An Index-Based Approach to Assessing Recalcitrance and Soil Carbon Sequestration Potential of Engineered Black Carbons (Biochars)

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Ⓢ Supporting Information

ABSTRACT: The ability of engineered black carbons (or biochars) to resist abiotic and, or biotic degradation (herein referred to as recalcitrance) is crucial to their successful deployment as a soil carbon sequestration strategy. A new recalcitrance index, the R_{50}, for assessing biochar quality for carbon sequestration is proposed. The R_{50} is based on the relative thermal stability of a given biochar to that of graphite and was developed and evaluated with a variety of biochars ($n = 59$), and soot-like black carbons. Comparison of R_{50}, with biochar physicochemical properties and biochar-C mineralization revealed the existence of a quantifiable relationship between R_{50} and biochar recalcitrance. As presented here, the R_{50} is immediately applicable to pre-land application screening of biochars into Class A ($R_{50} \geq 0.70$), Class B ($0.50 \leq R_{50} < 0.70$) or Class C ($R_{50} < 0.50$) recalcitrance/carbon sequestration classes. Class A and Class C biochars would have carbon sequestration potential comparable to soot/graphite and uncharred plant biomass, respectively, whereas Class B biochars would have intermediate carbon sequestration potential. We believe that the coupling of the R_{50}, to an index-based degradation, and an economic model could provide a suitable framework in which to comprehensively assess soil carbon sequestration in biochars.
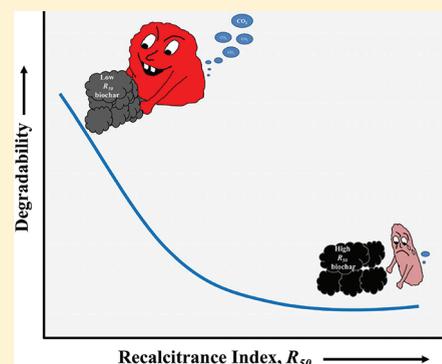
INTRODUCTION

The role of black carbon (BC; pyrogenic organic materials derived from incomplete biomass combustion) in biogeochemical cycles has received much attention in recent years. In addition to its role as an effective sorbent,[1−3] and viable soil amendments,[4−6] BC is widely recognized as an important carbon sink in the global carbon cycle.[6−9] The significance of BC as a carbon sink is due to its relatively high recalcitrance, or resistance to abiotic and biotic degradation.[10,11] Research on BC recalcitrance suggest turnover times ranging from less than a century to several millennia.[8,12−14] In general, slow turnover rates and high carbon content have led to increased interest in land application of engineered BC materials (often referred to as "biochars") as a key component in an integrative strategy for carbon sequestration to mitigate global climate change. Estimated carbon sequestration potential in these biochars range as high as 9.5 PgC yr[−14], which is of the same magnitude as current emissions estimates from fossil fuels (9.1 pgC y[−115]). A more recent estimate that takes competing uses and sustainable harvesting of biomass into account suggests a

maximum net greenhouse gas offset from biochars of 1.8 pgC y[−1.6].

The inherent variability of biochars (stemming from different feedstocks and production conditions) coupled with that of soils to which they are applied[5] suggests that the production and use of biochars, as a carbon sequestration strategy, will need to be customized for each situation. A comprehensive framework for evaluating quality and assigning value (in terms of carbon sequestration potential) or carbon credits to the different biochars, prior to land application will therefore be required. We believe an index-based framework would be a viable option for the assessment and valuation of biochars produced for carbon sequestration. Such a framework would require; (i) an index for screening/categorizing biochars based on their carbon sequestration potential; (ii) an index-based

model for predicting how long carbon would be sequestered in different biochars; and (iii) a tool for assessing the economic benefits associated with the land application of a specific category(s) of biochars.

The current study addresses the first requirement of the index-based approach, by using thermal analysis to develop an index for evaluating biochars produced for carbon sequestration. The use of thermal analysis techniques such as thermogravimetry (TG) and differential scanning calorimetry (DSC) have proven very useful in the characterization of soil organic matter (including BC).[16−20] Correlations between thermal stability and biogeochemical stability of soil organic matter have also been found.[21,22] To quantitatively evaluate the thermal stability of organic matter some indices have even been proposed.[16,17,20] However, as will be discussed later, the applicability of these indices to BC materials is limited. Leifeld[18] utilized DSC to characterize different BC materials in soils and proposed the maximum DSC peak temperature as a qualitative measure of the thermal stabilities for BC materials.

We developed and evaluated a new recalcitrance index (the R_{50}) for quantifying biochar recalcitrance and screening biochars with respect to their carbon sequestration potential. In developing the R_{50} it was hypothesized that biochars of increasingly higher environmental recalcitrance, and therefore higher carbon sequestration potential, will require increasingly higher energy inputs to oxidize/mineralize a unit mass of biochar-C to CO_2. Hence by comparing the energy required to oxidize a given mass of different biochars, a quantitative indicator of their carbon sequestration potential can be obtained. The R_{50} uses the energy required for thermal oxidation of the biochars (normalized to that for oxidation of graphite) as a measure of recalcitrance.

To evaluate the utility of the R_{50} as a screening tool for biochars of different carbon sequestration potential, we studied a broad array of biochars that were produced from different feedstocks and heat treatment conditions. The relationship between R_{50} and mineralization of biochar-C was also assessed. For comparative purposes, the R_{50} values for sootlike-BC and nonpyrogenic (e.g., cellulose, uncharred plant material, and humic acids) carbonaceous materials were also determined.

■ MATERIALS AND METHODS

Carbon Materials and Their Properties. The plant-derived biochars ($n = 59$) studied were used in three previous studies and represented 10 plant species; heat treatment temperatures (HTT) ranging from 150 to 1050 °C; full atmospheric to oxygen-limited conditions; and heat treatment durations (HTD; at desired HTT) from 0.5 to 72 h. Plant species represented include honey mesquite (*Prosopis glandulosa*), cordgrass (*Spartina spartinae*), loblolly pine (*Pinus taeda*), swamp laurel oak (*Ouercus laurifolia*), Eastern red cedar (*Juniperus virginiana*), bubinga (*Guibourtia demeusei*), Eastern gamma grass (*Tripsacum dactyloides*), sugar cane bagasse (sugar cane following industrial processing, provided from Florida Crystal Corp.), rice straw (*Oryza sativa*), and chestnut wood (*Castanea sativa*). Elemental composition (CHO) data on the plant-derived biochars were also obtained from the three studies. Details on the heat treatment conditions and analysis of biochar elemental composition are outlined in the respective studies.[11,23,24]

In addition to the plant-derived biochars we also prepared biochars from microcrystalline cellulose powder (Avicel, Sigma-Aldrich, St. Louis, MO). Cellulose biochars were prepared in a

muffle furnace under oxygen-limited condition; HTTs between 200 and 600 °C; and a HTD of 1 h. Ramp rate on the muffle furnace (up to desired HTT) was 20 °C min^{-1}. Fourier transform infrared spectroscopy was used to assess functional group chemistry of the cellulose biochars according to Harvey et al.[3]

Other BC materials studied include acetylene carbon black (Alfa Aesar, Ward Hill, MA), lampblack, *n*-hexane soot,[25] and graphite (<149 μm, purity 99.9995%; Alfa Aesar, Ward Hill, MA). The nonpyrogenic materials studied included the uncharred plant[23] and cellulose feedstocks, lignite,[26] a soil humic acid,[26] and three standard humic acids (Elliott soil humic acid, Pahokee peat humic acid, and Leonardite humic acid) purchased from the International Humic Substances Society .

Biochar Degradability. Fifteen of the biochars (produced from loblolly pine, swamp laurel oak, Eastern red cedar, bubinga, Eastern gamma grass, and sugar cane bagasse feedstocks) was previously used in a BC mineralization study.[11] Data for total biochar-C loss after 1 year from this earlier study was utilized in the current study. The BC mineralization study was conducted at 32 °C in the dark under uninoculated or microbially inoculated conditions. Uninoculated treatments consisted of 20 mg of biochar, 200 mg of cleaned quartz sand, 80 μL of aqueous nutrient solution and 20 μL of sterilized water. Microbially inoculated treatments were the same, except the sterilized water was replaced with a microbial inoculate. Further details on the composition of the nutrient solution, sampling, sample analysis and the microbial inoculate are outlined in Zimmerman.[11]

Thermal Degradation of Carbons. Weight loss and heat flow characteristics associated with the thermal oxidation of all carbon materials were studied in air (flow rate = 10 mL min^{-1}) using thermogravimetry/derivative thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC), respectively. The instrument used was a differential scanning calorimeter with capabilities for simultaneous TG-DSC analysis (SDTQ600; TA Instruments, New Castle, DE). A ceramic crucible (without lid) was used in all the analyses. With the exception of lignite and the cellulose biochars, which were grounded and/or sieved, samples were analyzed as received or extracted. All samples analyzed had particle sizes less than 250 μm. Between 14 and 16 mg of a given sample was analyzed, with the exception of the soot-like BC samples where only approximately 5 mg could be analyzed due to the lower comparative densities of these materials. Thermal analysis started at an oven-temperature of 30 °C and increased at a ramp rate of 10 °C min^{-1} until no further weight loss was observed. Cut-off temperatures were between 700 and 1100 °C.

■ RESULTS AND DISCUSSION

Thermal Degradation Characteristics of Carbons. Typical DTG and DSC thermograms obtained for the biochars and other BC materials are presented in Supporting Information Figure S1−S8. For a given black carbon material, up to three general regions of weight loss (and associated heat flow) were apparent. The first general region of weight loss and associated endothermic heat flow was apparent below 200 °C and was attributable to the loss of free and nonstructural water from the surfaces or pores of the materials.[27,28]

A second weight-loss and exothermic heat-flow peak observed in the 300−350 °C region, (and apparent only for biochars produced at HTTs <350 °C), were attributable to the thermal oxidation of cellulosic components.[27] Multiple over-

lapping weight loss and exothermic heat flow peaks with centers above 350 °C reflected thermal oxidation of more recalcitrant organic structures (e.g., lignin and thermally produced carbonized/aromatic structures). For soot-like BC, graphite and biochars produced at HTT ≥350 °C weight-loss and exothermic heat-flow peaks were focused toward much higher temperatures than exhibited by low-temperature biochars. Such differences were reflective of differences in thermal oxidation characteristics of the different BC and was consistent with qualitative assessments which suggest that biochars produced under increasing HTT will be more recalcitrant.[11,18,29]

DTG and DSC thermograms for uncharred feedstocks, humic acids and lignite also indicated differences in the thermal oxidation characteristics among nonpyrogenic carbon materials (Supporting Information Figure S9). Differences in thermal oxidation characteristics among nonpyrogenic carbon materials have long been recognized and have been used to develop various quantitative indices for characterization and assessment of thermal stabilities of nonpyrogenic soil organic matter.[20] These thermal stability indices are usually of two general forms:

$$I_x = \mathrm{Exo}_{x,m}/\mathrm{Exo}_{x,n} \tag{1}$$

or

$$I_x = \mathrm{Exo}_{x,m,\,\mathrm{or}\,n}/\mathrm{Exo}_{x,\mathrm{total}} \tag{2}$$

where, the index value I for sample x is calculated as a ratio of either (1) the weight loss associated with exotherms m and n, or (2) the weight loss associated with a given exotherm (m or n) to that for all exotherms ($\mathrm{Exo}_{x,\mathrm{total}}$). Exotherms occurring at lower temperature ranges on DTG or DSC thermograms are typically attributed to less stable or so-called "labile" organic fractions, whereas those occurring at higher temperatures are attributed to more thermally resistant or stable organics.

One critique of these types of thermal stability indices is that weight loss regions are not rigorously defined and vary significantly between studies, due to significant overlaps in the exotherms.[20] Plante et al.[30] found that even with peak deconvolution, interpretation and comparison of results would be difficult.

We found that, even with well-defined weight loss regions, current thermal stability indices may have only limited applicability to highly heterogeneous organic materials such as BCs. For instance, while an $\mathrm{Exo}_{x,1}$ (e.g., 200−350 °C) and $\mathrm{Exo}_{x,2}$ (e.g., 350−550 °C) could be defined for low temperature biochars (HTT <350 °C), no such delineation could be made for biochars produced at HTT >350 °C or highly condensed BC forms, due to the absence of a distinctive $\mathrm{Exo}_{x,1}$ in these BCs.

Rather than the weight-based approach of eqs 1 and 2, we adopted an energy-based approach for quantitatively evaluating the thermal stability of BC materials. The premise of this energy-based approach was that the amount of energy required to oxidize/volatilize a given quantity of BC will depend on the bonding environment of carbon atoms in the respective materials. That is, thermal stability is a function of bond energy. Hence, BC materials dominated by a larger proportion of C−C single bonded structures would have a lower thermal stability than those dominated by C=C, conjugated and aromatic structures.

Based on this alternative approach and the use of temperature as a measure of energy input, we propose a new recalcitrance index for quantifying the relative thermal

degradability of a broad array of BC materials. The new recalcitrance index, which we term the R_{50}, is calculated as:

$$R_{50,x} = T_{50,x}/T_{50,\mathrm{graphite}} \tag{3}$$

where $T_{50,x}$ and $T_{50,\mathrm{graphite}}$ are the temperature values corresponding to 50% oxidation/volatilization of BC material x and graphite, respectively.[31] Values for $T_{50,x}$ and $T_{50,\mathrm{graphite}}$ are obtained directly from TG thermograms (for x and graphite) that have been corrected for water and ash content. Details on how thermograms were corrected are provided in Supporting Information 2.

Equation 3 differs fundamentally from eqs 1 and 2 in several ways. Equations 1 and 2 uses weight loss as input parameters, whereas eq 3 uses temperature as a input parameter. Also in eqs 1 and 2, the index value I is defined by the thermal degradability of one organic fraction (labile or stable), is based on loosely defined temperature ranges and; uses a self-standardization approach (i.e., denominator is always from the sample of interest). In contrast, calculation of R_{50} in eq 3; considers the overall thermal degradability of a sample (i.e., both labile and stable organic fractions); is based on a single consistently defined criterion (T_{50}), and uses a common external standardization factor ($T_{50,\mathrm{graphite}}$) across all materials to be tested. The use of T_{50} in eq 3 as the only criterion for defining a sample's thermal degradability eliminates the problems associated with peak overlaps in earlier stability indices calculated using eqs 1 and 2. Standardizing to $T_{50,\mathrm{graphite}}$ also facilitates calculation of index values across a broader array of BC materials with the potential for interstudy comparison.

Thermograms for selected BCs that have been corrected for water and ash content are shown in Figure 1. These
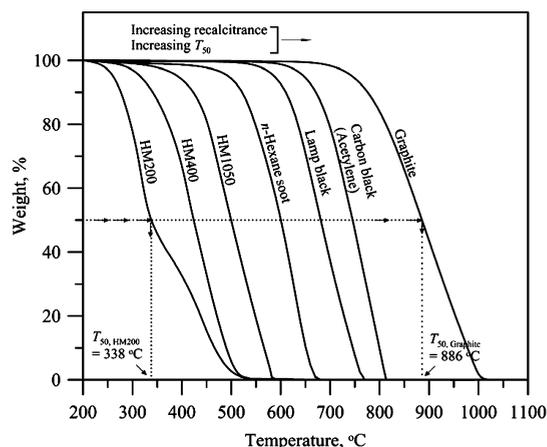
Figure 1. Water and ash content-corrected thermogravimetric thermograms for honey mesquite biochars (HM; produced at HTT of 200, 400, or 1050 °C), soot-like black carbons (n-hexane soot, lampblack, and carbon black), and graphite.

thermograms were selected to represent the full range of T_{50} values observed among the BC materials studied. Under the study conditions (10 mL min^{-1} air and 10 °C min^{-1}) the largest T_{50} observed was for graphite ($T_{50,\mathrm{graphite}} = 886$ °C), while the lowest was for biochars produced at HTTs ≤200 °C (e.g., $T_{50,\mathrm{HM200}} = 338$ °C). Trends observed with increasing T_{50} were consistent with expectations based on the BC continuum[32] and show a transition from slightly charred biomass to char/charcoal-BC to soot-BC to graphitic-BC. That is, a transition from the least environmentally recalcitrant to most environ-

Table 1. Recalcitrance Index (R_{50}) Values for Biochars Produced from Different Source Materials under Different Heat Treatment Temperatures (HTT), Heat Treatment Duration (As Hours; In Parentheses) and Atmospheric Conditions

| HTT	cellulose[a]	honey mesquite[b]	swamp laurel oak[c]	bubinga[c]	chestnut wood[d]	loblolly pine[b,c]	eastern red cedar[c]	cord grass[b]	eastern gamma grass[c]	sugar cane baggase[c]	rice straw[d]
unburnt	0.37	0.39				0.37		0.37			
200 °C	0.37(1)	0.38 (1)				0.39 (1)		0.37 (1)			
250 °C	0.42(1)	0.40 (0.5); 0.41 (1); 0.43 (3); 0.45 (5)	0.48 (3)			0.41 (1); 0.48 (3)		0.42 (1)	0.47 (3)		
300 °C	0.52(1)	0.46 (1)				0.47 (1)		0.47 (1)			
350 °C	0.55(1)	0.48 (1)				0.50 (1)		0.48 (1)			
400 °C	0.57(1)	0.48 (1)	0.48 (3)[e]			0.51 (1); 0.49 (3)[e]		0.49 (1)	0.46 (3)[e]		
450 °C	0.58(1)	0.48 (1)			0.54 (5)[e]	0.53 (1)		0.50 (1)			0.42 (5)[e]
500 °C	0.58(1)	0.52 (1)				0.53 (1)					
525 °C			0.57 (3)[e]								
550 °C	0.59(1)	0.52 (1)				0.55 (1)		0.50 (1)			
600 °C	0.61(1)	0.53 (1)				0.56 (1)		0.52 (1)			
650 °C		0.53 (1)	0.52 (3)[e]; 0.60 (72)[e]	0.54 (3)[e]		0.59 (1); 0.58 (3)[e]; 0.57 (72)[e]	0.56 (3)[e]		0.52 (3)[e]	0.54 (3)[e]	
850 °C		0.55 (1)									
1050 °C		0.56 (1)									

[a]Biochars produced for this study. [b]Biochars from Kuo et al.[23] [c]Biochars from Zimmerman.[11] [d]Biochars from Hammes et al.[24] [e]Produced under full nitrogen, instead of oxygen-limited conditions.

mentally recalcitrant BCs.[32] The fact that graphite had the largest T_{50} of all BC is consistent with its position as the upper-end member in the BC continuum and serves to normalize the R_{50} values on a scale of 0 to 1.

Relationships between R_{50}, Biochar Formation Conditions and Biochar Properties. Calculated R_{50} values for the biochars ranged from 0.37 to 0.61 (Table 1). Values at the lower end of the R_{50} range were obtained for those biochars produced at HTT ≤200 °C, and were comparable to those obtained for uncharred plant material. On the other hand, values at the upper-end of the range were obtained for biochars typically produced at HTT ≥350 °C but were lower than R_{50} values for soot-like BC (0.68−0.84), and reflected an increase in R_{50} with HTT.

Pearson correlation analysis revealed that R_{50} was indeed significantly correlated with HTT ($r = 0.812$, $n = 59$, $p < 0.01$). For biochars produced under oxygen-limited conditions and a heat treatment duration of 1 h the R_{50}-HTT correlation was higher ($r = 0.921$, $p < 0.01$). There was also some evidence to suggest that R_{50} was also influenced by charring duration (Table 1). This was not surprising since charring duration is known to have similar effects on biochar properties as HTT.[33] However, regardless of biochar formation conditions, we found no significant differences (Mann−Whitney U test, $p > 0.10$) in R_{50} across the three major plant categories (hardwoods, softwoods, grasses). Our data thus suggests that biochar formation conditions were the primary factors controlling thermal stability of the biochars.

The highest R_{50} values were observed in biochars with the highest carbon contents, suggesting that the influence of formation conditions on the degree of biochars carbonization/aromatization was a major factor driving their thermal recalcitrance (Figure 2). This was also supported by evidence from a modified van Krevelen plot, which shows that R_{50} generally increases along the course of condensation toward the
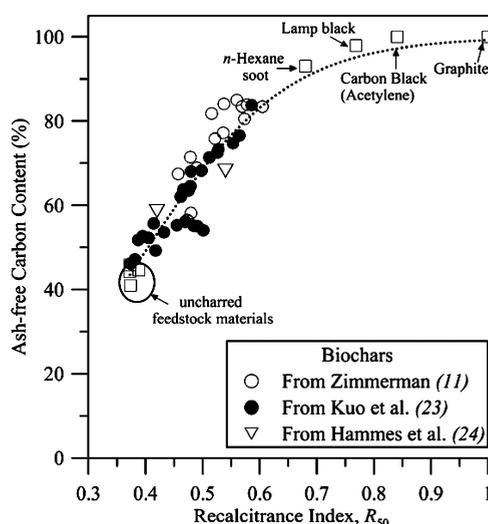
Figure 2. Variation in recalcitrance index (R_{50}) with carbon content of biochars, soot-like black carbon (*n*-hexane soot, lampblack, and carbon black) and graphite.

more aromatic carbon forms (Figure 3, refs 23,24,34) and was consistent with observations from previous studies which show that increase in environmental recalcitrance of BC was attributable to thermal transformation of feedstock materials to form increasingly carbonized/aromatized structures.[10,29,35−38] Figure 3 also suggested that in some cases BCs (e.g., graphite and carbon black, *n*-hexane soot and HM850, or CW450 and RS450) may have comparable H/C and O/C ratios, but very different thermal recalcitrance (as determined by R_{50}). One plausible explanation for such occurrences is that, despite similar atomic ratios, the O, H, and C atoms in the structure of these BC materials are arranged differently. For example, although carbon black and graphite
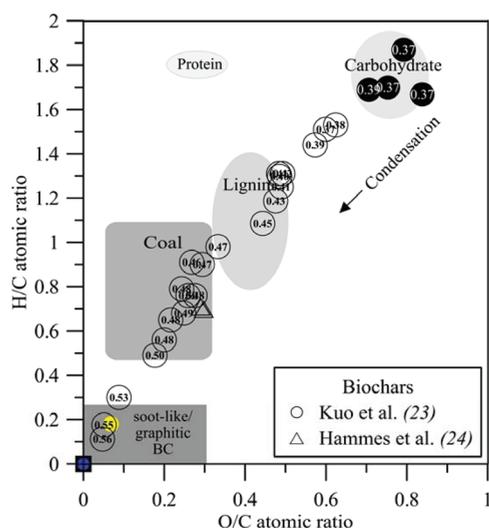
Figure 3. van Krevelen plot showing relationship between elemental composition (H/C and O/C atomic ratios) and recalcitrance index value (R_{50}; numbers in symbol) for uncharred plant materials (black circle), biochars (open circle and open triangle), soot (yellow circle), carbon black (black square) and graphite (blue circle). The shaded areas represent different biomolecules or refractory materials.[24,34].

samples both had no detectable quantities of H or O, graphite is known to have higher aromaticity and therefore a higher recalcitrance ($R_{50} = 1$) than carbon black ($R_{50} = 0.84$). Differences in thermal recalcitrance between *n*-hexane soot ($R_{50} = 0.68$) and biochars (e.g., HM850; $R_{50} = 0.55$) of comparable H/C and O/C ratio, or biochars (e.g., CW450 and RS450 biochars from Hammes et al.[39]) of equal H/C or O/C ratios, could also be plausibly explained by differences in degree of carbonization/aromatization. In the case of the CW450 and RS450 biochars, in addition to a 13% difference in carbon content, solid state 13C NMR data from Hammes et al.[39] suggested a 12−13% higher aromaticity (2−3% more of total C as aromatic C) in CW450 ($R_{50} = 0.53$) than RS450 ($R_{50} = 0.42$). Other factors such as particle size and surface area could also influence thermal oxidation results.

Available infrared spectroscopic data on the biochars also provided additional evidence to support a link between R_{50} and biochar physicochemical properties. Harvey et al.[3] presented infrared spectra for 12 of the 59 biochars used in this study (HM and PI biochars produced at HTT 200, 300, 350, and 650 °C; plus CG biochars produced at HTT 200, 300, 350, and 550 °C). They found that, as with the R_{50} values for these biochars (Table 1 of this study), biochar condensation (as evident by decreased OH, C=O, C−CH$_n$ character and a increased in C = CH$_n$ and C=C character) increased with HTT. The same trends were also apparent from R_{50} and infrared spectra for cellulose biochars (made in this study; Supporting Information Figure S10).

Links between R_{50} and Biochar Environmental Degradability. Although thermal analysis has proven useful in differentiating organic materials of varying physicochemical properties, experimental results pertaining to a direct link between thermal and environmental degradability are mixed.[22,40] We used available carbon mineralization data from Zimmerman[11] and corresponding R_{50} data from 15 biochars to assess the link between thermal and environmental recalcitrance. The biochars represented a range of plant feedstocks (grass, softwood, and hardwood) and biochar formation

conditions (HTT, HTD, as well as oxygen-limited and nitrogen atmosphere).

Within the limit of R_{50} values obtained in this study for BC materials (0.37−1) and the one-year incubation period (of the degradation study), a strong negative exponential-type relationship between BC degradability and thermal recalcitrance was apparent (Figure 4).
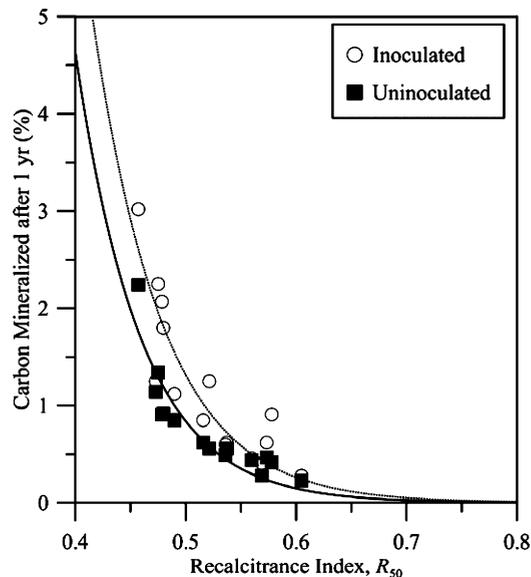
Figure 4. Relationship between recalcitrance index (R_{50}) and the amount of carbon mineralized (after 1 year of incubation) in quartz sand, under uninoculated and inoculated conditions.[11].

Changes in the slope of the mineralized carbon-R_{50} relationship defined in Figure 4 suggest that biochars (or BC and organic matter in general) can be classified into at least three groups having different susceptibilities to environmental degradation. In light of ongoing research, we tentatively define three of these groups as Class A, Class B, and Class C carbons. Class A carbons have $R_{50} \geq 0.70$ and exhibit minimal susceptibility to biodegradation under the experimental conditions employed.[11] Under the same conditions, Class B carbons ($0.50 \leq R_{50} < 0.70$) exhibit some susceptibility to biodegradation, but to a much lesser extent than Class C carbons ($R_{50} < 0.50$).

Interestingly, the less recalcitrant Class C carbons in Figure 4 were all produced under low HTT conditions (HTT = 200 or 400 °C), while the more recalcitrant Class B carbons were produced under high HTT conditions (HTT = 525 or 650 °C). This matches well with expectations based on earlier discussions on biochar physicochemical properties, and recently published data on solvent-extractable biomolecules.[41] Kuo et al.[41] found that detectable quantities of solvent-extractable/leachable anhydrosugars and methoxylated phenols (from thermal degradation of cellulose/hemicellulose and lignin, respectively) were only present in biochars formed at HTT <400 °C. Considering that these leachable biomolecules are likely to form a significant part of the bioactive or "labile" fraction of the biochars, it would be reasonable to suggest that biochars in Class A and B are more recalcitrant (than those in Class C) at least partly due to the removal of labile biopolymers and the significant increase of aromatic structures during the pyrolysis process. This could also explain the converging nature of the uninoculated and inoculated mineralization data sets

shown in Figures 4, with biodegradability shifting from being microbial population-limited in low R_{50} (Class C) biochars to being labile substrate-limited in high R_{50} (Class A and B) biochars.

Environmental Significance and Future Research. The successful, large-scale deployment of land application of biochars as a carbon sequestration strategy will require both pre- and postapplication assessment of biochar quality with respect environmental recalcitrance. To our knowledge, an established framework in which to conduct such quality assurance/quality control checks does not currently exist. Although many advanced biochar characterization techniques are available, the associated cost and time of analysis make them prohibitive to extensive application. We believe that the R_{50}, as part of an index-based framework, provides an easy, inexpensive, fast and universally applicable approach for assessing the environmental recalcitrance (and carbon sequestration potential) of biochars. As presented in this paper, the R_{50} could be immediately applied to the pre-application screening of engineered carbons into Class A ($R_{50} \geq 0.70$), Class B ($0.50 \leq R_{50} < 0.70$), or Class C ($R_{50} < 0.50$) recalcitrance/carbon sequestration classes. In a given soil environment, Class A and Class C biochar would have comparable recalcitrance and carbon sequestration potential to soot/graphite and uncharred plant biomass, respectively, whereas a Class B biochar would have intermediate recalcitrance and carbon sequestration potential. By coupling R_{50} with other important parameters such as water holding and cation exchange capacity, biochars could be screened to find an "optimum" biochar when custom applications involving auxiliary benefits (e.g., soil improvement) are targeted.[42]

We are also cognizant of the fact that absolute environmental recalcitrance will be a function of both biochar properties and soil environment.[43] For example, sorption of soil organic matter to biochar has been proposed to result in greater carbon sequestration than by the added biochar alone.[35] Therefore, any framework for assessing biochar should account for the effect of environmental factors such as temperature, moisture, mineralogy, and organic matter of soils on degradability.[43−46] To this end, we have initiated the development of a R_{50}-based model that would account for variability in pertinent environmental conditions and predict degradation and carbon sequestration potential of a given biochar over time. In addition to estimates of carbon loss over time, such a model could also be coupled to an economic model to assess the long-term trade-offs of land applying a biochar of a given R_{50} compared to other alternatives.

ASSOCIATED CONTENT

ⓈSupporting Information
Additional data on the thermal degradation of the various carbons are presented in Supporting Information 1. Information on correcting TG thermograms for ash and water content is provided in Supporting Information 2. Tabulated values of R_{50} for other materials tested in Supporting Information 3. Additional data on link between R_{50} and biochar properties are presented in Supporting Information 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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