from the original biochar particle, these biochar pieces are chemically equivalent to the original biochar as confirmed by SEM−EDS data (Table 1). In other words, these fragments do not show signs of oxidative or other chemical weathering, just physical comminution. In the evaporated portion of the water extraction, we observed <20 μm and nanoscale particles of BC that were not removed by filtration (Figure 3). The presence of nanoscale particles has been previously demonstrated for pyrolyzed BC materials[40] and could alter the mobility of sorbed organic compounds on these fragments.[41] The presence of this DBC is important, because the typical DOC analysis via persulfate UV might not adequately detect these fragments of DBC without more intense chemical oxidation conditions[42] (Table S2 of the Supporting Information). This lack of quantification might further account for the "black carbon paradox" and confirms the suggestion by Jaffe et al.[17] To put this rapid mass loss in perspective, a recent study observed <5% of the carbon in biochar was mineralized over a 8.5 year laboratory incubation.[5]

Others have observed that once biochar is exposed to soils, soil particles can fill exposed cavities and fissures[16] (Figure S4 of the Supporting Information). These sealing processes could be accelerated by exothermic water sorption onto BC surfaces[19] and accelerate desiccation drying. It is conceivable that the physical accumulation of colloidal, dissolved, and particulate material, including soluble inorganic salts and/or aluminosilicates, would rapidly infill fractures and pores[43] (Figure S4 of the Supporting Information). This infilling could potentially stabilize the BC particle from further physical degradation, analogous to the soil mineral protection of native soil organic material.[44] Soil particle stabilization of biochar does require further scrutiny but could be an essential mechanism for extending biochar's longevity, particularly in clay-rich soils.

It is well-known that natural physical processes cause abrasion on geologic materials and shape their external morphology. We hypothesize that once charcoal is placed in the soil environment, it is subject to similar weathering and aging processes that act upon all geologic materials. While a majority of the current research has focused on surface chemical and microbial reactions, our observations stress the overwhelming importance of the physical friability of biochar and the need to account for the corresponding protection mechanisms when predicting long-term soil behavior.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional SEM images of biochar structural and physical alterations and dissolved concentrations of the rinse waters (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*USDA-ARS, 1991 Upper Buford Circle, 439 Borlaug Hall, St. Paul, MN 55108. E-mail: kurt.spokas@ars.usda.gov.

Notes

The authors declare no competing financial interest.

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