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Persistence of biochar in soil

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Introduction

A key property upon which the interest in biochar rests is the period that it remains in soil compared to the uncharred biomass that it was produced from (Lehmann et al, 2006). It follows that the factors governing the period for which biochars may remain in soil need to be understood. The empirical and basic scientific principles agree that charring results in changes in material properties of biochars (Chapter 6) that confer greater persistence and therefore longer residence times. This means biochars mineralize more slowly than the biomass they were produced from. The extent of biochar mineralization varies and its dependency on material properties as well as on a variety of other conditions are discussed in this chapter. This chapter uses the term persistence (a measurable, numerical parameter, e.g. expressed as mean residence time (MRT), Box 10.1) to characterize the length of time that biochars remain in soils.

A greater persistence of biochar compared to the uncharred precursor biomass can enhance ecosystem services in several ways: (i) the net CO_2 emissions from biomass converted to biochar is reduced which offers opportunities for climate change mitigation (Whitman et al, 2010; Chapter 27); and (ii) any benefits of the presence of biochar in soil continues for a longer period of time, such as effects on nutrient (Chapters 7, 9, 15) and water availability (Chapter 19) or mitigation of agrochemicals (Chapter 23) or toxins (Chapters 20–22). The enduring presence of the biochar may not always translate into a continuation of any initial positive effects, as its properties can change during exposure to soil (Chapter 9) such as loss of its acid neutralizing ability (Chapter 7) or ability to adsorb PAH (Chapter 22). However, a desirable property may also emerge as in the case of surface oxidation and development of cation retention (Chapter 9). The properties of anthropogenic soils specifically in Amazonia, locally referred to as *Terra Preta de Indio* (Lehmann et al, 2003), are often seen as a proxy for long-term effects of biochar on soil productivity, but have to be taken with some scrutiny (Lehmann, 2009) due to their complex history of formation. This chapter also recognizes the variability of biochar properties that do not allow generalizations to be made across all biochar materials. Instead a careful consideration of different biochars is required.

This chapter will: (i) synthesize the available knowledge on the extent of biochar persistence; (ii) outline the mechanisms for its relative persistence compared to uncharred organic matter; (iii) discuss the effects of management or a changing environment on its persistence; and (iv) develop a rationale for its assessment and prediction in soil.

General persistence of biochar

There is overwhelming anecdotal evidence for the persistence of biochar-analogues in soil, which spurred research of biochar as a persistent carbon (C) source. These analogues may include chars from natural vegetation fires (Krull et al, 2006; Knicker et al, 2012), anthropogenic additions such as charcoal residues from iron ore production (Cheng et al, 2008) or agricultural and domestic charcoal residues in archaeological sediments (Calvelo Pereira et al, 2014; see Chapter 1 for terminology). Often, pyrogenic C (PyC) from charring or vegetation fires is found to be the oldest organic C form in soil as determined by ^{14}C dating (Pessenda et al, 2001). Anthropogenic soils with an identifiable archaeological record and large accumulation of biochar-type materials often show large amounts of PyC even after several millennia (Glaser et al, 2001; Chapter 2).

However, mere quantification of presence of large amounts of biochar-type material or PyC in soil does not allow quantification of MRT, even if their age can be quantified using C-14 dating. For estimating the persistence of such biochar-analogues from measurements of their stocks, several conditions have to met: (i) the input has to be known or approximated; (ii) physical mass losses other than mineralization have to be quantified, such as erosion, leaching or burning; ignoring physical losses will allow a minimum MRT to be calculated that could lie significantly higher; and (iii) more than two points in time have to be available for using differences in PyC stocks. If only one or two measurable time points are available, a single exponential approximation of decay can only give a minimum value for MRT ignoring basic principles of temporal mineralization dynamics for reasons discussed later in this chapter. Fundamentally, the shape of the mineralization function needs to be known to make predictions about MRT. A mineralization rate (slow or fast) observed during the early stages of an experiment does not necessarily remain constant and does therefore not constitute a robust predictor for MRT. If the data comes from observations in mature ecosystems the numerical estimate will not adequately represent the slow mineralization phase. Thus, the fact that some authors find MRTs of over 2000 years while others observe less than 100 years (Table 10.1) is not a contradiction – it reflects the part of the mineralization curve that was observed and used for extrapolation (Box 10.1), in addition to differences in other experimental conditions. Finally, an important unknown in estimates of MRT is the future state (management system, disturbance, change in redox regime, etc.) of the soil, as these factors are all able to modify mineralization rates in both directions.

Another group of issues lies in the methods of analyses and the cycles of pyrogenic organic materials (PCM) when relying on quantification of residual PCM stocks in soil: (i) We may intend to measure char or charcoal but what we in fact typically quantify is PyC which is a proportion of PCM that also contains non-PyC (Chapter 1 for definitions); (ii) General issues arise in quantifying PyC that is often analytically defined and results therefore depend on the method used (Hammes et al, 2007; Chapter 24); (iii) PyC may not only mineralize to CO_2, but may also be altered by abiotic and biotic processes to other C forms (Chapter 9) that are not quantified as PyC. However, it would still be present in soil as non-PyC. This may be important if it can be shown that the turnover of metabolites produced from charred and uncharred organic matter differs. To facilitate this discussion, we therefore use the term 'mineralization' to indicate a transformation of organic C to CO_2, whereas the term 'decomposition' is used in the context of a transformation to other organic substances, typically microbial metabolites and debris.

The use of stable C-13 isotopes (see sections below) alone or in combination with PyC quantification would in theory allow better distinction of the different transformation and movement processes. However, the opportunity may rarely arise from existing char or charcoal deposits, as the source of PCM may be the same as that of non-PCM in soil. To date, no study has been published where a C-13 isotopic difference was utilized to track PyC from ancient fires or historic anthropogenic additions. The use of C-13 isotopic differences may rather be suitable in experiments where biochar with contrasting stable isotopic composition is added to soil, both in laboratory or field studies. Except for dating, C-14 radioisotopes have not been used to model or otherwise quantify the mineralization of PyC of existing char or charcoal in soil. The opportunities may be limited to do so, but should be explored in the future.

Field studies of PCM mineralization

Even though we intend to present an overview of the scientific evidence concerning the persistence of biochar in this section, the discussion is heavily influenced by methodological considerations, because the choice of methods greatly affects the estimates. Field studies are separately discussed here from laboratory studies below as both types of studies have greatly differing constraints and therefore caveats pertaining to the interpretation of results. Field studies allow quantification of biochar turnover under the most realistic conditions including differential climate, soil type, constant organic C input, soil management (e.g., tillage), presence of plants, etc. However, using field studies poses constraints on distinguishing mineralization from other pathways by which biochar may disappear from the topsoil, where it is typically applied. More so than laboratory studies, field studies restrict the number of comparisons between biochar types, which is shown by the low number of treatments per field study in Table 10.1.

Reported MRT of PCM studied under a variety of field conditions range from 6 to 5448 years (adjusted to 10°C mean annual temperature, Table 10.1). This range is wide considering the intent for biochar applications to serve as a long-term improvement of soil or as a means of C sequestration. Major portions of this variation stem from different PCM properties which are not random but are becoming predictable using material properties and environmental and biotic differences (discussed in later sections). This is in principle not different from well-known variations in decomposition of uncharred litter (Zhang et al, 2008), even though the material properties to predict mineralization are fundamentally different for biochar compared to uncharred residues. Another source of variation is the different experimental approaches and extrapolations used, which are discussed in the following sections.

Purposeful addition of biochar

Several studies over annual to decadal time scales have indicated neither mass loss nor increases in CO_2 emissions after biochar-type materials are added to soil (Wardle et al, 2008; Kimetu and Lehmann, 2010; Zhang et al, 2012), but these studies did not allow separate assessment of sources of CO_2. Monitoring the CO_2 evolution of applied biochar that can be isotopically distinguished from other sources of CO_2 is the most reliable and relevant method to quantify biochar mineralization (Major et al, 2010). Repeated measurements of C-13 in the soil to detect unique signatures of isotopically labelled biochar-type materials also capture all relevant effects of soil ecosystems on biochar mineralization (Kimetu and Lehmann, 2010). The limited number of MRT for biochar C estimated in these ways varies widely between 11 and 1314 years (values adjusted to a global mean annual temperature of 10°C, Table 10.1). Neither of the two approaches distinguishes between C from biochar remaining in soil in the form of the original added biochar material (dominated by PyC) and any decomposition products such as microbial metabolites or debris. Additional experiments would need to be included such as tracing the isotopes in microbially derived lipids (Santos et al, 2012; Farrell et al, 2013) or separately in PyC known (after analytical separation, Chapter 25) to be derived from the applied biochar to assess decomposition products.

Either approach has its strengths and weaknesses. Challenges to quantification of residual C-13 isotopic difference from applied biochar in soil arise from the large pool of soil organic C, only relatively small mineralization of biochar and the limitation to measure frequently over time which is needed for calculation of a MRT (Box 10.1). Challenges to quantifying CO_2 include the need to sample multiple locations in an experimental plot separately, detection of low isotopic differences over long periods of time and the effort and expenses associated with frequent or continuous measurements (Major et al, 2010). These challenges resemble those for MRT quantification of any organic amendments or plant litter.

No field studies have so far been reported that quantify PyC forms as proxy for applied biochar, except for studies on fire-derived char (Nguyen et al, 2008; Schneider et al, 2011). Quantification of residual PyC after biochar additions may generate valuable information in combination with C-13 isotopic techniques. Measurements of PyC on its own as an assessment of its persistence, however, leaves questions open about methodological constraints and choices as to what form of PyC is captured (Chapter 24).

For all these approaches, physical losses such as translocation into the subsoil or erosion on the soil surface would need to be assessed separately. Repeated measures even of soil C-13 derived from the biochar application would give an erroneous and low estimate of MRT if a significant proportion was eroded or leached as seen in Major et al (2010).

Box 10.1 Terminology for quantification of persistence

Persistence is typically measured through assays of the CO_2 evolved or the changes in amounts remaining in soil over time. A numerical value is commonly modelled by assuming an exponential decay, with the resultant dynamic expressed as decay rate, mean residence time (MRT, equivalent to mean life time), half-life or turnover time, which can also be applied to biochar. These are not synonymous but are mathematically related (Six and Jastrow, 2002). A decay rate is the exponent (k, as a function of environmental conditions) in the exponential decay function and has a unit of 1/time:

$$\text{Biochar}_{(\text{at time t})} = \text{biochar}_{(\text{at time 0})}\ e^{-kt}$$

MRT is the inverse of the decay rate (1/k) and is the average time that biochar is present. Half-life is the time that elapses before half of the biochar mineralizes and can be obtained by multiplying the MRT by the natural logarithm of 2. For computing the turnover time, information about the stock of biochar is required. It is calculated by dividing the stock at equilibrium by the loss per unit time.

Heterogeneous composite materials such as biochar and other natural organic matter are typically composed of a mixture of individual compounds or groups of compounds, here called 'fractions', each with different rates of decay. This may necessitate assignment of multiple exponential functions to describe the overall decay process, using distinct (although usually conceptual) 'pools'. For biochar, since more recalcitrant fractions seem to predominate, simplification may be possible when considering long time scales. Such equations can be solved mathematically to yield an estimate for 'k', provided that the assumption of no interaction between C pools and no transfer of decomposition products to other C pools can be made. Although this assumption cannot hold for all soil organic C forms, it may be used to conservatively estimate persistence of biochar. The alternate approach is multi-pool modelling typified by soil organic C models such as Century (Parton et al, 1994) and RothC (Coleman et al, 1997), in which material entering a pool as the product of one or more other pools is accounted for and the status of each pool is re-assessed at each successive calculation 'time step' (dynamic simulation).

Quantification through a PyC balance in natural char cycles

In practice, deliberate application of biochars as discussed above allows only relatively short-term assessment compared with predicted MRT of hundreds to thousands of years, as experiments lasting more than a few years are challenging to sustain. In addition, results from truly long-term experiments in the range of hundreds of years will naturally not be available for some time. However, there are several opportunities that can be explored, calculating a PyC balance of natural char dynamics being one of them (Czimczik and Masiello, 2007).

Fire has been part of Earth's C cycle for time periods well exceeding those relevant for estimating biochar persistence in soil (Bowman et al, 2009). Fire residues have therefore been deposited in soil over very long periods of time and may be used as analogues for those types of biochars made from similar biomass and under similar conditions. Chars from archaeological soil in the Amazon and from natural fires in an Iowa Mollisol shared similar molecular properties (Mao et al, 2012).

The requirements for calculating MRT from natural char cycles would include: (i) a known and preferably quasi-continuous input of chars over time; (ii) an input over a period that well exceeds MRT; and (iii) quantifiable char inputs and minimal char export beyond mineralization. A significant yet unknown export of chars would underestimate persistence and estimates can therefore be considered conservative with respect to expectations of high MRT. Grasslands may be more appropriate for such an approach as they burn frequently, whereas forest fires may prove too sporadic and the most recent fire may dominate the char record (Ohlson et al, 2009). Assumptions of char input significantly affect estimates of MRT but may in some instances be reasonably constrained by experimental data and resulted in MRT estimates between 1300 and 2600 years for a range of grasslands in northern Australia (Lehmann et al, 2008). It is also possible to extend this approach to regular anthropogenic burning of rice straw in paddies which have calculated to MRT values between 113–920 years in China (Lehndorff et al, 2014).

Chronosequences

Chronosequences substitute space for time by sampling soils that received biochar-type PCM at different times in the past (Bird et al, 1999; Preston and Schmidt, 2006; Hammes et al, 2008; Nguyen et al, 2008; Vasilyeva et al, 2011; Alexis et al, 2012). They are also called 'false time series' as they are not actually derived from sampling repeatedly over time, yet are used to draw conclusions of changes over time and have historically been used for a variety of processes beyond biochar and soil management (Huggett, 1998). The challenge is to identify a sufficiently large number of sites that have received the same amount and type of biochar, under near-identical environmental conditions (vegetation, soil type, climate) and management (tillage, cropping system). The assessment is also restricted to those PCM that are typically produced by fires rather than deliberate additions of a range of biochar types. The advantage of this approach is that biochar mineralization can theoretically be examined over longer periods of time up to hundreds (Hammes et al, 2008; Nguyen et al, 2008) or thousands of years (Preston and Schmidt, 2006, calculated from Gavin et al, 2003) than would ordinarily be accessible through field observations using researcher-managed biochar additions. Similar to field studies, significant challenges arise to either estimate or exclude physical movement of biochar. Since erosion can be the major pathway explaining disappearance of biochar from soil (Chapter 11), neglecting to consider this shortcoming will result in erroneous estimates of biochar mineralization (Nguyen et al, 2008). Chronosequences may therefore at best provide a lower estimate of mineralization and should not be used unless erosion and leaching rates are known to be low.

Laboratory studies of biochar mineralization

Laboratory studies allow for much greater control over experimental conditions to investigate effects of different environments and biochar properties, for example. However, their short-comings are their typically limited duration (even though the longest published observations to date stem from incubation studies) and absence of litter input, macrofauna, plants or soil management also affecting re-inoculation with microorganisms, water and temperature dynamics. Expectedly, variations in calculated MRT from 6 to 4419 years is large between and within studies that include a wide variety of different PCM and experimental conditions even when adjusted to the same incubation temperature (Table 10.1). Much of this variation can be explained with different biochar properties and experimental conditions (including soil properties, soil biota etc.) and are discussed in later sections as already pointed out for the results of field studies.

One important advantage of incubation studies is the opportunity to utilize so-called aged biochars. Such aged biochars have been obtained from storage sites of historic charcoal production (Cheng et al, 2008; Calvelo Pereira et al, 2014), isolated char fractions of fire-prone soils (Shindo, 1991), collected on the soil surface (Zimmermann et al, 2012) or experimentally produced in the laboratory

Table 10.1 *Mineralization of biochars and fire-derived chars and their methods of assessment (ordered by mean residence time)*

Calculated MRT[1] (years)	*Persistence as reported[2]*	*Method of calculation[3]*	*Type of study*	*Temperature of mineralization (°C)*	*Period of assessment (years)*	*Feedstock*	*Production[4]*	*Soil type or soil textural class*	*Reference*
6	94.50%	S	Incubation of fresh biochar	23	0.18	Wheat straw	Pyrolysis for several seconds; 525°C	Sandy loam	Bruun et al (2012)
7	91%	S	Incubation of fresh biochar	25	0.31	Barley roots	Burning for 40 min; 375°C	Sandy loam	Bruun et al (2008)
11	99.19%	S	Incubation of fresh biochar	30	0.04	Sugarcane bagasse	Pyrolysis for 40 min; 350°C	Quartz sand, microbial inoculant	Cross and Sohi (2011)
11	84%	n/a	Field trial of fresh biochar, recovery of biochar ^{13}C	Variable (average 21)	1–2 (repeat applications)	*Eucalyptus saligna*	Pyrolysis in charcoal kiln for appr. 2 days; 500–600°C	Nitosols	Kimetu and Lehmann (2010)
12	97.10%	S	Incubation of fresh biochar	23	0.18	Wheat straw	Pyrolysis for 2 hrs; 525°C	Sandy loam	Bruun et al (2012)
13	4 HL	D	Incubation of fresh biochar	30	2.33	Rye grass	Combustion for 1-4 min; oxic conditions; 350°C	Cambisol	Hilscher and Knicker (2011)
14	98%	S	Incubation of fresh biochar	20	0.16	Corn silage	Pyrolysis for 2 hrs; 600°C	Silty arable soil	Bamminger et al (2014)

Table 10.1 *Continued*

Calculated MRT[1] (years)	*Persistence as reported[2]*	*Method of calculation[3]*	*Type of study*	*Temperature of mineralization (°C)*	*Period of assessment (years)*	*Feedstock*	*Production[4]*	*Soil type or soil textural class*	*Reference*
27	89.50%	S	Incubation of fresh biochar	32	1.37	Gamma grass	Pyrolysis for 3 hrs; 250°C	Mollisol	Zimmerman et al (2011)
35	99.75%	S	Incubation of fresh biochar	30	0.04	Sugarcane bagasse	Pyrolysis for 40 min; 550°C	Quartz sand, microbial inoculant	Cross and Sohi (2011)
38	21 MRT	S	Incubation of fresh biochar	20	0.16	Corn straw	Pyrolysis for 2 hrs; 350°C	Quartz sand, microbial inoculant	Hamer et al (2004)
41	19 MRT	D	Incubation of fresh biochar	30	0.13	Rye grass	Combustion for 4 min; oxic conditions; 350°C	Cambisol	Hilscher et al (2009)
41	23 MRT	S	Incubation of fresh biochar	20	0.16	Rye straw	Pyrolysis for 2 hrs; 350°C	Quartz sand, microbial inoculant	Hamer et al (2004)
43	16 HL	S	Incubation of fresh biochar	25	0.55	Miscanthus straw	Pyrolysis for 20 min; 575°C	Loamy sand Mollisol	Bai et al (2013)
51	96.80%	S	Incubation of fresh biochar	25	1.92	Oak wood pellets	Fast pyrolysis; 550°C	Phaeozem, Luvisol, Gleysol	Stewart et al (2013)
58	20 HL	D	Incubation of fresh biochar	25	0.55	Miscanthus straw	Pyrolysis for 20 min; 575°C	Sandy Inceptisol	Bai et al (2013)

58	99.16%	S	Incubation of fresh biochar	25	0.24	Miscanthus	Pyrolysis for 30 min; 350°C	Aquic Paleudalf, pH 7.6	Luo et al (2011)
61	95.10%	S	Incubation of fresh biochar	32	1.37	Gamma grass	Pyrolysis for 3 hrs; 400°C	Mollisol	Zimmerman et al (2011)
62	95.20%	S	Incubation of fresh biochar	32	1.37	Gamma grass	Pyrolysis for 3 hrs; 250°C	Alfisol	Zimmerman et al (2011)
76	96.10%	S	Incubation of fresh biochar	32	1.37	Gamma grass	Pyrolysis for 3 hrs; 400°C	Alfisol	Zimmerman et al (2011)
79	99.39%	S	Incubation of fresh biochar	25	0.24	Miscanthus	Pyrolysis for 30 min; 350°C	Aquic Paleudalf, pH 3.7	Luo et al (2011)
81	39 MRT	D	Incubation of fresh biochar	27	0.43	Ryegrass	Pyrolysis for 4 hrs; 450°C	Cambisol	Maestrini et al (2014a)
92	48 MRT (own calculation)[5]	D	Incubation of fresh biochar	22	0.2	Wheat shoots	Pyrolysis for 40 min; 450°C	Aridic Arenosol	Farrell et al (2013)
107	97.20%	S	Incubation of fresh biochar	32	1.37	Gamma grass	Pyrolysis for 3 hrs; 650°C	Mollisol	Zimmerman et al (2011)
111	62 MRT	D	Incubation of fresh biochar	20	0.33	Eucalyptus wood	Pyrolysis for 40 min; 450°C	Vertisol	Keith et al (2011)

Table 10.1 *Continued*

Calculated MRT[1] (years)	*Persistence as reported[2]*	*Method of calculation[3]*	*Type of study*	*Temperature of mineralization (°C)*	*Period of assessment (years)*	*Feedstock*	*Production[4]*	*Soil type or soil textural class*	*Reference*
113	63 MRT	S	Incubation of fresh biochar	20	0.16	Oak wood	Pyrolysis for 2 hrs; 350°C	Quartz sand, microbial inoculant	Hamer et al (2004)
121	56 HL	D	Incubation of fresh biochar	30	0.13	Pine wood	Combustion for 4 min; oxic conditions; 350°C	Cambisol	Hilscher et al (2009)
122	60 MRT	S	Incubation of fire-affected soil (second exponential rate was taken as char)	25	0.6	Pine and oak litter	Fire-derived char	Dystric Cambisol	Knicker et al (2013)
130	56 HL	S	Chrono-sequence of fire-cleared soil, recovery of char by chemical oxidation	Variable (average 17.7)	51	Savanna grass	Fire-derived char	Sand to clay	Bird et al (1999)
131	46 HL	D	Incubation of fresh biochar	25	0.55	Miscanthus straw	Pyrolysis for 20 min; 575°C	Sandy loam Inceptisol	Bai et al (2013)

133	67 TOT (from 99.25%)	S	Incubation of aged and fresh char	Variable (20–50, average 24)	0.5	Acacia	Fire-derived char	Over glass beads	Zimmermann et al. (2012)
141	28%	S	Chrono-sequence of fire-cleared soil, recovery of char by NMR	Variable (average 19–21)	100	Natural woody vegetation	Fire char	Nitosols	Nguyen et al (2008)
146	99.43%	S	Incubation of fresh biochar	Variable (0–25, average 8.4)	0.83	Pine saplings	Pyrolysis for 5 hrs; 450°C	Cambisol	Maestrini et al (2014b)
170	89 MRT	D	Incubation of fresh biochar	22	5	Cow manure	Pyrolysis for 40 min; 400°C	Vertisol	Singh et al (2012)
173	80 MRT	S	Incubation of soil with 100-yrs aged biochar	30	0.48	Hardwood	Pyrolysis in charcoal kiln for appr. 2 days; 500–600°C	Varying soil NE United States	Cheng et al (2008)
179	100 MRT	D	Incubation of fresh biochar	20	0.33	Eucalyptus wood	Pyrolysis for 40 min; 550°C	Vertisol	Keith et al (2011)
181	82 MRT	D	Incubation of fresh biochar	32	1	Bubinga wood	Combustion for 3 hrs; 250°C	Quartz sand, microbial inoculant	Zimmerman (2010)
183	60 HL	D	Incubation of fresh biochar	28	0.3	Primary forest trees	Archaeo-logical charcoal (Papamoa)	Quartz sand, microbial inoculant	Calvelo Pereira et al (2014)

Table 10.1 *Continued*

Calculated MRT[1] *(years)*	*Persistence as reported*[2]	*Method of calculation*[3]	*Type of study*	*Temperature of*[5] *mineralization (°C)*	*Period of assessment (years)*	*Feedstock*	*Production*[4]	*Soil type or soil textural class*	*Reference*
196	88 MRT	D	Incubation of fresh biochar	32	1	Sugar cane bagasse	Combustion for 3 hrs; 250°C	Quartz sand, microbial inoculant	Zimmerman (2010)
198	99.58%	S	Incubation of fresh biochar	Variable (0–25, average 8.4)	0.83	Pine saplings	Pyrolysis for 5 hrs; 450°C	Cambisol	Singh et al (2014)
201	105 MRT	D	Incubation of fresh biochar	22	5	Papermill sludge	Pyrolysis for 40 min, steam; 550°C	Vertisol	Singh et al (2012)
212	99.76%	n/a	Incubation of fresh biochar	21	0.27	Mixed wood	Pyrolysis for 1–3 sec; 500°C	Typic Hapludoll	Spokas et al (2009)
217	98 MRT	D	Incubation of fresh biochar	32	3.2	Gamma grass	Pyrolysis for 3 hrs; 400°C	Quartz sand, microbial inoculant	Zimmerman and Gao (2013)
220	72 HL	D	Incubation of fresh biochar	28	0.3	Primary forest trees	Archaeological charcoal (Horotiu)	Quartz sand, microbial inoculant	Calvelo Pereira et al (2014)
231	96 MRT	D	Incubation of fresh biochar	32	1	Cedar wood	Combustion for 3 hrs; 250°C	Quartz sand, microbial inoculant	Zimmerman (2010)
239	125 MRT	D	Incubation of fresh biochar	22	5	Poultry litter	Pyrolysis for 40 min; 400°C	Vertisol	Singh et al (2012)

244	127 MRT	T	Incubation of fresh biochar	Variable (13–25, average 19)	1.4	Corn stover	Pyrolysis at 36°C min^{-1}; 550°C	Alfisol	Herath et al (2014)
251	113 MRT	D	Incubation of fresh biochar	32	1	Cedar wood	Pyrolysis for 3 hrs; 525°C	Quartz sand, microbial inoculant	Zimmerman (2010)
260	128 MRT (own calculation)	D	Incubation of fresh biochar	25	1.13	Barley roots	Pyrolysis with some air for 24 hrs; 500°C	Low clay	Bruun et al (2013)
262	129 MRT (own calculation)	D	Incubation of fresh biochar	25	1.13	Barley roots	Pyrolysis with some air for 24 hrs; 400°C	Low clay	Bruun et al (2013)
268	132 MRT (own calculation)	D	Incubation of fresh biochar	25	1.13	Barley roots	Pyrolysis with some air for 24 hrs; 600°C	Low clay	Bruun et al (2013)
269	99.82%	S	Incubation of fresh biochar	25	0.24	Miscanthus	Pyrolysis for 30 min; 700°C	Aquic Paleudalf, pH 7.6	Luo et al (2011)
269	93 MRT	D	Incubation of fresh biochar	32	1	Sugar cane bagasse	Pyrolysis for 3 hrs; 400°C	Quartz sand, microbial inoculant	Zimmerman (2010)
269	121 MRT	D	Incubation of fresh biochar	32	1	Bubinga wood	Pyrolysis for 3 hrs; 400°C	Quartz sand, microbial inoculant	Zimmerman (2010)
275	98.90%	S	Incubation of fresh biochar	32	1.37	Gamma grass	Pyrolysis for 3 hrs; 650°C	Alfisol	Zimmerman et al (2011)

Table 10.1 *Continued*

Calculated MRT[1] (years)	*Persistence as reported[2]*	*Method of calculation[3]*	*Type of study*	*Temperature of mineralization (°C)*	*Period of assessment (years)*	*Feedstock*	*Production[4]*	*Soil type or soil textural class*	*Reference*
293	75%	S	Chrono-sequence of fire-cleared soil, recovery of char by BPCA	Variable (average 6.6)	97	Natural grassland vegetation	Fire-derived char	Mollisol	Hammes et al (2008)
311	162 MRT	T	Incubation of fresh biochar	Variable (13–25, average 19)	1.4	Corn stover	Pyrolysis at 36°C min^{-1}; 350°C	Andisol	Herath et al (2014)
311	140 MRT	D	Incubation of fresh biochar	32	1	Sugar cane bagasse	Pyrolysis for 3 hrs; 525°C	Quartz sand, microbial inoculant	Zimmerman (2010)
325	147 MRT	D	Incubation of fresh biochar	32	1	Cedar wood	Pyrolysis for 3 hrs; 400°C	Quartz sand, microbial inoculant	Zimmerman (2010)
331	149 MRT	D	Incubation of fresh biochar	32	3.2	Oak wood	Pyrolysis for 3 hrs; 400°C	Quartz sand, microbial inoculant	Zimmerman and Gao (2013)
341	178 MRT	T	Incubation of fresh biochar	Variable (13–25, average 19)	1.4	Corn stover	Pyrolysis at 36°C min^{-1}; 550°C	Andisol	Herath et al (2014)
346	99.86%	S	Incubation of fresh biochar	25	0.24	Miscanthus	Pyrolysis for 30 min; 700°C	Aquic Paleudalf, pH 3.7	Luo et al (2011)

359	200 MRT	S	Incubation of fresh biochar	20	3.2	Rye grass	Pyrolysis for 13 hrs; 400°C	Haplic Luvisol or loess	Kuzyakov et al (2009)
369	166 MRT	D	Incubation of fresh biochar	32	3.2	Pine wood	Pyrolysis for 3 hrs; 250°C	Quartz sand, microbial inoculant	Zimmerman (2010), updated to 3.2 years
369	192 MRT	T	Incubation of fresh biochar	Variable (13–25, average 19)	1.4	Corn stover	Pyrolysis at 36°C min^{-1}; 350°C	Alfisol	Herath et al (2014)
381	213 MRT	D	Incubation of fresh biochar	20	1	Eucalyptus wood	Pyrolysis for 40 min; 450°C	Entisol	Fang et al (2014a)
381	172 MRT	D	Incubation of fresh biochar	32	3.2	Oak wood	Combustion for 3 hrs; 250°C	Quartz sand, microbial inoculant	Zimmerman and Gao (2013)
390	217 MRT	D	Incubation of fresh biochar	20	1	Eucalyptus wood	Pyrolysis for 40 min; 450°C	Vertisol	Fang et al (2014a)
420	234 MRT	D	Incubation of fresh biochar	20	1	Eucalyptus wood	Pyrolysis for 40 min; 450°C	Oxisol	Fang et al (2014a)
441	199 MRT	D	Incubation of fresh biochar	32	1	Sugar cane bagasse	Pyrolysis for 3 hrs; 650°C	Quartz sand, microbial inoculant	Zimmerman (2010)
458	207 MRT	D	Incubation of fresh biochar	32	3.2	Pine wood	Pyrolysis for 3 hrs; 400°C	Quartz sand, microbial inoculant	Zimmerman (2010), updated to 3.2 years

Table 10.1 *Continued*

Calculated MRT[1] (years)	*Persistence as reported[2]*	*Method of calculation[3]*	*Type of study*	*Temperature of mineralization (°C)*	*Period of assessment (years)*	*Feedstock*	*Production[4]*	*Soil type or soil textural class*	*Reference*
463	258 MRT	D	Incubation of fresh biochar	20	1	Eucalyptus wood	Pyrolysis for 40 min; 450°C	Inceptisol	Fang et al (2014a)
506	228 MRT	D	Incubation of fresh biochar	32	1	Bubinga wood	Pyrolysis for 3 hrs; 650°C	Quartz sand, microbial inoculant	Zimmerman (2010)
510	267 MRT	D	Incubation of fresh biochar	22	5	Eucalyptus leaves	Pyrolysis for 40 min, steam; 400°C	Vertisol	Singh et al (2012)
549	248 MRT	D	Incubation of fresh biochar	32	3.2	Gamma grass	Pyrolysis for 3 hrs; 525°C	Quartz sand, microbial inoculant	Zimmerman and Gao (2013)
551	303 MRT	B	Modeling of fire chars	Variable (average 20.4)	n/a	Rice straw	Fire-derived char	Paddy soil	Lehndorff et al (2014)
552	250 MRT	D	Incubation of fresh biochar	32	3.2	Gamma grass	Combustion for 3 hrs; 250°C	Quartz sand, microbial inoculant	Zimmerman and Gao (2013)
557	99.70%	S	Incubation of fresh biochar	25	1.92	Oak wood pellets	Fast pyrolysis; 550°C	Gleyic Phaeozem	Stewart et al (2013)
561	294 MRT	D	Incubation of fresh biochar	22	5	Eucalyptus wood	Pyrolysis for 40 min; 400°C	Vertisol	Singh et al (2012)

582	263 MRT	D	Incubation of fresh biochar	32	3.2	Pine wood	Pyrolysis for 3 hrs; 525°C	Quartz sand, microbial inoculant	Zimmerman (2010), updated to 3.2 years
594	311 MRT	D	Incubation of fresh biochar	22	5	Cow manure	Pyrolysis for 40 min, steam; 550°C	Vertisol	Singh et al (2012)
594	292 MRT	D	Incubation of fresh biochar	25	0.49	Pine wood	Pyrolysis for 5 hrs; 450°C	Granitic soil	Santos et al (2012)
605	273 MRT	D	Incubation of fresh biochar	32	1	Cedar wood	Pyrolysis for 3 hrs; 650°C	Quartz sand, microbial inoculant	Zimmerman (2010)
616	344 MRT	D	Incubation of fresh biochar	20	1	Eucalyptus wood	Pyrolysis for 40 min; 550°C	Inceptisol	Fang et al (2014a)
623	326 MRT	D	Incubation of fresh biochar	22	5	Eucalyptus wood	Pyrolysis for 40 min, steam; 400°C	Vertisol	Singh et al (2012)
709	320 MRT	D	Incubation of fresh biochar	32	3.2	Oak wood	Pyrolysis for 3 hrs; 525°C	Quartz sand, microbial inoculant	Zimmerman and Gao (2013)
736	362 MRT (own calculation)	D	Incubation of fresh biochar	25	1.13	Barley roots	Pyrolysis with some air for 24 hrs; 600°C	Intermediate clay	Bruun et al (2013)

Table 10.1 *Continued*

Calculated MRT[1] *(years)*	*Persistence as reported*[2]	*Method of calculation*[3]	*Type of study*	*Temperature of mineralization (°C)*	*Period of assessment (years)*	*Feedstock*	*Production*[4]	*Soil type or soil textural class*	*Reference*
751	393 MRT	D	Incubation of fresh biochar	22	5	Poultry litter	Pyrolysis for 40 min, steam; 550°C	Vertisol	Singh et al (2012)
755	371 MRT (own calculation)	D	Incubation of fresh biochar	25	1.13	Barley roots	Pyrolysis with some air for 24 hrs; 500°C	Intermediate clay	Bruun et al (2013)
785	386 MRT (own calculation)	D	Incubation of fresh biochar	25	1.13	Barley roots	Pyrolysis with some air for 24 hrs; 400°C	Intermediate clay	Bruun et al (2013)
788	94%	S	Chrono-sequence of fire-cleared soil, recovery of char by BPCA	Variable (average 5.5)	55	Natural grassland vegetation	Fire-derived char	Mollisol	Vasilyeva et al (2011)
807	450 MRT	D	Incubation of fresh biochar	20	1	Eucalyptus wood	Pyrolysis for 40 min; 550°C	Vertisol	Fang et al (2014a)
824	405 MRT (own calculation)	D	Incubation of fresh biochar	25	1.13	Barley roots	Pyrolysis with some air for 24 hrs; 600°C	High clay	Bruun et al (2013)

854	420 MRT (own calculation)	D	Incubation of fresh biochar	25	1.13	Barley roots	Pyrolysis with some air for 24 hrs; 400°C	High clay	Bruun et al (2013)
893	439 MRT (own calculation)	D	Incubation of fresh biochar	25	1.13	Barley roots	Pyrolysis with some air for 24 hrs; 500°C	High clay	Bruun et al (2013)
902	444 MRT	D	Incubation of fresh biochar	25	0.49	Pine wood	Pyrolysis for 5 hrs; 450°C	Andesitic soil	Santos et al (2012)
951	429 MRT	D	Incubation of fresh biochar	32	3.2	Oak wood	Pyrolysis for 3 hrs; 650°C	Quartz sand, microbial inoculant	Zimmerman and Gao (2013)
1037	578 MRT	D	Incubation of fresh biochar	20	1	Eucalyptus wood	Pyrolysis for 40 min; 550°C	Oxisol	Fang et al (2014a)
1090	571 MRT	D	Incubation of fresh biochar	22	5	Eucalyptus leaves	Pyrolysis for 40 min, steam; 550°C	Vertisol	Singh et al (2012)
1092	609 MRT	D	Incubation of fresh biochar	20	1	Eucalyptus wood	Pyrolysis for 40 min; 550°C	Entisol	Fang et al (2014a)
1114	503 MRT	D	Incubation of fresh biochar	32	3.2	Pine wood	Pyrolysis for 72 hrs; 650°C	Quartz sand, microbial inoculant	Zimmerman (2010), updated to 3.2 years

Table 10.1 *Continued*

Calculated MRT[1] (years)	*Persistence as reported[2]*	*Method of calculation[3]*	*Type of study*	*Temperature of mineralization[5] (°C)*	*Period of assessment (years)*	*Feedstock*	*Production[4]*	*Soil type or soil textural class*	*Reference*
1314	600 MRT	D	Field trial of fresh biochar, measurement of $^{13}CO_2$	Variable (average 26)	2	Mango wood	Pyrolysis in charcoal kiln for appr. 2 days; 400–600°C	Oxisol	Major et al (2010)
1558	703 MRT	D	Incubation of fresh biochar	32	3.2	Oak wood	Combustion for 72 hrs; 650°C	Quartz sand, microbial inoculant	Zimmerman and Gao (2013)
1905	882 MRT (re-calculated)	D	Incubation of soil with millennia-aged biochar	30	1.5	Unknown	Unknown char from burning or charring	Clayey Oxisols to sandy Spodosols	Liang et al (2008)
2425	1270 MRT	D	Incubation of fresh biochar	22	5	Eucalyptus wood	Pyrolysis for 40 min, steam; 550°C	Vertisol	Singh et al (2012)
2721	1300 MRT	B	Modeling of fire chars	Variable (average 27)	n/a	Natural grassland vegetation	Fire-derived char	Sandy Inceptisol	Lehmann et al (2008)
2736	1433 MRT (own calculation)	D	Incubation of fresh biochar	22	0.2	Eucalyptus globulus shoots	Pyrolysis for 40 min; 450°C	Aridic Arenosol	Farrell et al (2013)
3080	1613 MRT	D	Incubation of fresh biochar	22	5	Eucalyptus wood	Pyrolysis for 40 min; 550°C	Vertisol	Singh et al (2012)

3202	1444 MRT	D	Incubation of fresh biochar	32	3.2	Pine wood	Pyrolysis for 3 hrs; 650°C	Quartz sand, microbial inoculant	Zimmerman (2010), updated to 3.2 years
3857	1400 HL	n/a	Incubation of fresh biochar	Variable (17–27)	0.18	Pecan shells	Pyrolysis for 30 min; 700°C	Typic Kandiudult (loamy sand)	Novak et al (2010)
4419	1993 MRT	D	Incubation of fresh biochar	32	3.2	Gamma grass	Pyrolysis for 3 hrs; 650°C	Quartz sand, microbial inoculant	Zimmerman and Gao (2013)
5448	2603 MRT	B	Modeling of fire chars	Variable (average 27)	n/a	Natural grassland vegetation	Fire-derived char	Clayey Inceptisol	Lehmann et al (2008)

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[1] MRT adjusted to the average global land surface temperature of 10°C using the temperature conversion (Q_{10}) from Figure 10.3 (conversion equations explained in Box 10.1); MRT from recovery during a single measurement are calculated using a single-exponential single-parameter model

[2] MRT: mean residence time; HL: half life; TOT: turnover time (for double-exponential models, a weighted average was taken); MRT, HL and TOT given in years, recovery during a single measurement given as %, for the temperature under which the biochar mineralized in the study

[3] S: single exponential model; D: double exponential model; T: triple exponential model (models explained in later section); B: budget calculation; n/a if no model was used and only a one-time recovery measured (usually for experiments with only one measurement)

[4] Time at highest heating temperature

[5] calculation not available from the cited article but recalculated from original source data

using oxidants (Cross and Sohi, 2013). Also, incubations of soils with large proportions of PyC have been used to approximate mineralization rates and should be compared to adjacent soils with low or no PyC (Cheng et al, 2008; Liang et al, 2008; Knicker et al, 2013). Such aging may have two principal effects: (i) reduction of any easily mineralizable fraction of biochars; and/or (ii) weakening of aromatic structures. The former effect would avoid bias of long-term prediction of MRT through relatively large short-term mineralization of a non-PyC fraction. Resolving the question whether over very long time scales remaining biochars may have greater mineralization as suggested by the greater C-14 ages of the most easily chemically oxidizable PyC fraction (Krull et al, 2006), or indeed largely unchanged mineralization as suggested by similar functional group composition even over millennial time scales (Liang et al, 2008) may benefit from closer attention to interactions with minerals. Over decadal (McBeath et al, 2013), centennial (Schneider et al, 2011) and millennial (Liang et al, 2008) time scales, the evidence points towards rather unchanged bulk chemical composition of remaining chars in soils (not to be confused with changes in surface properties, which can be very large, Chapter 9).

Mechanism of biochar persistence

Different mechanisms determine on what time scale any organic materials mineralize, not just biochars. Environmental conditions such as moisture and temperature are likely the most important determinants of decomposition on a global scale and are discussed in the next section. At any given location, the rate of initial mineralization to CO_2 and decomposition to microbial products (process 1 in Figure 10.1) is a function of the chemical and physical characteristics of a given plant residue compared to other materials available to decomposers (all other conditions being equal). The current view is that the dominant processes for long-term persistence are spatial separation of decomposers from the organic matter or physical disconnection ('aggregation' shown as process 2 in Figure 10.1) and interactions with minerals ('mineral interaction' in Figure 10.1) (Schmidt et al, 2011), often together called 'stabilization'. This process of stabilization should be understood as the increase in persistence or MRT without a change in material property. The magnitude of persistence in soil is not discussed here (refer to other sections in this chapter), but the following briefly outlines the relative importance of these three different mechanisms: material preference, physical disconnection and mineral interactions.

Material preference is seen at best as a short-term mechanism for persistence of C from uncharred residues over time scales of days to months which largely depends on the adaptation of the microbial community to the litter quality and presence of alternative energy sources (Kleber, 2010). Plant C not mineralized to CO_2 is decomposed to microbial products for which chemical recalcitrance is not the dominant process determining persistence (Schmidt et al, 2011), but rather physical disconnection and mineral interactions contribute to their persistence as discussed later. This is different from biochar that has undergone significant changes in its chemical composition during pyrolysis (Chapter 6) in the sense that this initial phase of decay before relevant interactions with minerals (process 1 in Figure 10.1) has a greater quantitative importance for biochar over time scale comparable to decomposition of uncharred plant residues, but

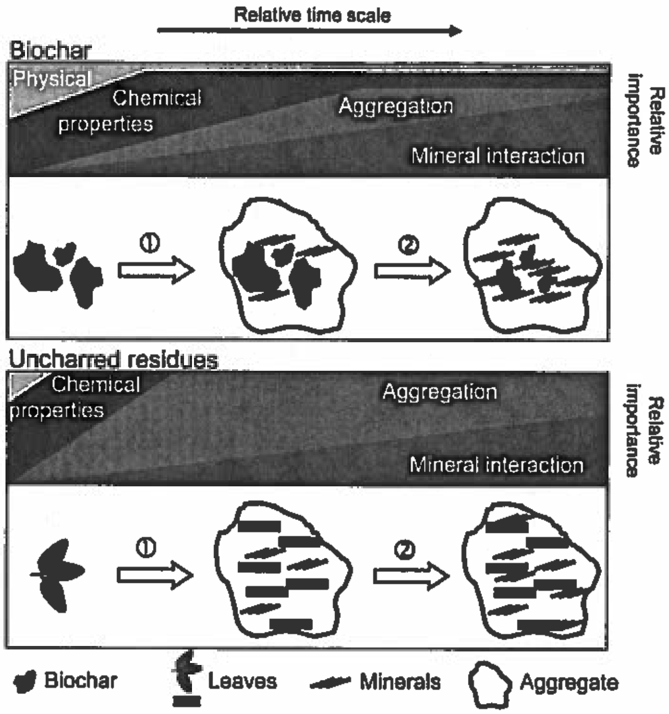

Figure 10.1 *Conceptual sketch of the relative importance of different mechanisms that determine persistence of biochar or uncharred organic matter in soil (the absolute time that C from biochar may reside in soil may be much greater); ① Relatively short-term decomposition and mineralization (similar to litter decomposition); ② Long-term persistence in aggregates and through mineral interactions (processes over long periods of time may differ for biochar, see text; greater importance indicated by a greater area in the plot)*

mechanisms over very long periods of time may not necessarily be qualitatively different (Box 10.2). The principle underpinning this phenomenon is that microorganisms prefer organic C forms that require less activation energy for their metabolization. The relevant change in material characteristics is that pyrolysis creates mineral-like properties which can be seen as a very early step towards the highly crystalline and well-ordered C mineral graphite, including: (i) the growth of graphene sheets that are much larger than those poly-condensed ring systems that have been reported as products of biological metabolism (and microorganisms therefore lack adaptation to utilize those as a source of energy); (ii) the assembly of turbostratic stacks with crystalline character; and (iii) the creation of unlimited molecular diversity of poly-condensed structures as a function of varying pyrolysis temperature and feedstock (Chapter 6).

These structural changes during charring are not homogeneous and vary considerably on a nanometer scale (Chapter 9) and depend on the biomolecule they are produced from (Knicker, 2011). The described ring structures have on average rather small cluster sizes that increase with greater pyrolysis temperatures: 18–40 C atoms were found in fresh biochars made from oak wood and corn residues at 350°C and 600°C using nuclear magnetic resonance (NMR) spectroscopy (Nguyen et al, 2010), 25 to 52 C atoms in biochars made from chestnut wood between 500°C and 700°C determined by adsorption of ^{13}C-labeled benzene (McBeath et al, 2011) and 20 or more C atoms in char residues in a Midwestern Mollisol and an Amazonian Dark Earth (Mao et al, 2012). These clusters are linked in larger PyC assemblages (Mao et al, 2012) which would remain in particulate form for long periods of time (Liang et al, 2008) and can also be seen to gain some degree of spatial ordering at temperatures around 600°C (Kercher and Nagle, 2003; Nguyen et al, 2010). How important the nano-scale spatial assemblage is for the persistence of biochars remains unclear (Lehmann et al, 2009), but could be important as different formations of onion-shape or fullerene-type structures are known to exist in PCM and possess different structural stabilities (Hata et al, 2000; Harris, 2005; Paris et al, 2005; Bourke et al, 2007; Cohen-Ofri et al, 2007). Within a given study, the net effect is a greater persistence of biochars that have been pyrolysed at higher temperatures (Figure 10.2).

Despite the dominance of aromatic ring structures, biochars also contain varying amounts of other compounds (Baldock and Smernik, 2002; Czimczik et al, 2002) that may mineralize more rapidly over relatively short periods of time of months such as those containing aliphatic C (Cheng et al, 2006; Hilscher et al, 2009; Nguyen et al, 2010). The proportion of non-aromatic C forms generally decreases with greater pyrolysis temperature (Nguyen et al, 2010; McBeath et al, 2014). However, considerable variation exists when examining the effects of pyrolysis temperature on mineralization (Figure 10.2) likely due to a combination of other pyrolysis conditions (e.g., duration, air flow) and feedstock properties (e.g., ash content), in addition to experimental conditions under which the mineralization was examined (see later sections). Understanding the molecular composition and indeed general properties is therefore important to quantification and prediction of the mineralization of different biochars in soil.

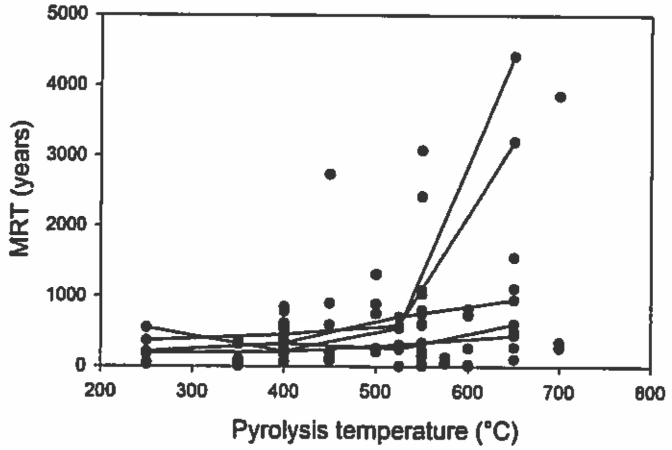

Figure 10.2 *Mean residence times (MRT) of biochars as a function of pyrolysis temperature (MRT adjusted to 10°C from Table 10.1; fire- and combustion-derived PCM were excluded); lines connect data from the same feedstock and mineralization experiment for which data were available for the greatest temperature range*

Box 10.2 The concept of persistence applied to biochar

It is irrefutable that charring decreases the mineralizability of organic materials supported by the empirical evidence provided in this chapter. From a mechanistic point of view, however, it would be incorrect to invoke an inherent material recalcitrance as responsible for greater longevity of biochars. Reconciling this apparent contradiction provides a useful conceptual framework for explaining the empirical evidence, for instilling confidence in the observed reduction in mineralization through charring and for designing biochar systems that maximize biochar persistence.

Any organic matter may in theory need to be considered mineralizable by microorganisms when the microbial community has the ability to adapt to the organic matter structure (Ekschmitt et al, 2005) and no additional mechanisms operate that confer greater persistence (such as low temperature, low moisture, interactions with minerals or aggregation, as discussed in the main text). Soil contains countless bacterial, fungal and faunal decomposers, many of which are accustomed to adapting to variations in food supply and substrate properties. In principle, compared to carbohydrates, aromatic C forms characteristic of biochars actually generate much greater energy yields when reacted with O_2 (about 40kJ g^{1} for a benzene ring compared to about 15kJ g^{1} for glucose, Chapter 6), creating a strong energetic incentive for decomposers to use aromatic rings as an energy source. Indeed, white-rot fungi are capable of developing enzymes that allow mineralization of small poly-aromatic rings (Hatakka and Hammel, 2011) and fullerol (Schreiner et al, 2009). However, biochar is both chemically unusual and energetically less advantageous to mineralize than most other organic C forms in the soil ecosystem (all other factors being equal). Microorganisms prefer substances that they are used to (home-field advantage, Ayres et al, 2009) and will therefore not prefer the introduced biochar. Other more prevalent C sources in soil are easier to metabolize for reasons of lower energy costs of producing the enzymatic tools needed (Schimel and Weintraub, 2003) and indeed plant litter additions to *Terra Preta* soils were shown to reduce the mineralization of PyC already present in soil (Liang et al, 2010). Therefore, the relationship between material properties determines the greater persistence of biochar in soil, rather than an intrinsic stability or recalcitrance. Traditional concepts of recalcitrance can be successful in describing observed mineralization dynamics, but a thermodynamically correct concept may account for a greater variation in environmental conditions.

Physical disconnection confers persistence to otherwise easily decomposable organic C through separation of the organic substrate inside aggregate (Tisdall and Oades, 1982) or occlusion in small pores that are inaccessible to microorganisms (Kaiser and Guggenberger, 2008). The extent to which this process is critical for biochar is not very clear. Char materials from vegetation fires have been observed inside aggregates (Brodowski et al, 2005; Lehmann et al, 2005), but to a greater extent in free light fractions outside aggregates (Glaser et al, 2000; Shindo et al, 2004; Murage et al, 2007) and in so-called heavy or mineral-associated fractions (Glaser et al, 2000; Liang et al, 2008). Chars from land clearing were macroscopically visible for about 30 years after deposition with particles larger than 50μm present and remained particulate over centennial (Nguyen et al, 2008) and even millennial time scales (Glaser et al, 2000; Lehmann et al, 2005; Liang et al, 2008). These particle sizes are too large to fit into the nanometer-size pores that would reduce access by microorganisms. Occlusion in small pores may therefore not be an important process conferring persistence to biochar. However, physical fractionation techniques developed for non-PyC with different specific densities, sizes and hydrophilicities may not automatically be suitable for biochars. Given the lack of strong evidence, aggregation and occlusion in pores are assumed to have a lower importance than interactions with minerals over long periods of time (Figure 10.1). This also agrees well with observed lower initial mineralization rates of biochars without interaction with minerals than that of uncharred residues (as seen in incubations with sand by e.g. Baldock and Smernik, 2002; Whitman et al, 2013).

On the other hand, the particulate nature of PCM maintained over long periods of time acts in itself in a way that may be described as 'self-aggregation'. The physical disconnection of the interior of a biochar particle with virtually unchanged chemical characteristics over millennia from the decomposer community surrounding the particle might reduce mineralization rates (Liang et al, 2008). Support for this process is provided by an incubation experiment with sand where smaller biochar particles mineralized faster than larger ones despite similar surface areas of the particles (Zimmerman, 2010). This should be classified as a physical property of biochars (process 1 in Figure 10.1) that likely remains important for biochar's persistence over longer periods of time in comparison to plant residues.

Interactions with minerals are a chief mechanism for long-term persistence of any organic matter in soil. Due to the mentioned small ring sizes of aged PCM, its high loading with negatively charged functional groups (Mao et al, 2012) and possibly due to its radical content and electrochemical properties (Joseph et al, 2013), opportunities for interactions with positively charged minerals are large. Such interactions could either occur with dissolved mineral elements including Al, Mn, Fe and Ca, or with soil minerals such as Fe or Al oxides or phyllosilicates. Direct spectroscopic evidence for both processes exists (Nguyen et al, 2008; Joseph et al, 2010, 2013; Chia et al, 2012; Heymann, 2012) and soil PyC contents were correlated with short range order minerals in fire-prone Hawaiian soils (Cusack et al, 2012). Mineralization of barley root biochar was significantly reduced with increasing clay contents from 11 per cent to 23 per cent of three Danish soils (Bruun et al, 2013), whereas a range of clay contents from 0.3 per cent to 27 per cent had no effect on mineralization rates of organic C dominated by old PCM in *Terra Preta* soils (Liang et al, 2008). The MRT of wood biochar determined in an incubation experiment was 22–35 per cent greater in an Oxisol (with greater proportion of short range order soil minerals) than in both Vertisol and Inceptisol from Australia (Fang et al, 2014a). Mineralization of biochar made from pine wood was reduced by half over six months when incubated in an andesitic soil with greater amounts of short range order clay minerals compared to a granitic soil; whereas there was no difference in mineralization for uncharred wood (Santos et al, 2012). In addition, mineralization of corn-stover biochar was unaffected by pyrolysis temperature in an Andosol, but reduced nearly by half to the level of the mineralization in the Andosol when incubated in an Alfisol (Herath et al, 2014). This may indicate a greater stabilization of charred compared to uncharred organic matter by reactive clay minerals. Whether or not these are rooted in different molecular interactions is not yet clear. Judging from the high proportion of negative surface charge of biochars in soil (Chapter 9) such stabilizing mechanisms may be larger for PCM than for uncharred organic matter, but differences in correlations with short range order minerals compared to other organic matter could not be verified (Cusack et al, 2012). In addition, biochars can remain particulate in soils over millennia (reaching at least 8000 years; Liang et al, 2008) and despite molecular interactions with mineral elements inside biochar particles (Joseph et al, 2010, 2013), the available surfaces may remain limited. On the other hand, biochars can have large surface areas (Chapter 5) and surface area in soils with high biochar contents remained high even after millennia (Liang et al, 2006). Yet a large proportion of pores of biochars assessed by conventional surface area measurements is likely smaller than what is accessible by clay minerals that have sizes greater than the N_2 or CO_2 gases used to assess surfaces. It is probable that biochar-mineral interactions are qualitatively and quantitatively different from those operating on uncharred organic matter. This requires further study recognizing the time dependence of biochar surface quality and quantity (Chapter 9).

Little known is whether the interactions with mineral elements or surfaces differ in terms of their time scale or relative importance at the stage when biochar C is decomposed by microorganisms to other microbial products (either metabolites or debris). Some authors have suggested that so-called 'black humic acids' decomposition products exist in soils that are different in chemical composition than decomposition products from uncharred organic residues (Shindo and Honma, 2001; De Melo Benites et al, 2004; Kramer et al, 2004). On the other hand, it is also possible that some or all decomposition products from biochar are chemically identical to those of uncharred plant residues (especially if functional group composition of alkaline extracts cannot be found at high spatial resolution, Heymann et al, 2014) and will behave identical to uncharred organic matter.

Mechanisms of mineralization

Biotic processes

Biochars are mineralized to CO_2 (Potter, 1908; Shneour, 1966) and decomposed to other organic materials by microorganisms (Wengel et al, 2006) as are all organic residues in soil. PyC, which makes up a major proportion of biochars, differs from other natural organic matter and the decomposer community will typically lack the full suite of enzymes required to decompose the multitude of thermally altered organic phases produced by pyrolysis (as discussed above and in Box 10.2). Possibly microorganisms preferentially colonize some biochars (Lehmann et al, 2011) and this may increase biotic mineralization of biochar (Farrell et al, 2013; Luo et al, 2013), which may be a function of the amount of easily mineralizable C in biochars (Luo et al, 2013). Some soil fauna groups such as earthworms have been shown to preferentially ingest soil containing fire-derived chars (Topoliantz and Ponge, 2003, 2005) or biochar (Van Zwieten et al, 2010). Earthworms may physically disperse biochar in the soil and decrease biochar particle sizes, but whether these processes decrease or enhance its mineralization is not known (Ameloot et al, 2013). However, biochars are diverse to elicit one uniform response and careful consideration has to be given to biochar properties.

Similarly, some evidence exists for preferential exploration of biochars by roots and root hairs (Chapter 14). Roots can exude protons or low-molecular acids thus changing the chemical environment and the biological activity in the rhizosphere. Whether any of these processes will have a net positive or negative effect on biochar mineralization is not known.

Chemical processes

Even though activity of soil biota is likely the major pathway of mineralization of biochar, also abiotic processes can lead to significant CO_2 evolution from biochars and specifically facilitate biotic mineralization. Inorganic carbonates invariably contained in some biochars (Enders et al, 2012) may be dissolved through dissolution reactions (Farrell et al, 2013). If present in significant quantity, the CO_2 released through the dissolution process can influence estimation of mineralization rates using the natural C-13 abundance and 2-pool mixing model approaches (Singh et al, 2012a; Bruun et al, 2013). In addition, these inorganic carbonates would not be included in prediction of persistence (e.g., by using H/Corg ratios), but are often not analytically separable in mineralization studies. None of the incubation studies used to calculate MRT of biochar (Table 10.1) have assessed this process separately. It would be worthwhile to explore whether accounting inorganic C separately from total C would improve predictions of mineralization from ash-rich biochars (Singh et al, 2012a; Farrell et al, 2013). This is relevant for certain waste streams (e.g., animal and human manures, sludges, food wastes) that may contain relevant proportions of inorganic carbonates (Enders et al, 2012), as well as biochars made with incomplete exclusion of O_2 (Bruun et al, 2013).

Abiotic oxidation of PyC surfaces may initially (after metabolization of non-PyC) be more important than biotic oxidation over monthly time scales (Cheng et al, 2006) and may facilitate biotic metabolization, even if it does not lead to C loss as such. In fact, it is plausible that abiotic processes (including physical diminution discussed later; Chapter 9) may be needed to allow biotic mineralization of fused aromatic ring structures. However, it should be noted that processes likely occur simultaneously and may greatly differ between different types of biochars. Abiotic mineralization of organic C to CO_2 has been calculated as a third (Zimmermann et al, 2012) to half (Zimmerman, 2010) or more (Bruun et al, 2013) of total mineralization over the first few months. Incubations of fresh biochar alone without microbial inoculants also showed in part significant evolution of CO_2 and were attributed to a variety of processes including abiotic reactions with water (Spokas and Reicosky, 2009; Spokas et al, 2009) and desorption of CO_2 (Bruun et al, 2013). Maintaining sterile conditions is challenging even in the laboratory and abiotic processes may require additional evidence, since they appear to be possibly significant.

Photo-oxidation may be important for biochars that remain on the soil surface as shown for uncharred plant litter (King et al, 2012). However, information on this process does currently not exist for biochar. Data on aged chars from forest fires collected on the forest floor surface point at a proportionally increasing fraction of leachable C (e.g., Abiven et al, 2011), but do not explicitly address photo-oxidation by excluding other processes. Skjemstad et al (1996) analytically defined PyC as the fraction of organic matter that is resistant to photo-oxidation, which suggests that the PyC fraction of biochars may be less prone to mineralization by this process than most uncharred organic matter.

Physical processes

Biochars may physically disintegrate, thereby increasing the opportunities for both mineralization and stabilization through interactions with soil minerals. Smaller particles were shown to mineralize more rapidly than larger particles in the absence of clay minerals (Zimmerman, 2010). No char particles with a diameter greater than 50μm could be found in a humid tropical upland soil thirty years after forest fires (Nguyen et al, 2008) pointing at disintegration over decadal time scales. Diminution may in general be a result of frost, temperature and moisture changes, salt weathering, roots or mechanic stress through soil tillage (Chapter 9). No indication exists whether any of the mentioned physical processes is specifically important to reduce or increase biotic mineralization of biochar. Proliferation of fine roots within biochar pores (Chapter 14) may motivate research on how this process affects biochar mineralization. Physical disintegration, as mentioned for chemical processes, may be analogous to weathering processes of minerals, which then allow biotic mineralization to occur.

Effects of environment and soil management on biochar persistence

Temperature

Temperature has profound effects on biological, chemical and physical processes in the environment and is therefore also expected to influence mineralization of biochar in soil. With important modifications depending on physical access to the organic C in soil, biological mineralization typically increases with temperature to a greater extent for those organic materials that mineralize more slowly (Davidson and Jannsens, 2006), expressed as the so-called Q_{10} (i.e., the increase in mineralization with a temperature increase of 10°C). Therefore, biochar mineralization may be expected to be more sensitive to temperature changes in soil than uncharred organic matter if all other factors are kept constant (which is difficult). Unfortunately, no direct comparison of the influence of soil temperature on mineralization between uncharred and charred organic matter is presently available. Fang et al (2014b) found that Q_{10} values were not influenced by the type of biochar (produced from a woody biomass source at 450 or 550°C) when incubated in soil, which suggests that interactions between soil minerals and biochar can reduce temperature sensitivity as was pointed out for uncharred organic matter (Davidson and Jannsens, 2006). In contrast, an increased Q_{10} of mineralization from corn stover biochar from 1.2 to 1.6 (at 10–20°C) with increasing pyrolysis temperature from 350 to 600°C (Nguyen et al, 2010) may serve as an indication for the magnitude of changes in temperature sensitivity of biochar mineralization without significant interactions with minerals (the incubations were done in sand) or other variables. Q_{10} values for an incubation on glass beads for an aged fire-derived char similarly lay at 1.7 (for 20°C; Zimmermann et al, 2012). Calculations based on C stock changes by Cheng et al (2008) yielded a Q_{10} of 3.4 at temperatures between 5 and 15°C, which is identical to results from oak wood biochar pyrolysed at 350°C from Nguyen et al (2010) when interpolated to the same temperature. Q_{10} values decreased non-linearly with increasing temperature of mineralization (Figure 10.3 (a)). The variation in this non-linear relationship was found to be to a certain extent a function of the H/C ratios of the biochars and thereby their mineralization (Figure 10.3 (b)). However, factors beyond material properties will also be important. This is illustrated by the different Q_{10} values found for incubations of identical organic materials (Feng and Simpson, 2008) and biochar (Fang et al, 2014b) in different soils.

The Q_{10} values so far obtained for biochars are above or at the upper range of values for uncharred plant litter mineralization (Gholz et al, 2000; Fierer et al, 2005). This also holds for comparisons between biochars that show greater Q_{10} values with lower H/C ratios (Figure 10.3 (b)). This Q_{10} dependency on biochar properties increases with lower mineralization temperature (Figure 10.3 (a)). However, conditions other than the material properties also play a significant role in determining Q_{10}, as mentioned before.

The Q_{10} values experimentally established so far may be biased towards the more easily mineralizable fraction of biochars, as the incubation results necessarily reflect the properties of the C that evolve during the first months of incubation. However, the studies that evaluate temperature sensitivity using mineralization of charcoal recovered from storage sites after 130 years (Cheng et al, 2008) or of naturally aged chars (Zimmermann et al, 2012) related well with the temperature sensitivity using incubation of fresh biochars (Nguyen et al, 2010). Very low temperature below freezing may still lead to oxidation as seen from changes in surface characteristics at -22°C (Cheng and Lehmann, 2009). Mineralization, however, may be limited and no information is available to suggest that this oxidation would be different compared to uncharred biomass at such low temperature.

Moisture

Moisture is a major factor controlling mineralization of organic C in soil. It is therefore not surprising that a model of biochar mineralization was very sensitive to variations in moisture and resulted in poor matches between observed and predicted mineralization especially during dry seasons (Foereid et al, 2011). Saturated soil water conditions (and possibly concurrent reduction in O_2 availability) did not significantly decrease mineralization of biochars that were pyrolysed at a greater temperature (600°C than 350°C) over a period of one year compared to unsaturated conditions (Nguyen and Lehmann, 2009). For biochars made from corn stover at 350°C, however, mineralization decreased by half under saturated conditions, with a similar decrease observed for biochars produced from oak wood at 350°C between alternating saturated/unsaturated conditions and saturated soil water contents. Conversely, it is presently not known, at what point a lack of moisture reduces mineralization and whether this is different to moisture

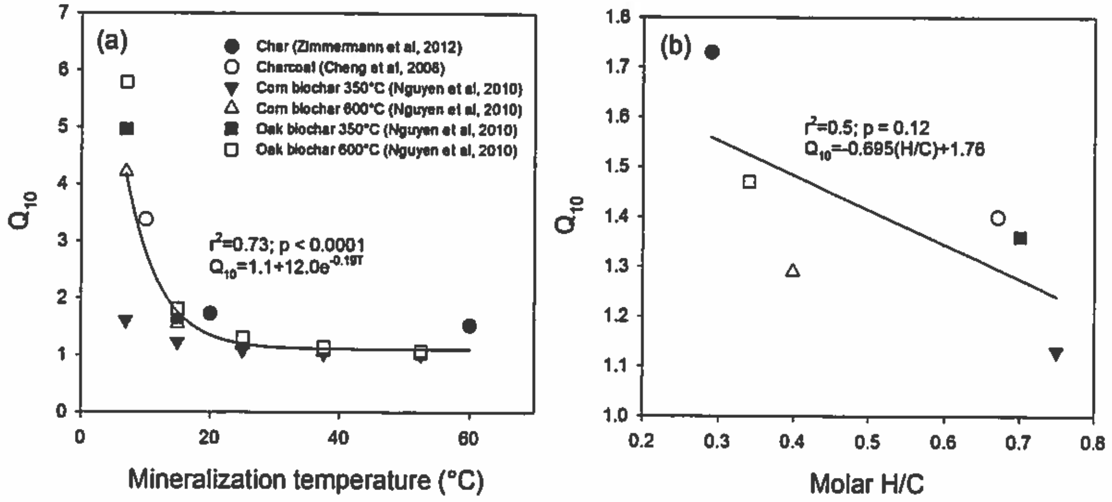

Figure 10.3 *Q_{10} values of biochar mineralization (a) with increasing temperature of mineralization and (b) as a function of molar H/C ratios of biochars (Q_{10} at a mineralization temperature of 20°C)*

contents observed for uncharred organic matter (e.g., below 5–15 per cent moisture as found for a pine forest and oak savanna by Yuste et al, 2007). Also interactions between moisture and temperature under field conditions and their effects on biochar mineralization have not been investigated so far.

Soil properties

The soil type and particularly soil texture and mineralogy play an important role for biochar mineralization (as discussed before), as is well known for uncharred organic matter due to their effects on aggregation and mineral interactions. Higher soil pH was also shown to increase mineralization of biochars (Cheng et al, 2008; Luo et al, 2011). Both a lower toxicity of free metals (e.g., Al) for microorganisms and a lower stabilization of biochar by short range order oxides may contribute to this lower persistence, outweighing any stabilizing effects of Ca-bridging that is more likely to occur in soil with alkaline pH values.

Tillage

Tillage of soil typically leads to greater mineralization of soil organic C through a variety of processes including aeration, destruction of macroaggregates or desorption from mineral surfaces. On the one hand, one may expect a greater acceleration of mineralization by tillage for biochar than other organic matter if biochar particles are physically broken and C surfaces exposed that would otherwise be protected in the particle interior. On the other hand, the opposite may be hypothesized since mineralization of biochar without mineral interactions or aggregate protection that are typically reduced by tillage the most, is lower than that of uncharred residues. Skjemstad et al (2004) reported virtually no decrease in char from vegetation fires over 8–18 years of tilling several soil types at two locations in Australia. Similarly, annual ploughing of a bare fallow did not significantly reduce PyC contents determined by the BPCA (benzene polycarboxylic acid) method, while total organic C decreased by 33 per cent over 55 years (Vasilyeva et al, 2011), not suggesting any detectable acceleration in biochar mineralization by tillage. Until further evidence is available, it may be assumed that proportional increases in mineralization of biochar by tillage are of the same order of magnitude as those documented for other soil organic C. This also means that evidence from mineralization of fire-derived chars in untilled soils must be corrected for the effect of tillage if those data are to be applied to inform on agricultural soil that is tilled.

Plant carbon input

Input of organic C by plants, such as roots, root exudates or leaf litter as well as any other organic matter inputs, such as animal manure, green manures or composts, will change mineralization of biochar in soil through co-metabolism or priming and are covered in Chapter 16. Greater existing soil organic C contents were also suspected to enhance biochar mineralization in four North American soils (Gomez et al, 2014). These effects have to be considered when extrapolating from incubation results without plants to application of biochar in agricultural soil.

Fires

In-situ burning in case of vegetation fires or crop residue burning may lead to CO_2 emissions from biochar. Burning of naturally produced chars in subsequent fires has been proposed as a possible reason for low char accumulation observed in natural ecosystems (Ohlson and Tryterud, 2000; Czimczik et al, 2005). However, experimental fire was found to only cause a 7 per cent loss of chars buried

20mm into the organic forest floor (Santin et al, 2013) and less than 8 per cent when attempting to maximize combustion by placing chars on the soil (Saiz et al, 2014), indicating very low rates of reburning. Any incorporation of biochar into mineral soil would probably even reduce such values, as temperatures during experimental fires reached only less than 50°C at a depth greater than 20mm (Bradstock and Auld, 1995). In modern soil management that likely includes incorporation of biochar and no significant crop residue burning in fields, this process may therefore not be as important as in natural ecosystems where most of the char is accumulating in organic horizons, on the soil surface or even on living or dead above ground woody vegetation.

Assessment of biochar persistence

Most of the current and likely also future assessments of biochar persistence are made by experimental additions of biochar to soil rather than using existing biochar-analogues such as fire-derived chars or residues from historic charcoal production. The main reason for this approach is that it includes better constraints on experimental conditions such as holding all factors except biochar mineralization constant and inclusion of appropriate controls, the ability to utilize isotopic differences and allowing for different biochar properties relevant to modern biochar management. Especially this last point is important, as differences in mineralization between biochars with varying properties and under different experimental conditions (two orders of magnitude from decadal to millennial time scales, Table 10.1) are similar to the differences between charred and uncharred materials (1.5 orders of magnitude; Baldock and Smernik, 2002; Santos et al, 2012; Maestrini et al, 2014b). Using natural or historic deposits of biochar analogues only permits the study of a segment of possible biochar types such as those derived from grass or forest fires and does not allow direct characterization of the starting materials (except for simulation of e.g. charcoal production or fires). However, assessments of such deposits give evidence for the persistence of biochar for time scales beyond what is directly quantifiable by experimental additions of biochars. Nonetheless, these are not further discussed here and the assessment concentrates on those experimental opportunities that allow biochar additions and monitoring.

Short-term assessments and long-term predictions

Strictly speaking, any experiments that use modern biochar to apply to soil will constitute a 'short-term' assessment relative to most expectations of information about 'long-term' mineralization rates. This would apply to both laboratory incubation experiments and to field experiments. The reason is that the time period that we seek information for likely exceeds the time period we monitor mineralization of biochar applied to soil at the beginning of the experiment. This requires extrapolation beyond the period of observation, which increases its uncertainty and requires multiple approaches to instil confidence about the calculated MRT. In addition to extrapolations, there are some opportunities to extend the time horizon of observation by: (i) exposing biochar to higher temperatures during what will likely be a laboratory study and therefore accelerate decomposition that may be mathematically corrected by using estimates of temperature sensitivities; or (ii) utilizing aged biochars as described in other sections. While field experiments are preferred for reasons discussed in an earlier section, such as realistic environmental and management conditions, they do not allow these two strategies to be used and are typically constrained to testing very few biochar types for reasons to keep work load manageable. In addition, the variability of environmental conditions such as soil moisture and temperature make extrapolations challenging especially in strongly seasonal climates (Maestrini et al, 2014b). Laboratory experiments offer more flexibility as to what biochars and experimental conditions are used (reflected in the larger number of treatments for incubations studies per publication than for field studies, Table 10.1) and extrapolate short-term data, but periods of observations typically do not exceed several years and are often much shorter than that. It is not fully evident, however, whether laboratory incubation experiments consistently over- or under-estimate mineralization as seen from experiments with uncharred litter (Bonan et al, 2013).

Furthermore, the objectives for adding biochar to soil may vary and with that also the data requirement. If climate change mitigation is sought, centennial to millennial data may be required depending on C trading periods. Information about annual or decadal time periods may suffice in cases where soil improvement is of interest that is likely to be considered 'long-term' already after several years.

If information is needed for time periods exceeding conventional experiments (whether laboratory or field experiments), an extrapolation is required. Such predictions of future mineralization is currently done by fitting equations through measured data and examining the behaviour for time periods exceeding the duration of measurements. Choosing the correct equation requires knowledge about the properties of biochar and the mineralization process. The equations or set of equations are therefore often called 'models' as they represent an understanding of the underlying mechanisms. These models can have different forms and allow calculation of half life or MRT (Box 10.1) that are typically longer than periods of observation.

Calculation methods

Mineralization of plant litter is commonly modelled using a single exponential function (1-pool; Box 10.1). However, the large difference in mineralizability of the comparably more labile fractions of fresh biochar composed of low-molecular acids and N-rich volatile compounds and the less labile fractions composed of cyclic C forms of varying formations (Chapter 6) requires the use of multiple pools with their own mineralization rate. The differences in calculated MRT are high when using either single or multiple pools and the number and duration of data available determine the options for computing MRT. Using conceptual data of biochar C remaining over 100 years assuming three fractions with varying MRT resulting in an average MRT of 712 years (Figure 10.4 (a)), the fitting of a single-exponential equation (1-pool) through either the data of the first 5 years, of all years or of the last 50 years of data produces vastly different MRT estimates ranging from 52 to 610 years (Figure 10.4 (b)). For an incubation experiment of 8.5 years, Kuzyakov et al (2014) calculated a MRT that was twice as long as the one calculated for the first 2.5 years (Kuzyakov et al, 2009). Therefore, the duration over which measurements are available as well as whether the comparatively rapid initial mineralization is accounted for has a profound effect on the calculated MRT.

Theoretically, it may be desirable to not only apply a model with two pools but with multiple pools (Bai et al, 2013; Zimmerman and Gao, 2013; Herath et al, 2014), recognizing that biochar C is composed of a continuum of PyC forms (Preston and Schmidt, 2006) with progressively slower mineralization rates.

The use of multiple pools poses another constraint to data requirements in addition to long-term observations: multiple measurements are needed to parameterize such models. However, often only one or two measurements of remaining biochar are made (Nguyen and Lehmann, 2009; Whitman et al, 2013) and using such data results in low estimates of MRT (Singh et al, 2012b). For an example mineralization experiment conducted by Singh et al (2012a), the 1-pool equation calculated a MRT of 966 years, the 2-pool equation a MRT of 1614 years and a model with infinite pools ('power model' introduced by Zimmerman, 2010) a MRT of 16,313,528 years (Figure 10.4 (c)). It seems indispensible to utilize at least two pools to adequately describe the mineralization dynamics. Alternatively, it may be possible to account for initial rapid mineralization in different ways, such as fitting curves by omitting the initial rapid mineralization (Figure 10.4 (b)). Inclusion of additional pools into the calculation may provide better approximation of long-term mineralization but extrapolation much beyond measured data may be more appropriate using fractions that are actually measured. Therefore, a 2-pool exponential model improves estimates when only a few years of data are available. An extrapolation beyond the period covered by the available data poses undeniable challenges to the assessment of biochar mineralization without scrutinizing the adequacy of the models used for a specific data set. This is illustrated by a very wide range in MRT values calculated by the three models shown in Figure 10.4 (c). In addition, the already mentioned variability in temperature and moisture conditions in field experiments provides challenges to extrapolation (Maestrini et al, 2014b). Dynamic models should be developed that include environmental factors as well as decomposers, which are currently only available in incipient form (Foereid et al, 2011).

The duration of an experiment also affects the results. Longer experiments that allowed the use of a 2-pool model included the highest estimates for MRT, and MRT estimates below 200 years were only calculated for experiments with a duration of less than one year (Figure 10.4 (d)). If only a single measurement was made at the end of the experiment, all of the computed MRT lay below 700 years. Regardless of which model was used, MRT of fire-derived chars were typically lower than pyrolysis-derived biochars and none exceeded a MRT of 500 years (Figure 10.4 (d)).

A direct comparison of MRT calculated either from a 2-pool model using multiple measurements over time or from the final biochar C remaining shows increasing underestimates with increasing MRT. Below a MRT of 1800 years estimated using two pools, the average drop in calculated MRT was 39 per cent for the data examined here, increasing to 93 per cent for the highest value (Figure 10.4 (e)). MRT estimates above 2000 years were rarely computed by a single measurement approach compared to continuous measurements and calculations using a 2-pool model. Even though the largest absolute difference in estimating MRT occurs for the biochars with the lowest mineralization, the difference is the largest for the biochars with the highest mineralization when calculating biochar remaining after 100 years (BC+100; Figure 10.4 (f)). The underestimate made for those biochars that showed a BC+100 of above 95 per cent estimated by a 2-pool model was relatively low (the largest change ranging from 99 per cent to 86 per cent of initial biochar). Similarly, over a 100-year time period, varying the mineralization rate of the pool with the low mineralization rate in a 2-pool model had little impact on the amount of biochar remaining (Foereid et al, 2011). The choice of the correct model and the use of a 2-pool over a 1-pool model may be more important for biochars than for uncharred organic matter, as the estimated MRT of biochars is typically greater than the duration of the experiments. This is usually not the case for plant residues.

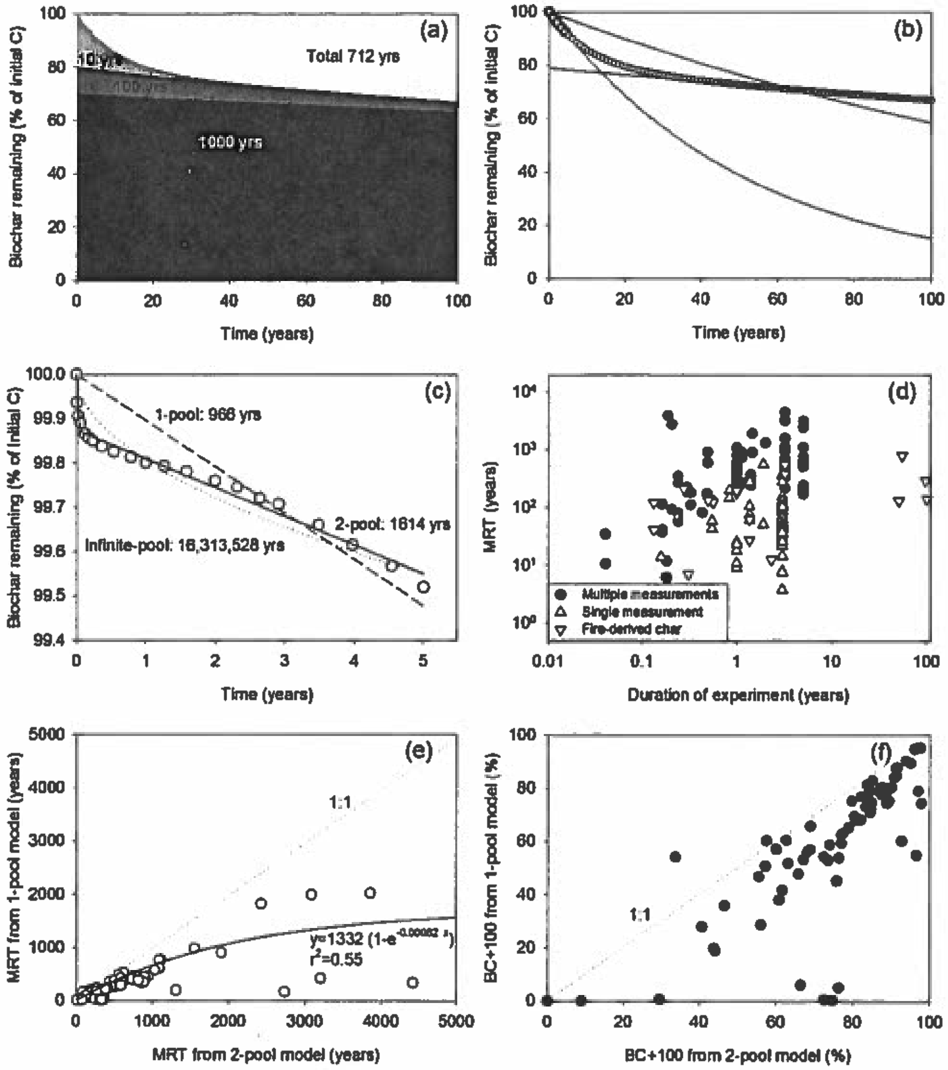

Figure 10.4 *Effects of different approaches for the calculation of MRT: (a) Concept of biochars containing different fractions of different sizes and MRT (20, 10 and 70% for 10, 100 and 1000 years MRT, respectively); (b) Three different methods of calculating MRT using a 1-pool equation and data from (a) shown as symbols (Biochar-C remaining=*ae^{-k*yrs}*)with (1) first 5 years of data and a=100, (2) 100 years of data and a=100 and (3) last 50 years of data and a=fitted; (c) Three different methods of calculating MRT from measured mineralization of wood biochar pyrolysed at 550°C (Singh et al, 2012a) using either a 1-pool (dashed line; biochar-C=*$100e^{-0.00104t}$*), a 2-pool (solid line; biochar-C=*$0.13e^{-58t}+99.87e^{-0.00065t}$*) or an infinite-pool (power, Zimmerman, 2010) model (dotted line; biochar-C=*$100-((100(1-e^{0.00081})/(1-0.63))t^{(1-0.627)})$*; (d) Temperature-adjusted MRT related to the duration of the experiment: using a 2-pool model of multiple measurements over the duration of experiment; using a 1-pool model of a single measurement after experiment; experiments with fire-derived chars (irrespective of calculation) (data from Table 10.1, including data from Whitman et al (2013), temperature sensitivity from Figure 10.2; n=156); (e) Comparison of temperature-adjusted MRT calculated either by using a 2-pool model of all data or a 1-pool model from the remaining biochar-C (from studies that allow a 2-pool model to be used, Table 10.1; n=76); (f) Biochar-C remaining after 100 years (BC+100) as a proportion of initial biochar-C from (e).*

Prediction of biochar mineralization from biochar properties

The prediction of biochar mineralization will only be fully aligned with basic theory if a comprehensive model is available that considers material properties, environmental factors (including soil properties) and decomposer dynamics. The use of biochar properties as a practical solution will at best generate a conservative estimate that can and should over time be improved through more sophisticated approaches. The requirements for an appropriate proxy for mineralizability to be used in application and as part of more comprehensive modelling include: (i) sufficiently low cost to allow routine measurements for research, monitoring and verification; (ii) relatively rapid analyses (ideally within hours); (iii) repeatability; (iv) robustness to different biochar properties and analytical capabilities; (v) strong and preferably linear relationship with mineralization; (vi) availability in different analytical laboratories; and (vii) ideally capturing a specific chemical property rather than an operational definition (adapted from Budai et al, 2013).

The material property most likely responsible for the relative persistence of charred organic matter compared to uncharred organic matter are the fused aromatic C forms discussed above and in Chapter 6. Plant residues do not contain fused aromatic C forms, which are created by charring and increase in proportion e.g. with higher pyrolysis temperature and duration (Chapter 6). In addition, feedstock properties play a role in changing the C forms in biochars, e.g. due to their mineral contents (Chapter 6). Total aromaticity may be quantified by using spectroscopic techniques such as NMR spectroscopy which has been shown to correlate well with mineralization for individual studies (Singh et al, 2012a). However, correlations including multiple studies (Figure 10.5 (a,b)) may be hampered by use of different NMR analytical approaches, in addition to different experimental conditions. For example, cluster sizes of aromatic C can vary significantly between biochars independent of aromaticity (McBeath and Smernik, 2009; Nguyen et al, 2010) and may be more important for persistence than aromaticity (Mao et al, 2012). Further refinement of predictive capability may be achieved by recognizing the different forms of fused aromatic C that have been quantified using NMR measurements of C-13 isotopically labelled benzene adsorbed to biochars (McBeath et al, 2011). However, improvements of correlations with mineralization of biochars using this methodology have so far been marginal over the use of total aromaticity (Singh et al, 2012a).

Less expensive, allowing a larger analytical throughput and more widely accessible are measurements of atomic O/C or H/C ratios that are valid proxies for aromaticity (Wang et al, 2013) and have been successfully correlated to mineralization (Spokas, 2010; Budai et al, 2013). For some feedstocks that are rich in alum (aluminium sulfates in sludges) or ash, additional correction for inorganic C, H and O is needed (Enders et al, 2012; Wang et al, 2013). Even more commonly accessible are measurements of volatile and fixed carbon that are often called proximate analyses, a protocol adopted from the coal and charcoal industry (ASTM, 2007). For low-ash biochars, volatile or fixed carbon contents may be sufficiently correlated with O/C or H/C ratios (Enders et al, 2012) and have been useful in predicting biochar mineralization (Zimmerman, 2010).

Measured MRT (at 10°C) consistently exceeded 1000 years for biochars with H/Corg ratios below 0.4 for the data available to date that include both field and laboratory experiments (Figure 10.5 (c)). This means that more than 90 per cent of the initial C will remain after 100 years (BC+100, Figure 10.5 (d)) for these biochars under similar conditions. Most biochars produced by slow pyrolysis above 500°C will have a H/Corg ratio below 0.4 (Enders et al, 2012; Schimmelpfennig and Glaser, 2012). Conservative thresholds below which MRT or BC+100 has not been observed to fall, may be more appropriate than correlations, since multiple factors beyond biochar properties determine mineralization as discussed above. Data sets from individual studies provide better control for those experimental conditions and the correlation between H/Corg and BC+100 was $r^2=0.96$ recalculated for ten biochars investigated by Singh et al (2012a), compared to $r^2=0.45$ for the global data set in Figure 10.5 (d). Much of the variation in addition to biochar properties stems from explainable differences in experimental conditions which include soil type for the

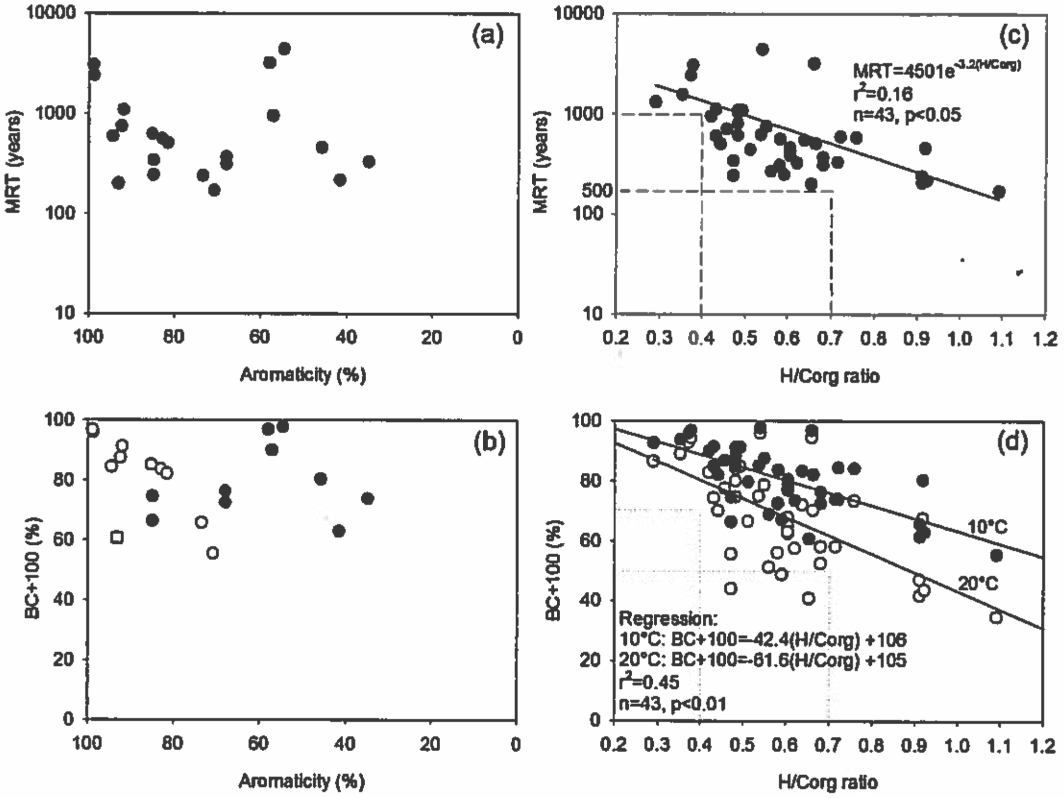

Figure 10.5 *Relationship of molar H/Corg ratios or aromaticity and either MRT or the amount of biochar C remaining after 100 years (BC+100); (a-c) at 10°C; (d) at both 10°C and 20°C (for (b), open symbols from Singh et al (2012a) with square symbol denoting paper sludge as feedstock) (only those temperature-adjusted data (and computed BC+100) included from Table 10.1 that allowed use of a 2-pool model of experiments conducted for one or more years using biochars from pyrolysis (not combustion or fire); note the logarithmic y axes for MRT graphs; additional H/Corg and aromaticity values provided by T. Wang, A. Zimmerman)*

laboratory experiments (as temperature was corrected for) and temperature, moisture, microbial community, clay mineralogy and texture among others (see previous sections) for the field studies. This illustrates that material properties of biochars alone will not be able to predict all of its mineralization dynamics as is clear from basic theory and known dynamics of any soil organic C (Box 10.2). Interestingly, the observed outliers for the currently available data are found to lie at the upper rather than the lower end of estimated MRT (Figure 10.5 (c)), suggesting combinations of management and site factors that may significantly increase persistence in soil beyond the average or thresholds predicted by a global data set.

Uncharred organic matter has H/Corg ratios well above 1 (Baldock and Smernik, 2002; Enders et al, 2012: 1.4–1.6), indicating that charring confers at minimum a one order of magnitude lower mineralization to organic residues. Direct experimentation with charred (at comparatively low temperatures of 350–450°C) and uncharred residues point to a 1.5 order of magnitude reduction in mineralization (Baldock and Smernik, 2002; Santos et al, 2012). Since different residues (e.g., leaves vs wood) already possess very different initial mineralization rates without charring (Santos et al, 2012; Whitman et al, 2013), the difference in absolute reduction of mineralization conferred by charring (e.g., BC+100) is smaller for those uncharred residues that show a lower mineralization. This has implications for the life cycle emission balance (Chapter 27).

Conclusions and recommendations

Charring significantly decreases mineralization of organic matter by at least one and a half orders of magnitude under otherwise identical environmental conditions (e.g., soil temperature or moisture, soil properties, decomposer community). Although biochar turnover is only to a certain degree explainable by material property, this relative decrease in mineralization is significantly related to its organic matter forms (such as H/Corg and aromaticity) which in turn depends on the way in which the biomass is pyrolysed (Chapters 5 and 6), mainly by variations in charring temperature and time, and by the property of the biomass, mainly by its ash contents, but possibly other properties that warrant further investigation. This specific variation is by now becoming better predictable through assessment of relevant material properties of biochars such as aromaticity, aromatic condensation and even the atomic ratios of organic C, H and O.

However, variation between locations, between experimental conditions (e.g., incubation temperature; incubation media; field vs laboratory experiments) and between extrapolation approaches to calculate MRT add a layer of complexity to the interpretation and future modelling efforts should capture all sources of variation. Recommendations for appropriate scrutiny and interpretation of experimental data should include the following:

- Accept the fact that biochar products are chemically and physically different. The behaviour of one specific biochar product does not allow us to extrapolate the behaviour of other biochar products without recognizing their differences.
- Compare apples with apples: for estimating the extent to which charring of biomass increases persistence in soil, mineralization of fresh biochar added to soil should only be compared to minerali-

zation of the corresponding uncharred biomass under identical experimental conditions. Misconceptions commonly arise by comparing mineralization of fresh biochar to: (i) mineralization of soil organic C that typically includes chars from vegetation fires, or to some extent has already been decomposed from a much larger source of biomass and is stabilized by mineral interaction that would also stabilize biochar; (ii) mineralization of uncharred biomass of a different feedstock; the variation between mineralization of uncharred wood and leaves is on the same order of magnitude as the difference between charring and not charring; (iii) mineralization of uncharred biomass under different experimental conditions; different incubation temperatures or the difference between sand and iron-rich clays as the incubation medium may have larger effects than charring (and future research will need to clarify whether all effects are similar irrespective of charring); (iv) no uncharred biomass; an experiment that focuses on assessing the effect of charring on mineralization should include a comparison to the corresponding uncharred biomass, preferably at conditions it would enter the soil (often fresh rather than dried plant residue).

- Apply the correct model: extrapolation and calculation of MRT and other measures of mineralization from fresh biochars must use at least a 2-pool model. A 1-pool model is unacceptable and at best gives minimum estimates.
- Distinguish between physical movement and mineralization: erosion and leaching (Chapter 11) can be significant pathways that lead to disappearance of biochar in field experiments but should not be confused with mineralization and in several instances 'mobility' has been confused with 'lability', or 'stationary' in the landscape with 'stable' against mineralization; in fact, eroded organic matter buried in lake or ocean sediments or organic matter in subsoils may rather mineralize to a lesser degree than organic matter in topsoils. Accounting for biochar movement and especially erosion in field mineralization studies is difficult; erosion should be prevented and leaching be measured.
- Attribute mineralization to the correct source: not only biochar contributes to CO_2 evolution from soil and the difference in CO_2 evolved from plots that received biochar and from those that did not, may not be additive. Therefore, isotopes must be used to distinguish CO_2 or remaining soil C from biochar and other sources.

In addition to appropriate interpretation of existing data, future research may need to set priorities to fill several knowledge gaps (Table 10.2). Experimental data from field trials are still scarce and a coordinated international effort is needed to stage comparative trials in sufficient locations and over sufficiently long time scales. Future experiments on biochar persistence, whether in the field or laboratory, may need to include the following components: (i) sufficient C-13 or C-14 isotope enrichment to distinguish biochar-derived CO_2 from other CO_2, preferably greater than what is possible by natural abundance; (ii) experimental periods exceeding annual time scales; (iii) a sufficient number of measurements to allow a 2-pool model to be used; (iv) adequate comparison to uncharred organic matter.

Whether biochar is applied on the soil surface or incorporated and what types of minerals are present in soil, are both known to affect mineralization of uncharred organic matter. There are a number of reasons to expect differential responses with charred residues, but their net effect on mineralization is not sufficiently quantified. Comprehensive modelling including all processes controlling biochar

Table 10.2 *Recommended research priorities to predict biochar persistence in soil*

Priorities	*Target knowledge gap*	*Comparison*	*Expectation*	*Challenges*
Field studies	Long-term mineralization across different agro-climatic regions; unknown variation from laboratory experiments	Field vs laboratory studies	Higher or lower mineralization	Quantification of losses other than mineralization are difficult to quantify; extrapolation is challenged by variations in soil moisture and temperature
Soil application	Photo-oxidation; differences between tillage methods; erosion	Incorporation vs surface application	Higher or lower mineralization	Often requires large amounts of biochar due to mechanization of application and field trials which are expensive (especially with isotopic labeling)
Soil minerals	Mechanism and magnitude of influence by soil minerals	Biochar vs corresponding uncharred organic residues	Similar or lower mineralization due to stabilization	In addition to laboratory incubations, requires long-term field assessment with accompanying spectroscopic quantification of the interaction
Modeling	Quantification of turnover mechanisms and prediction, inclusion in standard soil organic carbon models	Integration vs no integration of processes (e.g., stabilization, moisture, temperature, decomposers)	Higher or lower mineralization	Knowledge gaps in quantitative responses to environmental and soil conditions and decomposer dynamics for parameterization of the model (incl. interactions among them and with biochar properties)

mineralization will provide a step forward not only for prediction of the biochar remaining in soil after certain periods of time, but even more so for understanding biochar mineralization and the interaction between different factors controlling the persistence of biochars. This will also provide guidance to first fill those knowledge gaps that have the greatest sensitivity for understanding biochar mineralization and determine the way forward for both policy guidance, C trading approaches and prediction of future C management strategies.

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11

Movement of biochar in the environment

Cornelia Rumpel, Jens Leifeld, Cristina Santin and Stefan Doerr

Introduction

Due to its high persistence, biochar mineralization rates in soil most probably approach several centuries. Physical processes, which may determine biochar loss at much shorter timescales, are those leading to its transport off site. Biochar and associated nutrients or micropollutants may be transported by water, wind or animals. Transport can occur via vertical mobilization within the soil profile as well as off-site horizontal or lateral export. Transport processes of biochar have several controls. They may be controlled by biochar physical properties, such as particle size and density (Chapter 3) and/or chemical properties such as hydrophobicity and/or sorptive properties (Chapter 10). Moreover, fresh biochar even when incorporated into the mineral soil is characterized by absence of mineral interactions at the time of application, which makes it prone to export by leaching or erosion processes, similar to those affecting free particulate organic matter derived from plant material such as crop residues or composts. In the first few years after its application, removal of biochar off-site may be more important in terms of quantitative biochar fluxes than microbial degradation (Major et al, 2010; Foereid, et al, 2011). The direction and magnitude of its transport will be influenced by the form of its application and incorporation, soil type, terrain topography, land management practices (e.g. till *vs* no till), as well as climate. For example, application of biochar as slurry may favour vertical transport, particularly in sandy soils. Dry biochar application to clayey soils may favour off-site transport by wind or water erosion. On biologically active sites, biochar may be subject to vertical transport by anaeic earthworms and arthropods together with other organic matter. Under humid climate conditions water erosion may be the main process for off-site biochar export, especially in terrain with steep slopes. During dry conditions, wind erosion may be an important transport mechanism.

Processes leading to soil removal and transport are scale-dependent and therefore

First published 2015
by Routledge
2 Park Square, Milton Park, Abingdon, Oxon OX14 4RN

and by Routledge
711 Third Avenue, New York, NY 10017

Routledge is an imprint of the Taylor & Francis Group, an informa business

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Cataloging in Publication Data
Biochar for environmental management : science, technology and implementation / edited by Johannes Lehmann and Stephen Joseph. -- Second Edition.
pages cm.
Includes bibliographical references and index.
1. Charcoal. 2. Soil amendments. 3. Environmental management. I. Lehmann, Johannes, Dr. II. Joseph, Stephen, 1950-
TP331.B56 2015
662'.74--dc23
2014029398

ISBN: 978-0-415-70415-1 (hbk)
ISBN: 978-0-203-76226-4 (ebk)

Typeset in Plantin
by Saxon Graphics Ltd, Derby

Printed and bound in Great Britain by
TJ International Ltd, Padstow, Cornwall

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