

# The Stability of Biochar in the Environment

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## Introduction

### 1 Biochar Recalcitrance and Lability

### 2 Biochar Loss—Rates and Models

#### 2.1 Short-Term Laboratory Incubations

#### 2.2 Biochar Mineralization Models

#### 2.3 Field Studies

### 3 Mechanisms of Black Carbon and Biochar Loss

#### 3.1 Biotic Black Carbon Degradation

#### 3.2 Abiotic Oxidative Black Carbon Degradation

#### 3.3 Non-Oxidative Abiotic Black Carbon Loss

#### 3.4 Black Carbon Loss by Leaching

#### 3.5 Black Carbon Losses by Erosion/Translocation

#### 3.6 Black Carbon Losses by Later Fires

### 4 Biochar-Soil C Interaction and Stability

### 5 Mechanisms of Biochar Stabilization

## Conclusions and Summary

## References

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## Introduction

Pyrogenic organic matter (OM) is a carbon-rich material that is present in a variety of forms ranging from lightly charred biomass to charcoal to soot (Masiello 2004). It is known as 'black carbon' (BC) by geochemists and has come to be referred to as 'biochar' when created by pyrolysis in oxygen-limited conditions. An understanding of the effects of biochar amendment on soil nutrient cycling, water balance, ecology, soil fertility and other associated beneficial properties is still emerging. However, it has long been clear that biochar, as a relatively refractory form of OM, can be used as a carbon (C) sequestration tool. That is, biomass C in its pyrogenic form is less susceptible to remineralization (i.e., conversion back to  $\text{CO}_2$  and perhaps  $\text{CH}_4$ ) in the environment than its non-pyrogenic form.

Understanding and quantifying the longevity of different types of biochar in the soil environment is important for a number of reasons. First, making up between 5–30% of soil and sediment organic C (Skjemstad et al. 2002, Song et al. 2002, Masiello and Druffel 2003), BC represents a large but poorly quantified portion of the surficial global carbon cycle. Atmospheric  $\text{CO}_2$  concentrations and associated climate changes of the past, as well as the historical record of fire occurrence, may be linked to the stability of BC in the environment. And any changes in the incidence of fire that occur with global climate change may, through BC, represent either a positive or negative climate change feedback, depending upon BC-soil-fire dynamics. Second, one who amends a soil for the purpose of fertility enhancement with a specific biochar type surely would wish to know how long those benefits could be expected to last. Some of these benefits are likely related to total soil C content, while other benefits may be related to other characteristics of biochar which may change over time (Ding et al. 2010, Graber et al. 2010, Mukherjee 2011). Lastly and most relevant to the present discussion, the large scale adoption of biochar soil amendment could potentially offset a substantial portion of the C released by humans through the burning of fossil fuels and thus serve as an important climate change mitigation tool. A recent estimate based on available waste biomass quantities, available land not already dedicated to food production, and C conversion efficiencies, predicted that biochar could offset up to 12% of annual net  $\text{CO}_2$ -C equivalent emissions (Woelf et al. 2010). Additional benefits may be derived from improved water use efficiencies and, should C sequestration activities be assigned a monetary value such as by C offset trading, rural economies could benefit as well. For this to occur, however, an accurate and long-term accounting system of the effect of biochar amendments of specific types on soil C would need to be developed.

This chapter is intended to review current knowledge on the stability of soil-amended biochar C as well as its effect on non-biochar soil C. Aspects

of this subject have been reviewed previously (Lehmann et al. 2009, Spokas 2010, Knicker 2011). This work will focus on more recent advancements that have been made in this area, on topics not covered by those reviews, and will present previously unpublished data on these topics generated in our laboratories. We have also assembled data summary tables to compare rates of biochar C losses that have been measured in the field and laboratory by various means. The different measurement approaches will be evaluated in addition to models used to simulate degradation data and predict future C losses.

Although the focus of this chapter is on carbon, it should be understood that, as biochar is made up of 50–90% C by weight, the longevity of biochar C can represent the longevity of biochar as a whole. Also, the term biochar is used here when referring to pyrogenic material produced by humans, the term black carbon (BC) for pyrogenic material produced in nature. The terms are used somewhat interchangeably, however, when discussing generic concepts of pyrogenic OM.

## 1 Biochar Recalcitrance and Lability

According to Sollins et al. (1996), 'stabilization' of an organic material refers to its resistance to loss via degradation, erosion or leaching. The latter two processes will be discussed later, while biochar degradation or 'mineralization', i.e., conversion to an inorganic carbon form such as  $\text{CO}_2$  via abiotic or cellular respiration processes, is discussed here. The presumption of biochar's or BC's relative resistance to degradation, or 'recalcitrance', in soil rests on a number of observations. Simplest is the very presence of old charcoal in soil. Soil charcoal  $^{14}\text{C}$  dates can be thousands of years in age, much older than the organic carbon found in the same soil horizon (e.g., Glaser et al. 2001, Pessenda et al. 2001, Schmidt et al. 2002, Pessenda et al. 2005). *Terra preta*, BC-rich soils produced by pre-Columbian Amazonians through some method of burning, are surrounded by tropical soils with very little organic C, thus, are further testament to the relative recalcitrance of pyrogenic C.

The chemical recalcitrance of BC that has been observed in the laboratory also implies longevity in the environment. First, biochar is relatively resistant to acid, base and oxidant extraction. Thus, removal of non-BC carbon by chemical extraction followed by C analysis has long been used to quantify soil and sediment BC (Kuhlbusch 1995, Gustafsson and Gschwend 1998), though more recent research has found significant C losses using harsher extractants (Kurth et al. 2006, Hammes et al. 2007). Second, the molecular structures making up BC are known to be relatively resistant to microbial enzymatic attack (further discussion below).

On the other hand, some older and many recent studies have shown that BC degradation does occur. These include laboratory incubation experiments, measurements indicating C loss in the field over time, and observations of a degree of BC solubility. Each will be discussed in greater detail below and the various processes for C loss from biochar-amended soils compared. Assuming today's BC production rate via natural biomass burning of 50–270 Tg C year<sup>-1</sup> (Kuhlbusch and Crutzen 1995), it has been calculated that 25–125% of the total soil organic C would have been produced as BC in just 20,000 years (Masiello and Druffel 2003). It is clear, then, that there must be BC losses, otherwise soil carbon would now be primarily BC. Czimczik and Masiello (2007) have termed this apparent contradiction the 'paradox of refractory-labile BC'. A solution to this paradox is surely in the heterogeneous chemical composition of biochar, both within any particular biochar type and across the different forms of biochar produced by different methods and from different feedstocks.

Molecular analysis of biochars reveals that, with heat treatment, or 'charring', plant biomass undergoes chemical transformations toward progressively more refractory molecular structures. Elemental analysis, and solid-state <sup>13</sup>C nuclear magnetic resonance (NMR) and Fourier Transform Infrared (FT-IR) spectroscopy have shown that, starting at temperatures as low as 250°C, the cellulose, pectin and lignin that make up the majority of plant dry biomass, is altered, predominantly by dehydration, to phenol, furan, aromatic and some alkyl C structures with substantial O, H and S substitutions (Baldock and Smernik 2002, Knicker 2007, Knicker et al. 2008, Keiluweit et al. 2010). At higher temperatures of 400–500°C and beyond, progressive depolymerization, loss of functional groups, aromatization, dehydrogenation reactions and removal of substituents occurs, resulting in larger sheets of fused aromatic rings. These condensed structures would likely be very resistant to biotic or abiotic degradation, as would the graphitic 'turbostratic crystallites' that have been observed to form at temperatures >600°C (Kercher and Nagle 2003, Keiluweit et al. 2010). Thus, the idea of a 'combustion continuum', attributed to Goldberg (1985) and popularized by Masiello (2004), was introduced, representing the degree of condensation and range in chemical structures represented by BC and biochar, with increasing temperature from slightly charred biomass to soot, and by implication, the range in environmental recalcitrance.

While the above discussion implies that production of recalcitrant molecules via heating is the primary cause of biochar's recalcitrance, the resistance of organic materials to abiotic or biotic degradation depends on a great variety of factors. In fact, the very idea of 'molecular-recalcitrance', as reviewed by Kleber (2010), is one that is only a "semantic convenience and not a useful classification of material properties". The resistance of biochar to degradation will likely vary with many additional intrinsic

properties such as macro- and micro-pore structure, solubility, surface affinity for other soil components and extrinsic or environmental factors, such as pH, oxidant concentration, moisture level and soil composition and structure. The idea of biochar stability in the environment will evolve only as the understanding of its molecular composition grows, but also as we understand the biogeochemical interactions of each of its components with the environment in greater detail.

## 2 Biochar Loss—Rates and Models

### 2.1 Short-Term Laboratory Incubations

There have been a large number of recent publications investigating the stability of biochar. The great majority of them employ *in vitro* laboratory incubations of biochar alone or in soil and measure carbon dioxide (CO<sub>2</sub>) efflux into the headspace of incubation chambers. Incubations of biochar with soil measure net C efflux from both the biochar and the soil and include the effects of soil-biochar interaction. These will be discussed separately. Results of a number of studies of these types that have examined mineralization of biochar-alone are shown in Table 1. Most commonly, these experiments were performed in cleaned quartz sand brought to 65% water holding capacity (WHC), were inoculated with a soil microbial consortia and a nutrient solution, and were incubated at 30°C in the dark. Conditions departing from these are indicated in Table 1. In order to calculate the biochar C mean residence times (MRT) and half-lives listed in Table 1 from the cumulative amount of effluxed CO<sub>2</sub>, an exponential (first-order) decay pattern was assumed such that:

$$\text{BC mineralized}_{(\text{time } t - \text{end of incubation})} = \text{BC}_{(\text{initial})} (1 - e^{-kt}) \quad (\text{Eq. 1})$$

where  $k$  is the apparent first-order degradation rate constant with units of inverse time. The MRT can then be calculated as  $1/k$  and C half-life as  $\ln(2)/k$ . This has been called a '1G degradation model' because it assumes that the material, biochar in this case, is composed of one component degrading at a single rate.

The amount of biochar observed to have been mineralized in microbial incubations ranges from 0.3% (for oak wood pyrolyzed at 800°C for 24 h incubated over 60 d, Hamer et al. 2004) to 22.2% (for corn pyrolyzed at 250°C and incubated over 1 y at 60°C, Nguyen and Lehmann 2009). Calculated MRT of biochar C ranges from 3.1 y (for wheat straw pyrolyzed at 525°C for a few seconds incubated over 65 d, Bruun et al. 2012) to 658 y (for oak wood pyrolyzed at 650°C for 72 h and incubated over more than 3 y, extension of Zimmerman 2010 study). The data in Table 1 illustrate a number of trends that have been consistently observed in these types of studies. First, and

Table 1. Summary of results of studies measuring biochar mineralization in laboratory incubation by CO<sub>2</sub> efflux.

Source	Biochar Type (feedstock & production conditions)	Incubation Method <sup>1</sup>	Incubation period (d)	Biochar C (weight %)	Biochar C% mineralized <sup>2</sup>	Biochar C MRT <sup>3</sup> (y)	Biochar C Half-life <sup>3</sup> (y)
Baldock and Smerrik 2004	pine sapwood, 200–350°C, 72 h, w/O <sub>2</sub>	25°C	120	47.9–67.3	<2%		
Hamer et al. 2004	maize, 350°C, 2 h in muffle furnace in closed steel containers	20°C	60	66.4	0.8	21.0	14.6
"	rye straw "	20°C	60	66.3	0.7	22.7	15.8
"	oak wood, 800°C, 20–24 h	20°C	60	78.5	0.3	63.1	43.8
Nguyen and Lehmann 2009	corn residue, 350°C, 60% WHC	C loss determined by TOC difference	365	67.5	21.2	4.2	2.9
"	corn residue, 600°C, 60% WHC		365	79.0	11.2	8.4	5.8
"	oak wood, 350°C, 60% WHC		365	75.9	8.1	11.8	8.2
"	oak wood, 600°C, 60% WHC		365	88.4	8.9	10.7	7.4
"	corn residue, 350°C, 100% WHC		365	67.5	10.9	8.7	6.0
"	corn residue, 600°C, 100% WHC		365	79.0	9.4	10.1	7.0
"	oak wood, 350°C, 100% WHC		365	75.9	6.2	15.6	10.8
"	oak wood, 600°C, 100% WHC		365	88.4	8.6	11.1	7.7
Zimmerman 2010	Oak, 250°C, 3 hr		365	55.2	1.5	65	45
"	grass, 250°C, 3 hr		365	52.7	1.1	93	65
"	oak, 650°C, 3 hr	sterilized	365	78.8	0.6	169	117
"	grass, 650°C, 3 hr	sterilized	365	63.8	0.5	220	153
"	oak, 650°C, 72 hr	sterilized	365	77.3	0.3	329	228
"	oak, 250°C, 3 hr		365	55.2	2.5	39	27
"	grass, 250°C, 3 hr		365	52.7	1.2	85	59

"	oak, 650°C, 3 hr		365	78.8	0.8	124	86
"	grass, 650°C, 3 hr		365	63.8	1.1	92	64
"	oak, 650°C, 72 hr		365	77.3	0.4	278	193
Zimmerman <sup>4</sup>	Oak, 250°C, 3 hr	sterilized	1173	55.2	3.4	93	65
"	grass, 250°C, 3 hr	sterilized	1173	52.7	3.0	104	72
"	oak, 650°C, 3 hr	sterilized	1173	78.8	1.1	298	206
"	grass, 650°C, 3 hr	sterilized	1173	63.8	0.9	351	243
"	oak, 650°C, 72 hr	sterilized	1173	77.3	0.5	658	456
"	oak, 250°C, 3 hr		1173	55.2	3.9	81	56
"	grass, 250°C, 3 hr		1173	52.7	2.0	156	108
"	oak, 650°C, 3 hr		1173	78.8	1.1	279	193
"	grass, 650°C, 3 hr		1173	63.8	1.9	166	115
"	oak, 650°C, 72 hr		1173	77.3	0.5	587	407
Nguyen et al. 2010	corn, 350°C, slow pyrolysis (BEST Energies)	4°C	365	67.5	9.9	9.6	6.6
"	corn, 350°C, "	60°C	365	67.5	22.2	4.0	2.8
"	corn, 600°C, "	4°C	365	79	5.4	18.0	12.5
"	corn, 600°C, "	60°C	365	79	18.4	4.9	3.4
"	oak, 350°C, "	4°C	365	75.9	3.3	29.8	20.7
"	oak, 350°C, "	60°C	365	75.9	15.4	6.0	4.1
"	oak, 600°C, "	4°C	365	88.4	0.8	124.5	86.3
"	oak, 600°C, "	60°C	365	88.4	13.6	6.8	4.7
Cross and Sohi 2011	sugarcane bagasse, 350°C, 40 min		14	56.2	0.8	4.7	3.3

Table 1. contd....

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Source	Biochar Type (feedstock & production conditions)	Incubation Method <sup>1</sup>	Incubation period (d)	Biochar C (weight %)	Biochar C% mineralized <sup>2</sup>	Biochar C MRT <sup>3</sup> (y)	Biochar C Half-life <sup>3</sup> (y)
"	sugarcane bagasse, 550°C, 40 min		14	59.3	0.3	14.7	10.2
Bruun et al. 2012	wheat straw, 525°C, 2 hr	35% WHC	65	69.9	2.9	6.1	4.2
"	wheat straw, 525°C, few seconds		65	49.3	5.5	3.1	2.2

## Notes:

1. All incubation at 65% water holding capacity (WHC), in cleaned quartz sand, with microbial and nutrient inoculation added, in dark, at 30°C, unless otherwise indicated.
2. Portion of initial biochar mineralized as measured by analysis of CO<sub>2</sub> efflux.
3. MRT = Carbon mean residence time = 1 / apparent degradation rate constant  $k$ ;  $t_{1/2}$  = Carbon half life =  $\ln(2) \times \text{MRT}$ .
4. These data from an unpublished continuation of incubations reported on in Zimmerman (2010).

most apparent, biochars created at higher temperatures are more resistant to mineralization than biochar made at lower temperatures (e.g., Baldock and Smernik 2002, Hamer et al. 2004, Nguyen and Lehmann 2009, Nguyen et al. 2010, Zimmerman 2010, Cross and Sohi 2011, Bruun et al. 2012). In addition, biochar pyrolyzed for a longer period of time is also more recalcitrant than biochar made of the same feedstock and peak pyrolysis temperature (e.g., Zimmerman 2010, Bruun et al. 2012). In general, biochars made from grasses are more labile than those made from woody material, though this relationship is not as consistent.

Thus, loss of functional groups and aromatization and other chemical changes that occur with increasing pyrolysis temperature and time at elevated temperature, can explain variability in biochar recalcitrance. The volatile matter (VM) content of a charcoal has been suggested as a measure of the degree of thermal alteration or carbonization of a biomass (Antal and Gronli 2003) and high VM biochars have been shown to contain abundant phenolic compounds compared to very few in low VM biochar (Deenik et al. 2010). Though possibly having some adverse effects on plant growth (Deenik et al. 2010, Deenik et al. 2011, Wang et al. 2011, Yang et al. 2011), these compounds have been shown to be available C sources for microbial respiration (Saravanan et al. 2008, Lepik and Tenno 2012, Pradhan et al. 2012). Biochar VM content can be easily approximated according to an ASTM method (D1762–84 1990) as the weight lost when a charcoal is heated in a covered crucible at 950°C for 6 min. As such, it has been suggested that VM might be used as a convenient estimator of short-term biochar lability (Zimmerman 2010, Deenik et al. 2011). Using the set of 28 biochars described in Zimmerman (2010), which include six biomass types and charring temperatures ranging from 250 to 650°C, strong relationships were found between biochar VM content and %biochar C lost over a 1 year incubation with and without microbes (Figs. 1a and 1b, respectively). Similarly strong relationships were also found between %biochar C lost and other interrelated parameters that have been suggested as useful indices of biochar stability such as biochar molar O:C<sub>organic</sub> ratio (Spokas 2010) and molar H:C<sub>organic</sub> ratio (IBI 2012).

It is also clear from Table 1 that experimental conditions affect biochar C degradation. Among the factors that have been observed to increase biochar C mineralization in these types of short-term incubations are increases in temperature (Nguyen et al. 2010) and moisture level (Nguyen and Lehmann 2009), and decreases in biochar particle size (Zimmerman 2010). Other factors that are likely important but have not yet been shown to alter mineralization rate include microbial population size and type, oxygen and nutrient level, and biochar/support mineral ratio. Among the greatest influences on the calculated longevity of biochar, however, is the time period over which the incubation is carried out. This can be clearly

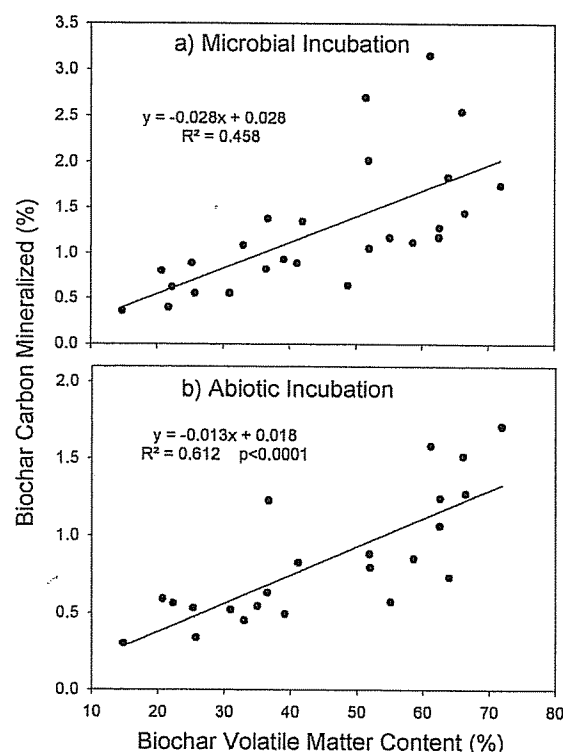


Figure 1. Relationship between biochar volatile matter content and C loss as measured by CO<sub>2</sub> efflux from a) microbial, and b) abiotic incubations. Recalculation of data presented in Zimmerman (2010).

seen by a comparison between the short incubations of Cross and Sohi (2011) and Bruun et al. (2012) which yielded biochar C half-lives ranging from 2 to 10 y (14 and 65 d, respectively), to that of Zimmerman (2010) which yielded half-lives ranging from 27 to 193 y (1 year incubation), to that of a previously unpublished extension of the Zimmerman (2010) incubations to 1173 d which yielded half lives of 56 to 407 y, almost two times greater on average. Thus, selecting an appropriate modeling approach becomes important for accurately predicting biochar C longevity.

## 2.2 Biochar Mineralization Models

The trend of increasing projected biochar C half-life with increasing incubation period can be explained by the realization that biochar is not a homogeneous material degrading at a single rate of exponential loss (as

assumed by the 1G model, Eq. 1). Though the short-term incubation data are well-fit to this model ( $r^2$  values in Table 2), this does not imply ability to predict long-term degradation. The biochar C losses predicted over 100 y range 13–61% (Table 2), do not seem realistic and are much greater suggested by field data (see below).

It is likely that biochar is, instead, a heterogeneous material composed of multiple components that degrade, both biotically and abiotically, at different rates. Thus, another approach commonly used is to model biochar (or soil as a whole) as a mixture of two components (thus, a '2G model'), one which degrades readily (BC<sub>1</sub>) and another more recalcitrant fraction (BC<sub>2</sub>). These may represent the VM or soluble portion of biochar and the fixed or condensed C fraction, respectively. To apply this approach, the course of CO<sub>2</sub> evolution from biochar can be fit to a double-exponential model using the equation:

$$BC_t = BC_1(1 - e^{-k_1 t}) + BC_2(1 - e^{-k_2 t}) \quad (\text{Eq. 2})$$

where  $k_1$  and  $k_2$  are the apparent first order degradation rate constants for the labile and refractory pools, respectively, and all biochar C is assumed to be degradable such that  $BC_{\text{total}} = BC_1 + BC_2$ . Results of this approach are also well-fit to the data and indicate that a very small portion of the biochars (0–2.4%) degrade very quickly (with half-lives of 1 y or less) and the remainder degrades with half-lives ranging 100's to 1000's of years (Table 2). However, predicted long-term loss rates of 2–59% still may be higher than expected given the longevity of charcoal in soil.

Another modeling approach, utilized by Zimmerman (2010), is one which assumes biochar to be composed of an infinite number of components, with a corresponding continuum of first-order degradation rates (i.e., a time-dependant  $k$ ). Reactivity continuously and exponentially decreases as the more labile, or perhaps, the more physically accessible organic compounds oxidize or solublize, leaving behind a progressively more refractory or more physically inaccessible residue. The assumption of a wide chemical heterogeneity for biochar is in line with the observation that biochars of different types degrade at different rates (e.g., Zimmerman 2010), are of variable chemical reactivity (Knicker et al. 2007, Knicker et al. 2008) and have organic compound sorption isotherms indicative of heterogeneous substances (e.g., Cornelissen et al. 2006, Kasozi et al. 2010).

The decrease in the reactivity of any organic matter mixture, biochar in this case, has been modeled with a power function (Middleburg 1989) that relates  $k$  to time ( $t$ ), and can be linearized as:

$$\log(k) = -m \log(t) - b \quad (\text{Eq. 3})$$

with  $m$  and  $b$  as the slope and intercept, respectively, of the  $\log(k)$  versus  $\log(t)$  relationship and can be solved graphically. Table 2 provides  $k$  values

Table 2. Comparison of laboratory incubation biochar degradation rate parameters using three different degradation models.

Biochar Type <sup>1</sup>	Abiotic Incubation			Microbial Incubation						
	Grass 250	Grass 650	Oak 250	Oak 650	Oak 650 (72h)	Grass 250	Grass 650	Oak 250	Oak 650	Oak 650 (72h)
1G Model <sup>2</sup>										
$k$ (yr <sup>-1</sup> )	4.6E-03	1.9E-03	5.7E-03	2.6E-03	1.0E-03	9.4E-03	5.2E-03	8.8E-03	3.7E-03	1.4E-03
$r^2$	0.98	0.93	0.97	0.92	0.91	0.95	0.98	0.95	0.95	0.93
C $t_{1/2}$ (y)	150	358	121	266	687	74	133	79	187	484
C loss-10y (%)	4.5	1.9	5.6	2.6	1.0	9.0	5.1	8.4	3.6	1.4
C loss-100y (%)	37.0	17.6	43.6	23.0	9.6	61.0	40.6	58.6	31.0	13.3
2G Model										
$k_1$ (yr <sup>-1</sup> )	1.50	0.56	3.61	4.51	4.33	3.74	0.61	2.58	3.29	6.38
BC <sub>1</sub> (%)	2.1	1.0	0.9	0.3	0.2	2.4	0.7	2.1	0.7	0.2
C $t_{1/2-1}$ (y)	0.5	1.2	0.2	0.2	0.2	0.2	1.2	0.3	0.2	0.1
$k_2$ (yr <sup>-1</sup> )	3.9E-03	2.1E-04	8.9E-03	1.1E-03	8.7E-04	4.4E-03	9.2E-06	6.1E-03	1.7E-03	1.1E-03
C $t_{1/2-2}$ (y)	177	3225	78	613	793	156	74921	114	405	646
R <sup>2</sup>	0.99	1.00	0.99	0.98	0.99	0.98	0.98	0.99	0.97	0.99
C loss-10y (%)	5.9	1.2	9.3	1.4	1.1	5.0	2.4	7.9	2.3	1.3
C loss-100y (%)	33.8	3.1	59.2	11.0	8.5	36.3	2.4	46.6	16.3	10.4

**Power Model**

$k$ -10y (yr <sup>-1</sup> )	-1.6E-03	-1.1E-03	-2.4E-03	-7.1E-04	-2.8E-04	-1.5E-03	-7.4E-04	-2.4E-03	-3.2E-04	-3.2E-04
$k$ -100y (yr <sup>-1</sup> )	-3.0E-04	-4.2E-04	-6.4E-04	-1.3E-04	-3.8E-05	-2.3E-04	-1.3E-04	-4.5E-04	-3.7E-05	-5.2E-05
$r^2$	0.91	0.66	0.68	0.95	0.89	0.87	0.77	0.95	0.89	0.79
C $t_{1/2}$ (y)	2.6E+04	2.7E+03	1.7E+03	8.9E+05	4.7E+11	1.6E+05	1.6E+06	5.8E+03	1.0E+07	1.7E+08
C loss-10y (%)	5.7	1.9	5.8	2.8	2.2	7.4	3.3	8.8	5.3	1.6
C loss-100y (%)	10.7	7.3	15.2	5.0	3.0	11.6	5.5	16.5	6.1	2.5

**Notes:**

1. Biochars used and experimental methods are those described by Zimmerman (2010) but extended to an incubation period of 1173 d. Names refer to biomass and charring temperature (3 h at peak temperature except where 72 h is indicated).

2. The three modeling methods are described in the text. Parameters listed are  $k$  = the apparent degradation rate constant,  $r^2$  = the correlation coefficient for fit of the model to the data, C  $t_{1/2}$  = biochar C half-life, C loss-10y and C loss-100y = percent of biochar C model-predicted loss after 10 y and 100 y, respectively. The Levenberg-Marquardt algorithm was used to estimate the value of the model parameters of the 2G model by minimizing the sum-of-the-squared differences between model-calculated and measured values as described in Zimmerman et al. (2011).



and %C loss calculations after 10 and 100 y predicted by this model. Losses of 5 to 17% after 100 y and half-lives ranging from thousands to hundreds of millions of years may be more reasonable given that charcoal fragments are found in ancient soils and sediments (e.g., Scott 2000, Dodson et al. 2005). While this model may be the most intellectually satisfying, it has the drawbacks of being more difficult to apply and requiring a longer period of data collection.

There are, however, major shortcomings to the laboratory incubation approach to estimation of long term biochar degradation which cannot be overcome simply by developing an appropriate degradation model. One is that a closed laboratory chamber can never truly simulate the open system that is the soil environment. Unaccounted for stimulatory effects on biochar degradation include UV exposure, rainwater infiltration, bioturbation, positive priming by soil OM and possible inhibitory/protective effect include mineral interaction and soil OM adsorption (see later discussion). Even the very variability in climate parameters such as temperature, freeze/thaw cycles and saturation/desaturation have been shown to stimulate microbial degradation (Sun et al. 2002, Cravo-Laureau et al. 2011). Oak biochar was found to mineralize most rapidly under alternating saturated-unsaturated conditions (Nguyen and Lehmann 2009). Another issue is the possible decrease in microbial biomass over incubation time due to non-ideal conditions such as nutrient limitation and buildup of metabolic products (Spokas 2010, and references therein). And laboratory incubations may not include either fungi or conditions conducive to fungi growth, which may be major players in biochar biodegradation (Lehmann et al. 2011). Thus, it is important to compare laboratory degradation data to that of field studies of different types.

### 2.3 Field Studies

A limited number of studies have been carried out using measurements of BC distributions in soil or sediment profiles with known accumulation rates and pyrogenic OM input histories to calculate apparent BC loss rates in the field. Their results range from showing no loss of pyrogenic OM at all to BC half-lives of 3.3 y (Table 3). Together, they show losses of biochar, to be substantial under some environmental conditions and negligible in others. The range may be due to the fact that each of these studies utilizes different BC materials, different analytical techniques and different soil and climate types. Only one study (Major et al. 2010) followed losses in the field using biochar of known starting composition and amount. The remainder relied upon BC produced by natural fires or slash and burn agriculture. These studies can yield results more nuanced than is indicated by a simple reading of a table such as this. For example, the chronosequences examined

Table 3. Biochar C loss rates derived from field studies.

Source	Location/Soil/BC/Experimental	BC quantification method	Time period (y)	Biochar C loss (%)	Biochar C <sub>t<sub>n</sub></sub>
Major et al. 2010	Colombia savanna Oxisol, mango prunings, charred in kiln, 400–600°C, 48 h	natural abundance d <sup>13</sup> C-OM	2	3.3	42
Nguyen et al. 2008	Western Kenya, Humic Nitosols, forest slash and burn sites of different ages with no subsequent burning	<sup>13</sup> C-CPMAS NMR	30	70	25
		hand picking	5	84	3
Hammes et al. 2008	Russian Chernozem sampled before burning cessation and 100 years later	benzene polycarboxylic acids (BPCAs)	97	24	245
			104	20	323
Schneider et al. 2011	Western Kenya, forest to ag. converted by slash and burn 100 y ago and less	BPCA	100	0	—
Vasilyeva et al. 2011	Russian Chernozem soil, cessation of burning (steppe and fallow)	BPCA	55	0	—
Bird et al. 1999	Zimbabwe sandy savanna soil, natural burning cessation	Acid-dichromate oxidation	51	47	56
Middleburg et al. 1999	Abyssal plain marine sediment exposed to oxygen	Thermal oxidation (soot only)	10–20 ky	63	7–14 ky

by Nguyen et al. (2008) after forest clearance by fire at different times, revealed an initial 30 y phase of rapid BC loss (or 5 y of visible charcoal loss) followed by at least 70 y of stable concentrations. One might conclude that this shows that a portion of the BC degrades on decadal timescales, while the residual portion is lost at much greater than centennial scales.

However, these types of studies are associated with their own set of uncertainties. Among them are: 1) the possibility that BC has been lost to erosion or vertical transfer with the soil profile, 2) reliance upon either the assumption that BC production in the natural environment was constant or ceased altogether at a known time, and 3) uncertainties associated with the quantification of charcoal or BC. Even if the assumptions of 1) and 2) can be satisfied, the last of these is still of much concern. Each technique only quantifies a portion of the pyrogenic C present. Thermal



oxidation, for example, is now known to preferentially detect soot C (Hammes et al. 2007) and the polycondensed aromatic domains detected by  $^{13}\text{C}$ -NMR spectroscopy have been shown to represent only a small portion of pyrogenic material in some cases (Sharma et al. 2004, Knicker et al. 2005). Further, it is not known that isotopic signatures, the proportion of condensed aromatic C as detected by  $^{13}\text{C}$ -NMR techniques, or the content of the biomarker benzene polycarboxylic acids (BPCAs) of BC remain constant as BC degrades. They most likely do not. For example, both the BCPA (Schneider et al. 2010) and spectroscopy preferentially detect the highly condensed portion of char more likely to be produced at higher temperatures and will be preferentially retained over time. And aged biochar was found to leach ~50 times more BCPA's than fresh biochar (Abiven et al. 2011). Thus, much as laboratory incubation experiments are most likely to overestimate the rate at which biochar is degraded by focusing attention on the most labile portion degraded early, field studies are likely to underestimate biochar degradation with their bias toward following the most recalcitrant portion of biochar. Additionally, laboratory incubations using  $\text{CO}_2$  efflux measurements underestimate true environmental stability by neglecting loss mechanisms other than microbial or abiotic oxidation while field measurements include the effects of, but do not necessarily properly evaluate, all types of BC loss.

### 3 Mechanisms of Black Carbon and Biochar Loss

Of the possible mechanisms for biochar loss from soils, degradation/mineralization (abiotic and biotic), erosion or downward translocation, leaching/solubilization, volatilization and consumption by later fires, only the first has been the subject of considerable research as yet. Aspects of each of these mechanisms are discussed in the following.

#### 3.1 Biotic Black Carbon Degradation

The evolution of  $\text{CO}_2$  from incubations of biochar are often attributed to microbial respiration of biochar when, in actuality, they are the net product of both abiotic and biotic processes. There is a good deal of evidence for the stimulatory effect of microbial processes on biochar degradation. Biological utilization of BC was first observed by Potter (1908) by recording  $\text{CO}_2$  evolution from 20-day charred wood and coal incubated with a *Diplococcus* culture. By comparison, Potter saw no  $\text{CO}_2$  evolution from either sterilized or dry incubations, confirming the involvement of microbes. In other early work, Shneour (1966) measured greater release of  $\text{CO}_2$  from a  $^{14}\text{C}$ -labeled charcoal than in parallel sterilized incubations. A longer term study (1 y) using a range of biochars showed up to twice the  $\text{CO}_2$  release from

incubations inoculated with a consortia of soil microbes (Zimmerman 2010) compared to sterilized incubations. The proportion of biochar C mineralized in these experiments that could be attributed to microbial involvement was greatest for chars produced at lower temperatures, thus richer in organic acids and phenols, suggesting a microbial preference for specific biochar OM components.

Measurements of increased microbial biomass via plate counting, DNA extraction, fumigation or phospholipid fatty acid extraction have also provided evidence of microbial response to pyrogenic OM additions. A number of researchers have also found increases in microbial biomass, along with basal respiration rate, that directly corresponded with increasing quantity of charcoal added to soil (Steiner et al. 2008, Kolb et al. 2009, Steinbeiss et al. 2009). The same result was found for amendments of pyroligneous acid, a condensate of the smoke produced during biomass combustion (Steiner et al. 2008). However, most studies of these types have not distinguished between increases in microbial biomass due to utilization of pyrogenic OM as substrates for microbial growth and activity versus that which may be due to the ability of charcoal, with its high surface area and porosity, to enhance the microbial soil environment by maintaining favorable moisture and aeration conditions and protection from grazers. The one study that has shown direct incorporation of pyrogenic C by microbes found that 1.5–2.6% of a  $^{14}\text{C}$ -labeled biochar produced from rye grass shoot litter at  $400^\circ\text{C}$  (13 h) was incorporated into microbial biomass after 624 d of incubation with soil (Kuznyakov et al. 2009).

There is also uncertainty as to the specific microbial organisms responsible for pyrogenic OM degradation. Likely candidates include fungi, Proteobacteria (O'Neill et al. 2009, Khodadad et al. 2011) and Actinobacteria (Baath et al. 1995, Khodadad et al. 2011). An important role of fungi in biochar degradation is widely hypothesized due to their known ability to decompose lignin, low-grade coals and other refractory OM (Scott et al. 1986, Gotz and Fakoussa 1999, Hofrichter et al. 1999, Wengel et al. 2006) and the often observed positive association between soil biochar and fungal mycorrhiza (reviewed in Warnock et al. 2007). The many effects of biochar on soil biota have been reviewed in detail elsewhere (Thies and Rillig 2009, Lehmann et al. 2011).

#### 3.2 Abiotic Oxidative Black Carbon Degradation

Oxidation of biochar, both on its surface and in bulk, clearly occurs over time. Rates of  $\text{CO}_2$  production and  $\text{O}_2$  consumption were strongly correlated in incubations of a variety of biochars (Spokas and Reicosky 2009). Boehm titration, Fourier-transform infrared (FT-IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) have shown increases in oxygen content

and phenolic and carboxylic functional groups to be initiated at biochar's surface both in 4-month laboratory incubations and over decades in the soil (Cheng et al. 2006, Cheng et al. 2008, respectively). Studies using  $^{13}\text{C}$ -NMR appear to indicate that oxidation may penetrate beyond biochar's surface with bulk aryl-C losses of up to 53% and carboxyl/carbonyl C and O-aryl C content increased to 29% over a twenty month incubation of grass biochar produced at 350°C (Hilscher and Knicker 2011a).

Attribution of biochar degradation or a portion of the observed degradation to purely abiotic causes is more difficult. While some studies report no or little loss of biochar C in the absence of microbes (Potter 1908, Shneour 1966, Santos et al. 2012), a number of studies suggest that abiotic processes play an important, perhaps even dominant, role in degrading biochar. Zimmerman (2010), for example, reported that, over 1 y, sterilized incubations of a range of biochars released 50–90% of the  $\text{CO}_2$  released by inoculated ones. While it can be argued that abiotic conditions are difficult to maintain during longer-term incubation experiments (Knicker 2011), the different pattern of microbial versus abiotic degradation observed suggests real differences in degradation mechanism between biotic and abiotic ones. In another study, addition of microbes did not alter the extent of oxidation of biochar surfaces during 4-month laboratory incubations (Cheng et al. 2006). And the lack of a lag phase at the start of charcoal incubations has been suggested as evidence for the predominance of non-microbial degradative processes, at least during early phases of degradation (Bruun et al. 2008). Finally, Nguyen et al. (2010) showed that biochar degradation rate increased as temperature was raised from 4 to 60°C, unlike what would be expected of microbial processes which are usually maximal closer to 30°C.

Most likely, both abiotic and microbial oxidative processes are important and, to some extent, interdependent. Chemical studies suggest a two part process in which aryl C structures are first abiotically oxidized, perhaps via oxygen chemisorptions reactions assisted by the high density of electron-donating pi-bonds (Contescu et al. 1998), or hydrolyzed to form catechol-like structures. The O-aryl rings can then be cleaved or converted to C-containing functional groups (Hilscher et al. 2009, Hilscher and Knicker 2011a). These organic components are now both more labile and more water-soluble, thus more accessible to microbes for use as respiratory substrates. Degradation experiments comparing fresh and biochars abiotically aged by oxygen, water, sunlight etc., in parallel and in series, should be carried out to explore the relationships between these processes.

### 3.3 Non-Oxidative Abiotic Black Carbon Loss

Dissolution of inorganic C minerals or amorphous phases, desorption of  $\text{CO}_2$  or volatilization of organic compounds have all been proposed as possible

biochar C loss mechanisms. While each of these processes would be expected to be short-lived (days to years?), they need to be better understood and accounted for when carrying out degradation experiments or C budget calculations.

Using X-ray diffraction spectra, a number of studies have reported the presence of calcite and other carbonate phases in biochar made by pyrolysis between 300 and 500°C (Cao and Harris 2010, Singh et al. 2010a, Inyang et al. 2011, Yuan et al. 2011). Calcite is not expected to be present in biochars made at higher temperatures as thermal decomposition of calcite begins to occur at about 600°C and is completed at 850°C (Rodriguez-Navarro et al. 2009). By measuring the release of  $^{14}\text{C}$  during acidification of biochar made from  $^{14}\text{C}$ -labeled barley root at 375°C, Bruun et al. (2008) calculated that carbonate represented up to 11% of the biochar C. They attributed the C released during early phases of incubation of this material wholly to this source. In another study, Jones et al. (2011) observed a 50% decrease in  $\text{CO}_2$  released from biochar incubations in soil after rinsing with water and a 5-fold decrease when biochar was pre-treated with acid. They concluded that abiotic release of mineral carbonate C contained in the biochar was a major factor but did not report having carried out measurements of inorganic C.

The set of 20 biochars (pyrolyzed at 250–650°C) reported on in Zimmerman (2010) was tested for inorganic C content by acidifying with 10% phosphoric acid and measuring evolved  $\text{CO}_2$  by coulometry (UIC Inc., Joliet, IL). After 5 min acidification,  $\text{CaCO}_3$ -C% (by weight) release ranged 0–0.5% and after 72 h acidification, 0.01–0.6%. Greatest carbonate contents occurred in high temperature (650°C) biochars and in grasses. Thus, we calculate that, while inorganic C could have accounted for <3.7% of the  $\text{CO}_2$  released from low temperature chars (produced at 250 or 400°C) during incubation, it could have accounted for as much as 42% (26% on average) of the C released from chars made at 525 or 650°C. However, the amount was probably far less given that strong acid was required for all of this carbonate C to be released. However, this should serve as warning that inorganic C should be considered during future degradation incubations.

Thus far, there have only been qualitative analyses of the volatile compounds able to be desorbed from biochar. Spokas et al. (2011) identified over 140 individual compounds released using headspace thermal desorption at 150°C coupled to capillary gas chromatographic-mass spectrometry. Lower temperature biochars produced the greatest amount and number of compounds and  $\text{CO}_2$  and other short-chain alkanes and alcohols were always among the volatile compounds detected. In only one indication of the amount of biochar C that may be lost to volatilization, Spokas et al. (2009) found that pre-treating biochar under a vacuum reduced  $\text{CO}_2$  efflux in incubation by 7%. Further research should be carried out in this area.

### 3.4 Black Carbon Loss by Leaching

A number of recent studies have examined losses of C, nitrogen and phosphorous as aqueous leachate from biochar-amended soils driven by interest in biochar's effect on plant-available nutrients. However, the quantification of leached dissolved organic carbon (DOC) from biochar itself is of interest from the standpoint of biochar's environmental longevity. The fate of that biochar-derived DOC is also of importance in establishing biochar's effect on soil C balance and global C cycling.

The production of colored leachate when pyrogenic OM is placed in water has long been noticed. Losses of C by this process may be significant as researchers have identified substantial amounts of pyrogenic substances in rivers and the ocean using BC analyses, molecular markers and ultrahigh resolution spectroscopic tools (Mitra et al. 2002, Mannino and Harvey 2004, Hockaday et al. 2006, Hockaday et al. 2007). This dissolved pyrogenic OM is identified as condensed aromatic ring structures of relatively low molecular weight (<1000 Da), and extensively substituted with oxygen-containing functional groups (Kim et al. 2004, Dittmar 2008). However, it should be understood that the similarity of these water-soluble condensed aromatics in natural waters to the degradative products of BC does not confirm their common origin. On the other hand, there may be many more pyrogenic compounds in natural waters not yet recognized as such.

Only a few studies have quantified the generally low amounts of C lost by biochar using laboratory aqueous leaching experiments. A mixed hardwood-derived biochar pyrolysed at 450°C for 48 h released only 0.04% of its total C after repeated rinsing with distilled water (Jones et al. 2011). And a 100 y-old charcoal yielded 0.2% of its C when extracted at pH 4.4 with HCl after 48 h (Hockaday et al. 2006). Abiven et al. (2011) extracted a fresh chestnut wood biochar (450°C for 5 h under N<sub>2</sub>) and 10 y aged natural charcoal using a more extensive routine (8 g bulk dry in 100 ml, 6 h repeated 6 times). They found that the fresh and aged biochars released 0.2% and 0.1% of their total C, respectively, in the combined soluble and colloidal fractions. Though these losses are small, the similarity between C leached from fresh and aged biochar, and our unpublished results (below) indicate that losses vary considerably with biochar type and can be more substantial over longer periods of leaching.

We tried to estimate long-term desorbable biochar C by carrying out both multiple consecutive batch and continuous flow-through column leaching experiments using the set of biochars described in Zimmerman (2010). For batch leaching, 20 g of each biochar was added to 400 mL distilled deionized (DI) water in 500 ml plastic bottles and placed horizontally on a mechanical platform shaker (150 rpm) in the dark. Weekly, over 3 months, the bottles were centrifuged (4500 rpm) and the supernatant was carefully

removed via pipette. The remaining sample was weighed to determine the amount of entrained solution present before addition of 400 mL more DI water. The DOC in the supernatant was measured by TOC analyzer (catalyzed high temperature combustion) and leached DOC was calculated after taking into account the entrained DOC left in each new round of leaching. Flow-through column desorption was carried out using a packed chamber filled with 10 g biochar plumbed with water flowing upward for full contact and driven by a column of water of a height adjusted to achieve the desired flow rate of about 150 ml d<sup>-1</sup>.

The results point to a number of interesting trends in biochar C leaching (Fig. 2). First, after nine rounds of leaching, biochar C losses ranged from 0.1 to 1.3% for all biochars tested. As expected from their greater VM content, biochars created at lower temperatures lost the greatest proportion of C via leaching. Second, biochar C leachability varied with parent biomass type following the trend pine wood  $\approx$  oak wood < grass. The much lower C losses measured previously by others can be attributed to their examination of low VM biochars or to their use of only a single leaching period. Lastly, batch and column C leach rates were similar after normalizing for amount of biochar and volume of extractant (water). We have conducted a number of other leaching experiments using the same materials but different solid/solution ratios, contact times, flow rates, etc., which all have yielded similar normalized C yields (Mukherjee and

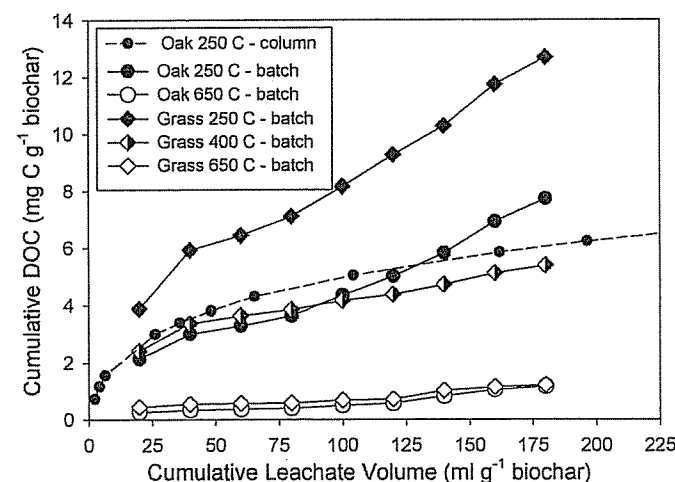


Figure 2. Relationship between cumulative leached C and cumulative leachate volume during successive batch (solid lines) and continuous flow column (dashed line) DI water extractions of biochars made from Loral Oak wood and Gamma grass combusted at 250°C (in oven with atmosphere) and 400 and 650°C (under flowing N<sub>2</sub>) as described in Zimmerman (2010).

Zimmerman. In press). Further indication that biochar C loss by leaching may be significant, though column leaching experiments were carried out to a total leach volume of 7.4 L (almost four times that depicted in Fig. 2), we never observed a decrease in C leach rate. Similar leaching experiments carried out on these same biochars which had been aged for 1 y outside in north Florida, during which time 109 cm of rain fell (fully described in Mukherjee 2011), yielded similar, even greater leach rates in some cases than non-aged biochars. We calculate that, assuming these laboratory-observed leaching rates remain constant, losses of biochar C by leaching over 1 y of average north Florida rainfall would be ~1% and 2% for high and low temperature biochars, respectively. These C loss rates are similar to those measured via laboratory CO<sub>2</sub> efflux experiments during 1 y and could be modeled similarly. However, if leaching C losses remain constant over time rather than decrease as do mineralization rates, it could add up to much greater long-term C losses.

There are two likely explanations for these observations of seemingly continuous leaching of biochar C. First, desorption of organic compounds from biochar may be driven by a chemical equilibrium at the solid-solution interface. Thus, movement of chemisorbed organic compounds such as organic acids and phenols between biochar's surface and the solution, which likely occurs in the confined space of biochars pores, would progress incrementally with each change of solution chemistry via reversible reactions that could be described by thermodynamic equations. On the other hand, hydrophobic compound sorption-desorption is more typically described using partitioning theory, which would liken the situation to volatile molecules permeating a more stable organic framework. Certainly, more work is needed in this area.

A second explanation for continuous leaching is that, over time, abiotic or biological degradation increases the solubility of organic compounds on biochar's surface by adding polar functional groups to aromatic units. For example, oxidation of soot has been reported to produce water-soluble organic compounds (Decesari et al. 2002, Kamagawa et al. 2002). Similarly, Reiss (1992) found that fungi was able to solubilize up to 78% of coal, by mass, and this ability varied directly with its VM and oxygen content. Knicker (2011) pointed out that this increase in biochar solubility would be expected to occur when carboxyl groups are deprotonated, which would occur more readily under the alkaline conditions that are typically produced by biochar amendments to soil (e.g., Atkinson et al. 2010).

But the effect of biochar solubilization on the C content of a biochar-amended or natural fire-impacted soil hinges on the fate of these leached organic compounds, which could include 1) percolation through the soil and export out of the watershed via rivers and groundwater, 2) sorption onto soil OM or minerals and long-term retention, or 3) mineralization through

abiotic or microbial degradation. A case could be made for the occurrence of each of these, depending upon biochar and soil type, climate etc. Claims of detection of abundant products of BC degradation in natural waters would argue for persistence and mobility through soil. However, in the few studies where C leaching from biochar-amended soils has been measured, very little dissolved pyrogenic C was detected. For example, Major et al. (2010) only measured biochar C losses of ~0.02% in percolating water collected by soil lysimeters over almost 2 y from a biochar-amended Oxisol.

Some biochar-amended soils show increased DOC fluxes over non-amended controls (e.g., Bell and Worrall 2011, Mukherjee 2011), which may also be due to increases in plant or microbial productivity, while others do not (Novak et al. 2010). No biochar C was detected in the K<sub>2</sub>SO<sub>4</sub>-extracted DOC of a <sup>14</sup>C-labeled ryegrass biochar after 624 d incubation with soil. In laboratory column experiments with grass biochar-amended soils, we found evidence of 20–40% of biochar-C leachate sorption by a sandy Entisol, but its full mobility through a clayey Ultisol (Mukherjee 2011). Sorption of aromatic phenols and carboxylic acids to soil minerals (Huang et al. 1977, Kaiser and Guggenberger 2000, Hyun and Lee 2004) and to biochar-itself (Kasozi et al. 2010) has been shown experimentally. However, the extents to which these sorbed components may be later desorbed or are microbially available is an area for future research.

Abiotic or microbial mineralization is another likely fate of leached dissolved biochar C. Soil exposed to the water soluble portions of wood smoke had enhanced rates of CO<sub>2</sub> respiration and O<sub>2</sub> consumption (Focht 1999, Steiner et al. 2008). We carried out *in vitro* abiotic (autoclaved) and microbial (inoculated with a consortia of soil-extracted microbes and nutrients) incubations of biochar leachates. For each biochar type, 35 ml leachate adjusted to a DOC concentration of 25 mg L<sup>-1</sup> was incubated in the dark at 30°C over 313 d and evolved CO<sub>2</sub> was measured monthly. We found the portion of biochar C mineralized in abiotic incubations to range 10–61% (35% on average) and in microbial inoculated incubations, 75–37% (56% on average) (Fig. 3). Thus, on average, 61% of the mineralization observed could be attributed to abiotic processes, assuming these incubations remained sterile. There was no consistent correspondence between biochar type and mineralizability of leachate. However, the highest temperature biochars produced somewhat more refractory leachate.

In summary, it is likely that, both in laboratory and in the field studies, the amount of biochar C measured as mineralized by CO<sub>2</sub> efflux is controlled by processes of OM desorption and mineralization of dissolved BC because 1) the quantity of biochar-C mineralized (~1–2% over a year) is roughly equivalent to the amount likely to be leached, and 2) correlations between the quantity of biochar-C mineralized and biochar VM contents or other proxies of potential solubilization. Between mineralization and sorptive

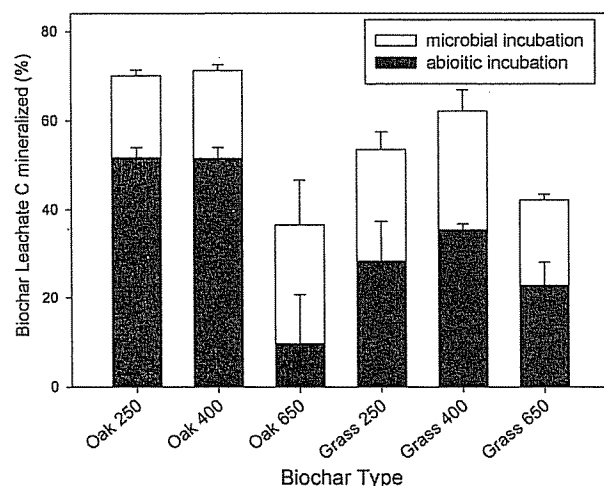


Figure 3. Portion of C in biochar leachates mineralized to  $\text{CO}_2$  after 313 d sterile and microbial inoculated incubation. Error bars represent standard deviations calculated from duplicate treatments. Biochar types are the same as shown in Fig. 2 and described in Zimmerman et al. (2010).

retention of dissolved BC, it seems there would be little pyrogenic C export from the soil. This needs to be reconciled with the apparent contradiction of observations of large amounts of dissolved BC in natural waters.

### 3.5 Black Carbon Losses by Erosion/Translocation

While there have been few direct quantifications of losses of particulate soil BC or biochar by horizontal movement (erosion) or vertical movement (downward translocation), there is quite a bit of indirect evidence that significant losses, perhaps even the majority of losses of soil BC, may occur by these processes. First, erosion is implied by the observation that BC makes up a large portion of the carbon in bogs and streams (Guggenberger et al. 2008) and riverine and marine sediment (2–38%, Masiello 2004). Strengthening the case for a soil BC source for this material, studies have found temporal correspondence between decadal-scale periods of regional drought and coastal deposits enriched in BC (Bird and Cali 1998, Pederson et al. 2005, Mitra et al. 2009).

Second, erosion of soil containing BC should be expected given that natural fires may denude the landscape of erosion-deterring vegetation and biochar-enriched soils may have been preferential sites of high intensity agriculture. Using experimental plots and a rainfall simulator, Rumpel et

al. (2006) found that soil erosion was most severe in an area under intensive slash and burn practice. And even within a specific soil, BC particles may be preferentially exported compared to other soil OM due to their predominantly small size and low density (Skjemstad et al. 1999). Rumpel et al. (2009) found that 7–55% of pyrogenic C added to the soil via a surficial grass fire was lost to erosion and another 23–46% was moved vertically to greater soil depths.

One might expect erosional losses of biochar to much less in level agricultural systems in which biochar is initially well-mixed into soil. However, downward movement of biochar, either as discrete particles, colloids or in dissolved form, may still be significant. Dai et al. (2005) found no effect of controlled burns on the BC content of a north Texas soil in the 0–10 cm depth interval, but a significant increase at the 10–20 cm interval suggesting downward movement of BC. Though homogenized into soil at the start of a laboratory column experiment, Hilscher et al. (2011b) found downward movement of 2.3% of the  $^{13}\text{C}$ -labeled biochar after 28 months and attributed this to leaching and re-adsorption of pyrogenic C or to translocation of clay-sized particles. However, in the one field study that attempted to follow all BC losses from a biochar-amended soil in the field, leaching, downward movement and mineralization only accounted for losses of <3% leading them to conclude that 20–53% of the applied BC must have been lost by surface erosion (Major et al. 2010). Clearly, losses of these types will vary with such factors as climate, topography, soil type and biochar application routine.

### 3.6 Black Carbon Losses by Later Fires

Indirect evidence for losses of pyrogenic C by consumption during later fires may be found in the observation that, in a number of studies, no additional soil BC was registered after multiple burning events compared to single events (Dai et al. 2005, Knicker et al. 2006). Also, studies have calculated BC stocks and ages much less than would be expected based on estimates of landscape fire frequency over long time periods (e.g., Czimczik et al. 2003, Ohlson et al. 2009). Of course, these losses could be due to other causes such as mineralization and erosion. Direct evidence for biochar losses by repeat fires is lacking.

### 4 Biochar-Soil C Interaction and Stability

While it appears that the greatest biochar C losses occur by microbial and abiotic oxidation (mineralization), it is not clear the extent to which this will be impeded or stimulated by the interaction of biochar with soil. For example, a few studies have found that some portion of soil BC can be



found embedded within microaggregates (Glaser et al. 2000, Brodowski et al. 2006) which could slow degradation by limiting access by oxygen or microbial enzymes. Soil OM, being a more labile C source than pyrogenic C, could stimulate the production of microbial exoenzymes, leading to the co-metabolism of BC. This accelerated mineralization of a refractory OM component when stimulated by the presence of a labile C source has been termed 'positive priming' (Kuzyakov et al. 2000). Making matters more complicated, the presence of biochar could either impede or accelerate the mineralization of soil OM. For example, given that biochar is both porous in nature and has high affinity for natural OM (Kasozzi et al. 2010), it could be expected to sequester non-BC soil OM within its pore network and protect it from degradation by oxidants and exoenzymes. Or biochar may sorb soil nutrients, limiting microbial activity. Alternatively, BC may accelerate soil C mineralization by providing nutrients or a habitat favoring increased microbial heterotrophic activity (Thies and Rillig 2009). Another idea is that following biochar-induced increased plant growth, microbial activity stimulation occurs in the rhizosphere (Graber et al. 2010).

At this point, a great number of studies have measured changes in CO<sub>2</sub> efflux following biochar amendment to soil. Generally, the results find either increased soil CO<sub>2</sub> efflux due to biochar addition (Kolb et al. 2009, Kuzyakov et al. 2009, Spokas and Reicosky 2009, Major et al. 2010, Zimmerman et al. 2011, Jones et al. 2012) or no significant change in soil CO<sub>2</sub> efflux (Kuzyakov et al. 2009, Spokas and Reicosky 2009, Novak et al. 2010, Singh et al. 2010b, Cross and Sohi 2011, Karhu et al. 2011, Case et al. 2012). One field litterbag study found greater losses of humus in the presence of charcoal than in its absence, possibly indicating positive priming (Wardle et al. 2008). All these results should be viewed with the understanding that they do not indicate positive priming or lack of priming of soil OM mineralization by biochar (or vice versa) if they do not correct for the increased C mineralization that would be due to biochar alone (from abiotic or microbial oxidation, or release of inorganic C in biochar).

A better understanding of the effects of the complex and multiple possible interactions between biochar and native soil OM can only be had by experimental methods which allow for the quantification of biochar C mineralization and native soil C mineralization separately. Results of studies that have done this are assembled in Table 4. In general, they show biochar C degradation rates similar to or greater than those carried out on biochar alone, ranging from losses of 0 to 9%, but with a median values of 1 to 2%. Further, the change in soil C mineralization rate observed with the addition of biochar ranged from +150 to -87%, with a median value of +6%, or almost no change. Clearly, the direction of priming is highly variable and seems dependent upon biochar and soil type and time. Likely due to their greater lability, low temperature biochars generally have been found to

Table 4. Biochar C and soil C loss rates derived from combined soil/biochar incubation studies.

Source	Biochar feedstock and production conditions	Soil	Incubation and Quant. Method <sup>1</sup>	Incubation period (d)	Biochar %C mineralized	Biochar C t <sub>1/2</sub> (y)	Soil C min. % change <sup>2</sup>
Kuzyakov et al. 2009	<sup>14</sup> C-labeled ryegrass, 400°C, 13 h	Haplic Luvisol	<sup>14</sup> C-CO <sub>2</sub> /scint. count	1181	4.0	55	0
"	"	loess	"	"	4.0	55	decrease
Steinbeiss et al. 2009	<sup>13</sup> C-labeled hydrothermal pyrolysis-glucose	arable Eutric Fluvisol	20-25°C	120	8.0	2.7	53
"	<sup>13</sup> C-labeled hy py yeast	"	"	"	9.0	2.4	150
"	<sup>13</sup> C-labeled hy py glucose	forest Cambisol	"	"	3.0	7.5	57
"	<sup>13</sup> C-labeled hy py yeast	"	"	"	6.0	3.7	108
Major et al. 2010	mango prunings charred in kiln, 400-600°C, 48 h	Colombia savanna Oxisol	static chamber CO <sub>2</sub> measured in field	730	2.2	62	25.5
Zimmerman et al. 2011	grass, 250°C under N <sub>2</sub>	forest Alfisol	50% WHC	90	2.9	5.8	61.3
"	grass, 650°C under N <sub>2</sub>	"	"	"	0.9	18.3	-15.6
"	grass, 250 °C under N <sub>2</sub>	wetland Mollisol	"	"	6.8	2.4	0.1
"	grass, 650°C under N <sub>2</sub>	"	"	"	0.2	114	-76.4
"	grass, 250°C under N <sub>2</sub>	forest Alfisol	"	90-500	1.9	41	-75.1
"	grass, 650°C under N <sub>2</sub>	"	"	"	0.1	613	-87.1

Table 4. contd...

Table 4. *contd.*...

Source	Biochar feedstock and production conditions	Soil	Incubation and Quant. Method <sup>1</sup>	Incubation period (d)	Biochar %C mineralized	Biochar C $t_{1/2}$ (y)	Soil C min. % change <sup>2</sup>
"	grass, 250°C under N <sub>2</sub>	wetland Mollisol	"	"	3.8	20	-9.9
"	grass, 650°C under N <sub>2</sub>	"	"	"	2.6	29	-49.8
Cross and Sohi 2011	sugarcane bagasse, 350°C, 40 min	fallow silty-clay loam		14	1.1	2.5	15.1
"	" 550°C, 40 min	"		"	0.1	29	18.0
"	" 350°C, 40 min	arable loam		"	0.7	3.6	25.1
"	" 550°C, 40 min	"		"	0.0	0	6.1
"	" 350°C, 40 min	grassland loam		"	0.4	7.1	-9.3
"	" 550°C, 40 min	"		"	0	0	-36.0
Keith et al. 2011	<sup>13</sup> C-depleted Eucalyptus, 450°C, 40 min pyrolysis	Vertisol		120	0.75	30	7.4
"	" 550°C, 40 min pyrolysis	"		120	0.4	57	19.4
Santos et al. 2012	<sup>13</sup> C-enriched pine, 450°C, 5 h under N <sub>2</sub>	forest - andesitic parent	55% WHC, 25°C	180	0.37	92	-10
"	"	forest - granitic parent	"	"	0.41	83	0

## Notes:

1. All incubation at 60–65% water holding capacity (WHC) in dark at 30°C, unless otherwise indicated. The amount and proportion of biochar C and soil C mineralized was measured by analysis of natural abundance of  $\delta^{13}\text{C}-\text{CO}_2$  efflux, unless otherwise indicated.

2. Change in soil C mineralized or mineralization rate with, relative to without, added biochar.

Luo et al. 2011	straw, Ar-flushed pyrolysis, 350°C, 30 min	Aquic Paleudalf, low pH	40% WHC, 25°C	87	0.61	27	304
"	"	" high pH	"	"	0.84	28	202
"	" 700°C, 30 min	Aquic Paleudalf, low pH	"	"	0.14	118	136
"	"	" high pH	"	"	0.18	92	74



stimulate soil OM mineralization to a greater extent than high temperature ones (Cross and Sohi 2011, Zimmerman et al. 2011). The effect of soil type is more difficult to discern. But soil C mineralization seemed to be inhibited by biochar to a greater extent in soils of lower organic C content (Kuzyakov et al. 2009, Zimmerman et al. 2011), suggesting that protective sorption of soil OM onto biochar is limited in extent.

As with biochar-alone incubations, time period of observation seems an important factor. For example, Luo et al. (2011) demonstrated the initiation, progress and termination of a positive priming effect by biochar on native soil C over the course of 3 months. Zimmerman et al. (2011) found that priming effect swung from positive to negative after a period of about 3 months (Table 4) and longer studies such as that of Kuzyakov et al. (2009) and Santos et al. (2012) tend to show a low or negative effect of biochar on soil OM mineralization. Finally, Liang et al. (2010) found that mineralization of native soil C was 64–82% lower in the BC-rich Anthrosols compared to nearby BC-poor soils. Together, these studies suggest that, following an initial stage of positive priming in which soil C mineralization may be stimulated (3 months?), an inhibitory effect of biochar on soil C mineralization takes over as soil OM is sorbed and perhaps encapsulated within biochar-OM mineral microaggregates. Organic matter sorption onto biochar surfaces has been shown to be kinetically limited by slow diffusion into the subnanometer-sized pores dominating biochar surfaces (Kasozi et al. 2010). This effect should be greater for higher temperature chars which possess greater porosity. These time-, soil- and biochar type-dependant trends explain the wide range of experimental degradation results obtained in various biochar-amendment studies. Some of the concepts described here for C, likely also apply, to some degree, to biochar-soil nutrient dynamics such as for N and P, particularly in organic forms.

## 5 Mechanisms of Biochar Stabilization

There have been a number of recently published reviews discussing the mechanisms which may stabilize BC or biochar in soil and account for biochar's longevity in the environment (Czimeczik and Masiello 2007, Lehmann et al. 2009, Knicker 2011). Certainly inherent chemical or molecular-recalcitrance is a major factor, though this is highly dependent upon environmental conditions, as discussed above. There has been much study of whether BC is physically stabilized by its interaction with soil minerals, soil OM, or occlusion within microaggregates that include both OM and clay-sized minerals. For example, Liang et al. (2008) found that BC-rich Anthrosols had a high proportion (72–90%) of its C in the organo-mineral fraction. Using X-ray spectromicroscopy, discrete particles of BC were observed embedded within intact microaggregates (Lehmann et al.

2008). And Al, Si, and to some extent Fe, were found associated with BC particle surfaces within 30 y after deposition in soil (Nguyen et al. 2008). However, Brodowski (2006) found soil BC to be widely distributed across a range of density fractions including microaggregates and discrete particles and major portions of the BC in soil can be found within the lightest soil fraction (Glaser et al. 2000, Rumpel et al. 2006, Murage et al. 2007). In addition, across a range of North American prairie soils, no correlation was found between BC content and soil properties including clay content (Glaser and Amelung 2003).

Though the importance of mineral-association to biochar preservation is debatable, soil C and soil BC abundances are usually correlated (Glaser and Amelung 2003, Czimeczik and Masiello 2007, Vasilyeva et al. 2011) indicating that BC and native soil OM are preserved by similar processes. For example, biochar particles or leachates and native OM may be stabilized separately or held together via ion bridging with  $\text{Ca}^{2+}$ , or with Al and Fe oxyhydroxides (Glaser et al. 2000, Czimeczik and Masiello 2007). These processes would likely grow in effectiveness with the surface oxidation that occurs with biochar aging. This may partially explain why aged soils enriched in BC such as *terra preta* are also enriched in non-BC OM.

Organic matter sorption onto surfaces as well as into mineral nanopores is an OM protection mechanism that has received wide attention (e.g., Keil et al. 1994, Kaiser and Guggenberger 2000, Mayer et al. 2004). Thus, OM sorption onto biochar's surface and within its pores may be an effective mutual preservation mechanism. While microbes may be excluded from micron-sized pores (those that are typically seen on SEM images of biochar particles), we have found that the majority of biochar surface area actually exists within nanometer diameter pores (Kasozi et al. 2010, Mukherjee et al. 2011). Thus, microbial enzymes and even water and oxidants may be excluded or severely kinetically inhibited from entering and degrading OM or biochar itself within pores of this size. This hypothesis was tested using experimental apparatus described elsewhere (Zimmerman et al. 2004) that measures enzyme activity via the oxygen consumption that occurs when the fungal-derived enzyme laccase reacts with its substrate, 2,6-dimethoxyphenol (DMP). When the substrate was sorbed to a biochar for only a few hours, the ability of the enzyme to degrade it decreased by 79 to 96% relative to the unbound substrate, depending upon the biochar type (Fig. 4).

Another potential biochar stabilization mechanism that has been little discussed is the inactivation of degradative microbial enzymes by pyrogenic OM. There are a wide range of enzyme-mineral and enzyme-OM interactions, the majority of which, though not all, lead to enzyme inhibition (Zimmerman and Ahn 2010). We found that when laccase was sorbed to biochar's surface prior to the introduction of substrate, enzyme activity

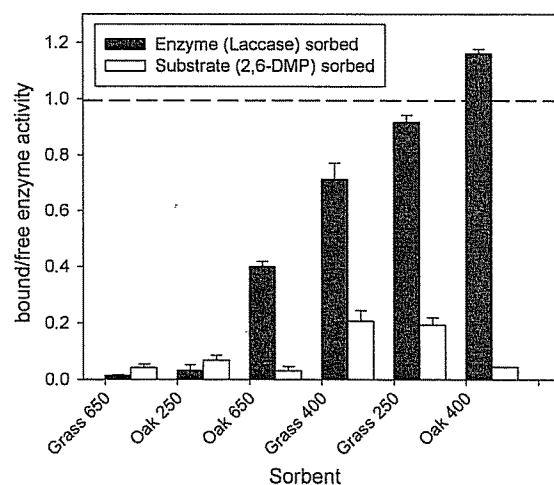


Figure 4. Enzyme activity inhibition (bound/free activity ratio) due to biochar sorption of enzyme (laccase) or sorption of substrate (2,6-dimethoxyphenol). Enzyme activity measured by  $O_2$  consumption (see Zimmerman et al. 2004 for methods used). Biochars are described in Zimmerman (2010).

ranged from 99% less to 16% greater than the free enzyme, depending upon the biochar type (Fig. 4). Thus, even though laccase was unlikely to enter biochar's small pores, its activity was inhibited either due to conformational restriction, surface charge distortions, or pH effects, etc. These mechanisms too may explain the correspondence between BC and non-BC OM preservation as well as the formation of long-lasting fertile biochar-enriched soils.

## Conclusions and Summary

Monolithic biochar degradation parameters, such as the oft quoted mean residence time of 1000–10,000 y should be abandoned in favor of an understanding of biochar as a heterogeneous material. A portion of biochar is lost with C half-lives on orders of years to decades. After this, the residual and more chemically recalcitrant component of biochar, such as that found as charcoal in ancient soils or detected as BC-soot in sediments, may have residence times of thousands to millions of years. As a practical concern, effort should be placed on developing analytical techniques that can predict the proportion of these biochar components and their associated lability, contained within a given biochar sample or naturally-derived pyrogenic material. However, much more work is needed on understanding the importance of environmental factors such as soil permeability and oxidant supply, moisture, pH and climate on biochar degradation.

Losses of biochar observed in the laboratory due to abiotic or microbial oxidation are generally in the range of 0.5 to 4% over a few years. Modeling approaches that take into account the heterogeneous nature of biochar predict losses of 3–20% over 100 y, while field studies that make use of long BC depositional records back-calculate biochar C losses in the range of 20 to 90%. While biochar leaching is a C loss mechanism that may explain this difference, it is likely that much of this C is remineralized or re-adsorbed. There is good evidence to suggest that the unaccounted for losses, which can be substantial, may be due to erosion. The particulate pyrogenic material that is exported from soil in this manner may be the source of pyrogenic C detected in natural waters.

Another area in which our understanding is sorely lacking is that of the changes to biochar that occur over time and with biochar-soil interaction. As biochar ages, through abiotic and microbial oxidation, it becomes both more soluble and, thus, even more microbially-available. With solubilization, sorption and ion-bridging, it may exchange pyrogenic OM for native soil OM, while soil minerals may gain a coating of pyrogenic OM, eventually leading to physical stabilization through aggregate formation. It is these processes that surely led to the creation of *terra preta* and other soils enriched in both pyrogenic and non-pyrogenic soil C.

While this chapter has focused on biochar C losses that may occur, it must be remembered that the majority of biochar's C, which it has in abundance, will likely remain in the soil. In fact, it is likely to increase total soil C even further over time as it builds non-pyrogenic soil C both through greater plant and microbial production and through the aforementioned preservation enhancement mechanisms. Thus, we may need to revise biochar's atmosphere  $CO_2$ -C sequestration potential upward rather than downward.

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## Biochar Impact on Plant Resistance to Disease

E.R. Graber<sup>1,\*</sup> and Y. Elad<sup>2</sup>

- 1 Why Biochar?
- 2 Plant Disease
  - 2.1 General
  - 2.2 Foliar Diseases
  - 2.3 Soil-borne Diseases
  - 2.4 Systemic Plant Responses to Disease
- 3 Biochar-mediated Protection of Plants from Foliar and Soil-borne Disease
  - 3.1 Possible Mechanisms by which Biochar May Protect Plants against Diseases
    - 3.1.1 Improved Nutrient Supply and Enhanced Plant Growth
    - 3.1.2 Increase in Beneficial Soil Microorganisms
    - 3.1.3 Sorption of Toxins Produced by Disease Pathogens
    - 3.1.4 Suppression of Soil-borne Pathogens by Biochar-Derived Toxic Organic Compounds

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List of glossary given at the end of the text.



# Biochar and Soil Biota

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## Preface

Biochar, a biomass that is burned at very high temperature in the absence of oxygen, has recently become an interesting subject of study. Biochar is highly stable and does not degrade; it possesses physical properties that assist in retention of nutrients in the soil. The use of biochar will undoubtedly have a significant impact not only on soil nutrients but also on soil organism communities and their functions.

This book focuses on how the ecology and biology of soil organisms is affected by the addition of biochar to soils. It takes into account direct and indirect effects of biochar addition to soils, on the soil carbon cycle, impact on plant resistance to foliar and soilborne disease, interactions with pathogenic, mycorrhizal and saprophytic fungi. The stability of biochar in soil environment is also discussed. Special focus has been put on application of biochar to remediate polluted soils, taking into account possible toxic effects of biochar on soil fauna. One of the chapters provides extended information on the role of biochar in soil using isotopic tracing techniques. An effort has been put to summarize the methods of traditional production of biochar, their material characteristic and how different biochars may change when applied to soils. Additional chapter is devoted to a comparison of methods to apply biochar into temperate soils.

The chapters have been written by experienced and internationally recognized scientists in the field.

This book will be useful to students and researchers in agronomy, biology, ecology, and environmental managers from both academic as well as industrial organizations.

Natalia Ladygina and Francois Rineau