Biochar Carbon Stability Test Method: An assessment of methods to determine biochar carbon stability

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Abstract

Twenty seven methods currently used to characterize biochar were assessed in terms of their usefulness to determine the stability of biochar carbon in the environment. The International Biochar Initiative (IBI), which led the effort, gathered fourteen world-class experts in different fields of biochar relevant to stability, who guided the process for obtaining a simple, yet reliable, measure for biochar stability. Important requisites were defined for the test, including cost, repeatability and availability. Identification of a cost-effective, scientifically valid test to measure the stable carbon component of biochar is imperative to distinguish biochar from non-biochar (non-stable) materials, and to develop a biochar offset protocol for carbon markets. The stability of biochar carbon in soils makes it a highly promising product for consideration as a strategy for climate change mitigation. The definition of the variable BC+100, which stands for the amount of biochar carbon that is expected to remain stable after 100 years, along with predictions of stability based on simple (Alpha) and more sophisticated (Beta)

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methods, allowed to correlate a molar ratio (H/Corg) to the relative stability of biochar. The process for identifying the Biochar Carbon Stability Test Method is summarized here, and the method itself is available as a separate, technical document.

1. Introduction

The stability of biochar is of fundamental importance in the context of biochar use for environmental management for two primary reasons: first, stability determines how long carbon applied to soil, as biochar, will remain in soil and contribute to the mitigation of climate change; second, stability will determine how long biochar will continue to provide benefits to soil, plant, and water quality (Lehmann et al., 2006). Biochar production and application to soil can be, in many situations, a viable strategy for climate change mitigation. Conversion of biomass C to biochar C via pyrolysis can lead to sequestration of about 50% of the initial C compared to the low amounts retained after burning (3%) and biological decomposition (<10–20% after 5–10 years) (Lehmann et al, 2006, figure 1), with the entirety of uncharred biomass being most likely decomposed after a century, which is a relevant time frame for the purpose of the stability test, as presented in subsequent sections.

Figure 1. Schematic of biochar and biomass degradation patterns. Source: Lehmann et al. (2006)
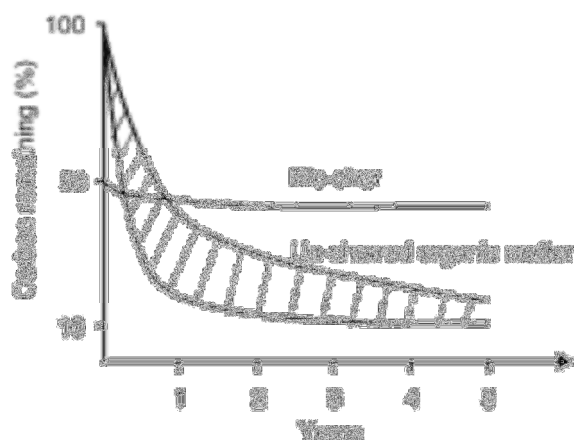
Biochar has been found to have a high stability or resistance to decomposition in soil. The Mean Residence Time (MRT) of different biochars has been found to fall mostly in the centennial to millennial scales, as shown in table 1, with some studies showing estimations of decadal scales.

Table 1. Mean Residence Time (MRT) of biochar across studies.

Publication	Scale of estimated MRT (years)
Masiello and Druffel, 1998	Millennial (2,400 – 13,900)
Schmidt et al., 2002	Millennial (1,160 – 5,040)
Cheng et al., 2006	Millennial (1,000)

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Laird, 2008	Millennial (1,000's)
Cheng et al., 2008	Millennial (1,335)
Kuzyakov et al., 2009	Millennial (2,000)
Major et al., 2010	Millennial (3,264)
Novak et al., 2010	Millennial (1,400-51,000)
Liang et al., 2008	Centennial to millennial (100-10,000's)
Zimmerman, 2010	Centennial to millennial (100-100,000)
Baldock and Smernik, 2002	Centennial (100-500)
Lehmann et al., 2006	Centennial (100's-1,000's)
Hammes et al., 2008	Centennial (200-600)
Schneider et al., 2011	Centennial (100's)
Hamer et al. 2004	Decadal (10's)
Nguyen et al. 2008	Decadal (10's)

Objective

The goal of this effort was to develop a method for testing and quantifying the stability of carbon in biochar, by specifying the amount of C that is predicted to remain present in soil 100 years[15] after land application, which for the purposes of the stability test is termed BC_{+100}. The fraction of carbon in biochar that decomposes during the same time period is termed BC_{-100}. Selection of methods was based on the following:

- Only analytical tests for biochar stability that have been published in the **peer-reviewed** literature before final issuance of this document were considered;
- Sampling procedures and test methods had to be considered **cost-effective**; and
- All assumptions made during the development of this test method followed the **principle of conservativeness**, i.e. the methodology should in every instance utilize conservative approaches in order to avoid over-estimating the stability of biochar carbon.

Scope of Work

The effort was built upon previous work completed by The International Biochar Initiative (IBI) to develop "**Standardized product definition and product testing guidelines for Biochar that is used in soil**" (aka **IBI Biochar Standards**). The present document constrains its scope to materials with properties that satisfy the criteria for biochar as defined by the IBI Standards.

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[15] Global Warming Potential (GWP) of Greenhouse gases (GHG) is assessed over a 100-year time horizon. One hundred years is commonly used to define permanence in carbon offset markets (e.g. Mechanisms under the Kyoto Protocol (Clean Development Mechanism - CDM, Joint Implementation - JI), Australia's Carbon Farming Initiative).

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This test method considers only the carbon stabilized in biochar via pyrolysis. Neither biochar impacts on plant productivity nor any effects on native soil carbon stocks or vice versa (i.e. positive or negative priming) are included (Figure 2) because scientific evidence is insufficient at this time to determine the direction and magnitude of these processes. Biochar may stabilize native soil organic carbon by sorbing organic compounds (Smernik, 2009). There are, however, cases where biochar addition to soil can produce an undesirable "positive priming effect" (Hamer et al., 2004; Wardle et al., 2008; Singh et al., 2010; Kuzyakov, 2010; Zimmerman et al., 2011; Cross and Sohi, 2011; Woolf and Lehmann, 2012; Singh et al., 2012), causing the release of additional CO_2 from soil. However, Woolf and Lehmann (2012) estimated that no more than 3 to 4% of initial non-pyrogenic SOC might be mineralized due to priming by biochar over 100 years. Even though this effect may be small compared to a possible negative priming effect, neither effect was included in the methodology. Further support for this decision is detailed in the Supplementary Information section.

Figure 2. Scope of work for the test method.
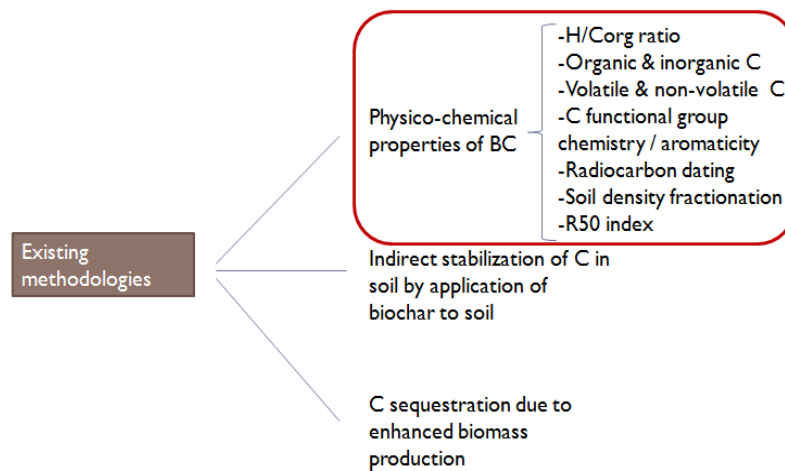
Even though there is evidence of increased net primary productivity (NPP) of soils after biochar addition (Lehman et al., 2006; Major et al., 2010), carbon sequestration due to enhanced biomass production was not included because insufficient data are available to quantify the effects of biochar additions to soil on crop productivity, which is likely to vary widely between soil types, feedstock and environments (Van Zweiten et al., 2010; Jeffrey et al., 2011). Additionally, the longevity of the impacts of biochar on NPP is unknown, as most experiments have been short-term. Furthermore, C sequestered in biomass of annual crops and pasture cannot be considered stable, mainly due to its fast turnover rate. The decision not to include these also reflects the conservative approach of this effort.

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2. Definitions

Types of methods

Through a review made by the Expert Panel consisting of fourteen world-class biochar experts, test methods were categorized into three groups: (1) Alpha methods, which may allow routine estimation of the BC_{+100} at minimal costs; (2) Beta methods, which directly quantify BC_{+100} and may be used to calibrate Alpha methods; and (3) Gamma methods, which may provide the physiochemical underpinning for the Alpha and Beta methods. These categories of methods are justified and described below.

2.1 Alpha methods

Alpha methods are defined as those which provide a simple and reliable measure of the relative stability of carbon in biochar, that are readily available, at a cost of less than 100 US dollars (USD) (defined as feasible by the Expert Panel) and within a timeframe of minutes or hours to, at maximum, a few days. Alpha methods are intended to be undertaken by a certified laboratory to be used by biochar producers.

Alpha methods do not provide an absolute measure of stability; rather, they assess a property (usually chemical or physical) that is related to stability. Alpha methods must be calibrated through comparison with Beta and/or Gamma methods.

Some Alpha methods have already been developed ("Alpha-1") and were found to be strongly related to the properties determined by the Beta and Gamma methods. It is expected that more Alpha methods will emerge as biochar stability research continues to develop, which could be placed in a category called "Alpha-2" methods.

The results of any Alpha method must correlate – ideally linearly – with results of at least one Beta (calibration) method, as well as those of the applicable Gamma methods. Some possible Alpha-1 methods are briefly described and discussed below.

Hydrogen to organic Carbon molar ratio (H:C$_{org}$) (Enders et al., 2012; IBI, 2012) and **Oxygen to Carbon molar ratio (O:C)** (Spokas, 2010): Both ratios reflect physical-chemical properties of biochar related to stability, as the proportion of elemental compounds (H and O) relative to carbon (C) present in biochar. These elemental constituents of biochar can be measured routinely, using an elemental analyzer, based on the manufacturer's protocol.

Increasing production temperatures lead to lower H/C and O/C ratios (Krull et al., 2009; Spokas, 2010), as the abundance of C relative to H and O increases during the pyrolysis process (Figure 3).

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Figure 3. Changes in biochar elemental composition with varying pyrolysis temperatures. Source: Krull et al. (2009).
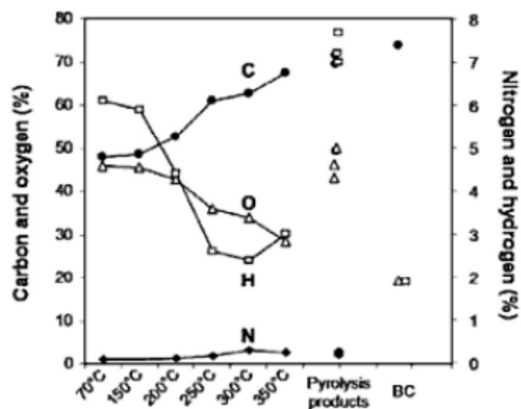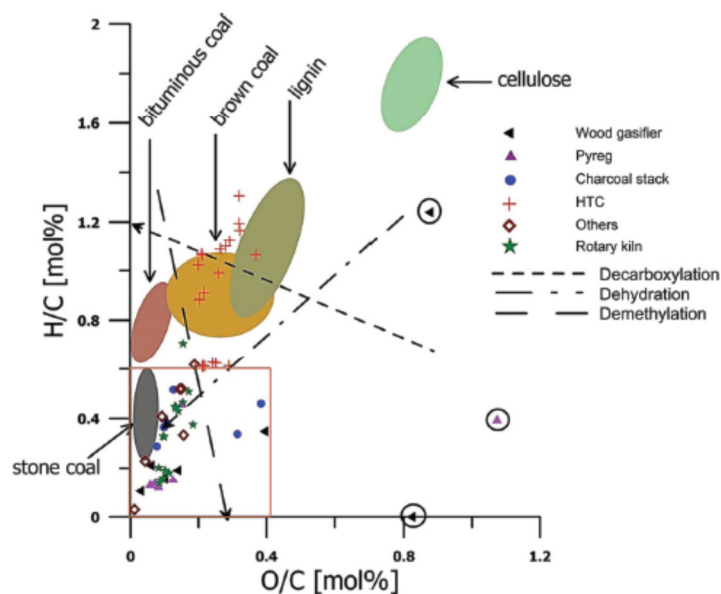

Materials with low H/C and O/C values are graphite-like materials (i.e. soot, black carbon, activated carbon), which exhibit high stability compared to uncharred biomass, which possesses high H/C and O/C values (Figure 4) and low resistance to degradation. Hence, as biochars resemble graphite-like materials, characterized by low ratios, they are expected to be more stable or inert, and less prone to degradation (Masiello, 2004).

Figure 4. Physical characteristics and ratios related to biochar stability. Source: Adjusted from Hammes et al. (2007)
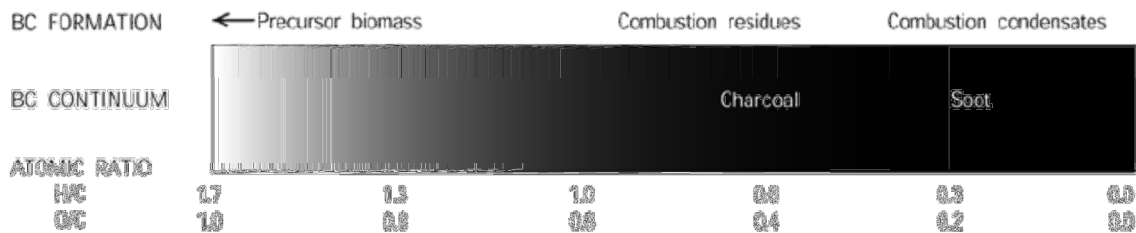
These two ratios can be plotted in a two-dimensional Van Krevelen diagram, which is a graphical representation of biochars based on elemental composition. In a study by Schimmelpfenning and Glaser (2012), different biochars are characterized based on the relation between the measured H/C and the O/C ratios, and compared to different types of coals (figure 5).

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Figure 5. Van Krevelen diagram. Source: Schimmelpfennig and Glaser (2012)

The use of the molar H/C_{org} ratio is proposed instead of the H/C ratio, as the former does not include inorganic C present in biochar mostly in the form of carbonates (e.g. calcite and, to some extent, dolomite) (Schumacher, 2002) and is not part of the condensed aromatic structure of C and thus is not expected to remain in soil on a centennial scale.

Volatile matter content: The content of volatile matter (VM) in biochar has also been observed to be related to biochar stability, calculated as mean residence time or half life (Enders et al., 2012; Zimmerman, 2010; Spokas, 2010). Volatile matter content can be measured through different paths, usually thermal treatment, e.g. the ASTM method D1762-84[16] (2007) (CDM SSM AMS.III-L; Major et al., 2010b; DeGryze et al. 2010; Enders et al., 2012), also termed proximate analysis, which covers the determination of moisture, volatile matter, and ash in a variety of materials.

VM is well correlated with elemental ratios (O/C and H/C), as shown in Figure 6, so it could be expected to be a good predictor of biochar carbon stability. However, Spokas (2010) found a weak correlation between VM content and the estimated biochar half-life using data from 37 biochar sample measurements from different studies (Figure 7). Therefore volatile matter is discarded as a well-suited predictor of stability.

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[16] Chemical analysis of wood charcoal

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Figure 6. Correlation of volatile matter and O/C molar ratio. Source: Spokas (2010) (R^2 = 0.76)
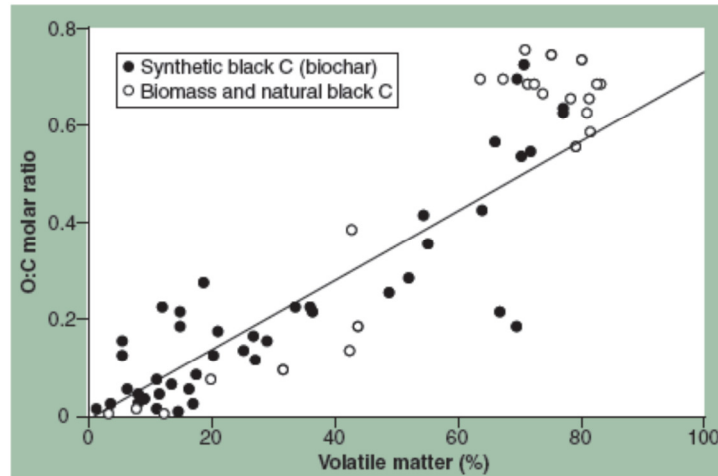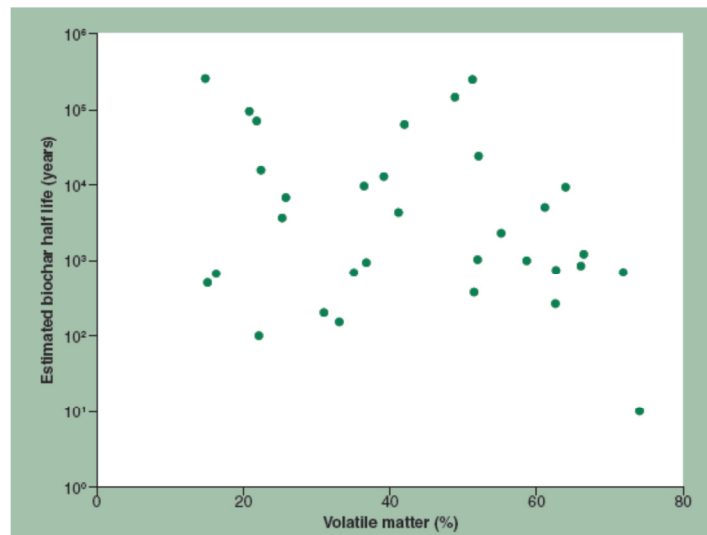

Figure 7. Comparison of volatile matter content with estimated biochar half life. Source: Spokas (2010) (R^2 not available)


2.2 Beta methods

Beta methods are those that (1) directly quantify BC loss over a period of time, and (2) demonstrate a relationship with results of an Alpha method (a more conveniently measured parameter) and Gamma values for a range of biochar types. At present, the Beta methods in use are laboratory and field-based incubations as well as field chronosequence measurements, all of which must be combined with modeling to estimate biochar C lost over the specific time interval of 100 years (BC_{-100}).

Beta methods provide an absolute measure for the carbon that will remain in biochar for at least 100 years (at minimum that is, a conservative estimate of stability). Beta methods are not widely available or obtainable at a cost or within the timeframes specified for Alpha methods. It is also not feasible to have

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registry of direct observations of biochar for 100 years, in order to demonstrate the suitability of a Beta method. Some Beta methods have been published and are presented below.

Incubation and field studies: Incubation studies of biochar under laboratory conditions (Zimmerman, 2010; Singh, 2012) and studies of biochar in soils (Major et al., 2010b; Cheng et al., 2008; Liang et al., 2008; Kuzyakov et al., 2009) have recorded temporal biochar decomposition patterns (see figure 8). Observations derived from incubation experiments are critical to the understanding of biochar behavior and, therefore, stability. The incubations (3-5 years of duration) were undertaken in controlled environmental conditions (e.g., moisture, temperature) and with addition of microbial inoculation and nutrient solution in order to promote decomposition. Because these are closed systems and non-variant conditions, estimates of stability based on these measurements can be considered conservative. Mineralization rates have been observed to decrease until reaching a constant rate at around 600-700 days, indicating that remaining biochar carbon may exhibit a certain degree of stability. In order to quantify stability a very conservative approach must be used for extrapolating measurements from short- to medium-term studies to 100 years, which is done in this report, as explained in subsequent sections.

Figure 8. Biochar mineralization rate. Source: Kuzyakov et al., 2009 (3.2 year incubation)
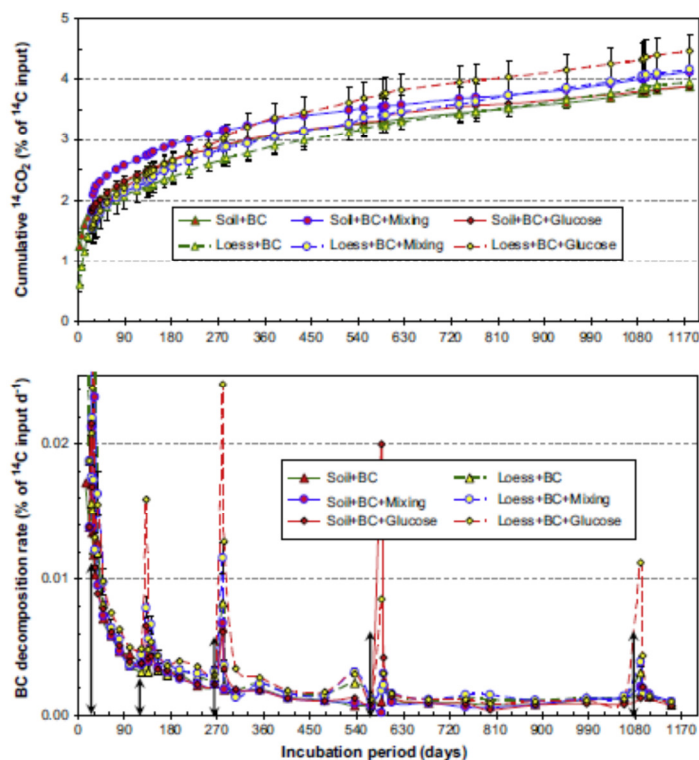
Both two-component (double exponential) models (e.g. Cheng et al., 2008; Zimmerman et al., 2011; Singh et al., 2012) and power regression models (e.g. Zimmerman 2010) have been used to extrapolate

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measurements from incubations of freshly produced and aged biochar to predict the longer-term stability of biochar. The second model may better represent the physical characteristics of biochar and assumes an exponentially decreasing degradation rate, whereas the first assumes biochar is composed of only two fractions – labile and stable. Thus, the two-component model is likely to underestimate stability of biochar C and will yield a more conservative estimate of C sequestration, since the greater the number of pools that are added, the greater predictions of stability will be.

Chronosquences: A biochar C loss rate can also be determined by using measurements of biochar distribution from sites that vary in time interval since biochar was applied (a chronosequence). However, results of these types of studies, thus far, range from no to complete C loss, and are likely affected by erosion or translocation (Nguyen et al. 2008; Major et al. 2010b; Foereid et al. 2011).

2.3 Gamma methods

Gamma methods measure molecular properties relevant to biochar stability and can verify the legitimacy of the Alpha and Beta methods through establishing strong relationships between the properties measured by them. Thus, Gamma methods would provide safeguard against selection of Alpha or Beta methods based on empirical correlations that do not reflect a functional relationship. Some Gamma methods are briefly described below.

NMR spectroscopy (Brewer et al., 2011; McBeath et al., 2011)**:** Direct polarization ^{13}C nuclear magnetic resonance spectroscopy with magic angle spinning (DP/MAS ^{13}C NMR) is a well-established technique for measuring the aromaticity (fraction of total carbon that is aromatic) of biochars. Aromaticity is strnogly correlated to C stability. The ^{13}C NMR spectrum of aryl carbon (i.e. derived from condensed aromatic carbon) is very characteristic, comprising a single resonance centered at approximately 130 ppm. Spinning side bands associated with the presence of aromatic carbon can be detected.

Pyrolysis Gas Chromatography mass spectrometry (Py GC/MS) – analytical pyrolysis (Kaal et al., 2008, 2009, 2012; Fabbri et al., 2012)**:** Analytical pyrolysis is a technique that uses controlled invasive thermal degradation to break down large molecules for identification. The resultant pyrolysis products are separated and identified using gas chromatography and mass spectroscopy. The sum of the most abundant fingerprints of charred material in pyrograms (i.e., monoaromatic hydrocarbons, polyaromatic hydrocarbons, benzonitriles/total quantified peak area) is related to the proportion of condensed aromatic carbon present in biochar.

Ring Current NMR (McBeath and Smernik, 2009; McBeath et al., 2011)**:** This method gauges the degree of aromatic condensation of biochars. It involves sorbing ^{13}C-labeled benzene to the biochar structure. The ^{13}C NMR chemical shift of the sorbed benzene (relative to straight ^{13}C-benzene) is affected by diamagnetic ring currents that are induced in the conjugated aromatic structures when the biochar is placed in a magnetic field. These ring currents increase in magnitude with the increasing extent of aromatic condensation.

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Benzene polycarboxylic acids (BPCA) (Glaser et al., 1998; Brodowski et al., 2005; Schneider et al., 2010)**:** The BPCA are molecules formed during the nitric acid oxidation of biochar. The maximum number of carboxylic groups reflects the number of quaternary C atoms initially present. Biochar with a higher degree of condensation should result in higher proportion of the penta (B5CA) and hexacarboxylic (B6CA) benzoic acids relative to BPCAs with less quaternary carbon atoms (B3CA, B4CA). The ratio of B6CA-C/total BPCA-C thus is positively related to the degree of condensed aromatic C present in biochar; the larger the ratio the greater the aromaticity. The concentration of the sum of BPCA can be used to quantify biochar in the environment, e.g. in soil amended with pure biochar or in mixture with other organic materials.

Gamma methods are not expected to be used by biochar producers for determining biochar C stability. This is mainly because of the high level of technical expertise required to perform these tests, specialized expensive instruments, high costs per analysis, and low availability. Instead, Gamma methods are intended to be used by scientists in order to calibrate Alpha and Beta methods for iterative improvement of a simple biochar C stability test method.

3. Material and methods – Biochar Carbon Stability Test Method selection process

Twenty-eight test methodologies currently used to assess biochar characteristics, mostly related to stability, were reviewed and evaluated by the Expert Panel. The process by which these were evaluated, the criteria used for this purpose, the categories defined, and other details are presented in Section 2 of the Supplementary Information. H/C_{org} was selected as the preferred Alpha method for being cost-effective, simple, replicable and published in peer-reviewed literature, in combination with the use of modeled data from observations of carbon degradation from 3 to 5-year incubation studies (Zimmerman, 2010 as extended in Zimmerman and Gao, 2013; and Singh et al., 2012) as the Beta method used to calibrate the predictions and determine BC_{+100}.

4. Results

In support of the selection of the proposed Alpha and Beta method, a strong relationship was found between the H/C_{org} values of 31 biochar samples from the two mentioned studies and the predicted BC_{+100} values, based on the two-component model (figure 9).

The observed behavior for carbon in each of the 31 samples followed the pattern shown in figure 8, where after some months, the turnover rate became stabilized, exhibiting little carbon loss. Q10 adjustments for harmonizing the data between both studies were not made, but if a low value were to be used, e.g. Q10 = 2, harmonizing the data from 30°C and lack of soil minerals (Zimmerman, 2010) to 22°C (Singh et al., 2012), would yield higher BC_{+100} values than the ones reported, thus complying with the conservative principle. Grouping the predicted BC_{+100} values, based on the two-component model, results in figure 9.

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Figure 9. The correlation between H/ C_{org} and biochar C predicted to remain after 100 years as predicted by a two-component model (i.e. BC_{+100}) was produced using data and calculations from Singh et al., 2012 (closed circles) and Zimmerman, 2010 as extended in Zimmerman and Gao, 2013 (open circles)..
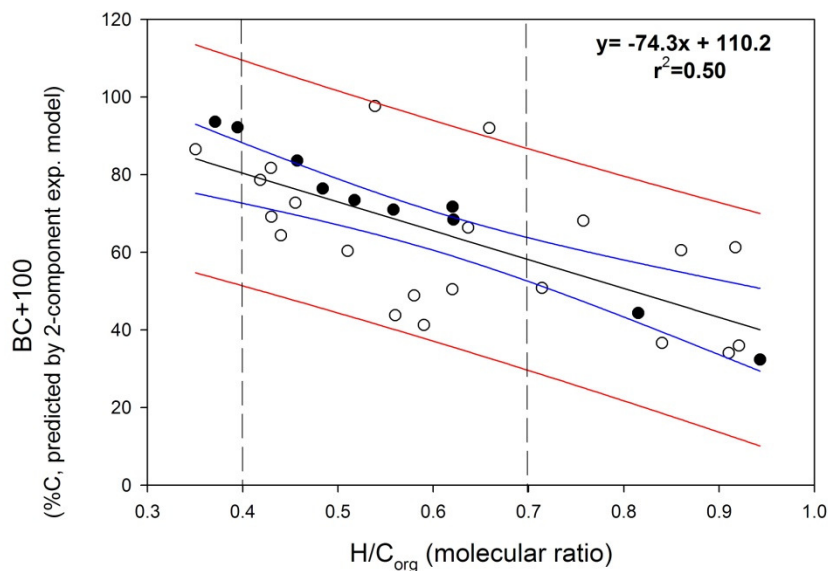
The vertical axis represents the percentage of organic carbon present in biochar that is expected to remain in soil after 100 years. Thus, a biochar sample with a H/Corg value of 0.6 would be predicted to have a BC_{+100} of 65.6% indicating that 65.6% of the organic carbon measured in biochar will likely remain stable for at least a century. The statistical basis for this inference is presented in the following.

The blue and red lines in the plot represent the 95% confidence upper and lower intervals, and the 95% prediction intervals, respectively. The correlation measure shows a modest value ($R^2 = 0.5$). However, as biochar is composed of various constituents, it is notable that this one parameter (H/C_{org}) explains 50% of the variation in the carbon stability of the biochar samples assessed. Furthermore, every individual sample but one falls within the 95% prediction interval, which predicts the range in which values of future samples will fall. Additionally, a p-value below 0.0001 indicates the strong statistical significance of the calculations. Thus, this regression model is judged adequate for determining BC_{+100} based on H/C_{org} measurements.

Defining cut-offs every 0.1 for H/C_{org} values in the range of 0.4 to 0.7 for the biochar samples, the equivalent mean, upper limit and lower limit BC_{+100} values are obtained for analysis (table 2). Two distinct levels can be evidenced: for an H/C_{org} value of 0.4, the lower limit of the confidence interval of BC_{+100} is above 70% (in a range of 88-72%). From this it is concluded that at least 70% of the C_{org} measured in biochar is predicted to remain in soil for 100 years with 95% confidence, for an H/C_{org} value lower or equal to 0.4. Confidence intervals are considered over prediction intervals, as they exhibit the probability that they will contain the true predicted parameter value, for the selected confidence level.

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On the other hand, for an H/C$_{org}$ value of 0.7, a BC$_{+100}$ of 50% can be conservatively expected. If a cut-off of BC$_{+100}$ is defined at 50%, most (17 out of 19) of the observed values in the 0.4-0.7 H/C$_{org}$ range would fall above this point, therefore underestimating stability. Thus, cut-offs at values of H/C$_{org}$ of 0.4 and 0.7 are defined to characterize "highly stable" (BC$_{+100}$ of 70%) and "stable" (BC$_{+100}$ of 50%) C$_{org}$ in biochars, respectively.

Table 2. H/C$_{org}$ and BC$_{+100}$ equivalences at 95% confidence

H/C$_{org}$	BC$_{+100}$ (%)			
	Mean	Lower limit	Upper limit	Chosen value
0.4	**80.5**	**72.6**	**88.2**	**70**
0.5	73.1	67.1	78.9	50
0.6	65.6	60.5	70.6	50
0.7	**58.2**	**52.5**	**63.8**	**50**

Biochar materials that obtain H/C$_{org}$ values higher than 0.7 are not considered to be biochar, as these materials would not meet the definition of biochar as defined by the IBI Standards.

5. Discussion

The comments in this section seek to provide guidance as to the possible next steps for the continuous improvement of the predictability of different Alpha, Beta and Gamma methods.

The members of the Expert Panel agreed upon the necessity of continued collaboration to further refine the proposed method. There emerged an interest to start the exchange of biochar samples to run different laboratory tests in the form of a ring trial. Additional funding would be needed for this very desirable initiative. As stated earlier in this document, as new findings emerge, they should be incorporated into the proposed methodology, with the aim of obtaining the most precise and, at the same time, economically feasible method for determining BC$_{+100}$.

5.1 Fate of biochar

5.1.1 Biochar transport mechanisms

The physical movement of biochar away from the point of soil application appears to occur at a similar rate to or possibly faster than for other organic carbon in soil (Rumpel et al., 2005; Guggenberger et al., 2008; Major et al., 2010). Eroded biochar C is considered to remain sequestered as it is typically buried in lower horizons of soil or in lake or ocean sediments (France-Lanord and Derry, 1997; Galy et al., 2007; Van Oost et al., 2007).

Biochar can move from the topsoil into the subsoil i.e. translocation (Major et al., 2010). It is not clear whether this transport occurs at the same rate as other organic matter in soil (Leifeld,

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2007). It may be assumed that different pathways operate for particulate biochars in comparison to dissolved organic C (Zhang et al., 2010). Biochar in subsoils can be considered stabilized to a greater degree than biochar in topsoils, as evidenced by the great age of organic carbon found in subsoils in general, and because microbial activity sharply decreases with depth (Rumpel and Koegel-Knabner, 2011).

Some studies indicate that a significant fraction of land-applied biochar can be exported within the first few years following amendment, even when biochar is incorporated into soil (Rumpel et al., 2009; Major et al., 2010). However, physical transport of biochar offsite does not necessarily result in a CO_2 flux to the atmosphere, as the final fate of charcoal erosion from the land surface may be deposition in marine sediments. The intrinsic refractivity of charcoal in marine environments may lead to its long-term storage in sediments (Masiello, 2004). It is reasonable to assume that mobilized biochar does not decompose, and remains a long-term carbon sink as it transits to the sea floor.

5.1.2 Combustion

Biochar can be combusted, either unintentionally due to inappropriate handling during transport, storage or application, or intentionally, by diverting it from the intended land application to a use as fuel, since many biochars can possess a significant energy value. This potential will need to be managed within the Biochar Protocol development. Another theoretical oxidation by combustion is through vegetation fires. Re-burning of previously deposited pyrogenic carbon from vegetation fires has been observed in Mediterranean forests (Knicker et al., 2006). It is unlikely that vegetation fires will lead to a significant re-burning of applied biochar that is incorporated into the soil. Temperatures during fires decrease dramatically with depth, and mixtures of biochar and soil will exhibit no greater combustibility than that of other organic matter in soil.

5.2 Resolution of information on carbon stability

Although there is a clear correlation between the H/C_{org} ratios and BC_{+100} over a wide range of values at a 95% confidence level (Fig. 9), variability will remain in the stability predictions. Future refinement and a greater data set with longer-term incubation experiments, including field data, will allow better constraint of the relationship. For the purpose of this first methodology, as mentioned previously, a very conservative approach was chosen (e.g. via the selection of the model to obtain BC_{+100} and the conditions of the incubation experiments) and thus predictability can be further improved over time.

The second analytical constraint stems from the quantification of inorganic and organic C (and H) in the biochar. Some uncertainties in the standard method using acidification and repeated determination of total C led to an initial recommendation of restricting the methodology to class 1

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biochars (as defined in the *IBI Biochar Standards*). For these biochars, which by definition contain more than 60% organic carbon, the proportion of inorganic carbon is likely negligible and organic carbon is roughly equivalent to total carbon. However, data analysis determined that this restriction yielded no change in the prediction results. Nevertheless, a method for calculating inorganic carbon in the sample was included, allowing the calculation of organic carbon by difference to total carbon. This exemplifies how the conservative approach mentioned was operationalized in the decisions made to arrive at a test method.

5.3 Future improvements to Alpha, Beta and Gamma methods

Alpha: The choice amongst routine analytical procedures that would reflect a robust, repeatable, and analytically sound result was limited to those that had been used in the peer-reviewed literature. These included the Standard Test Method for Chemical Analysis of Wood Charcoal, so-called proximate analysis (ASTM-D1762-84, 2007) and elemental ratios of O, H and C. Structural information beyond stoichiometric relationships between elements may provide better estimates of stability and may be attainable through spectroscopy or automated thermogravimetry. However, these have not been sufficiently developed or are not available at a sufficiently low cost or time requirement to be included at present, or both.

Beta: Longer periods of observation will likely provide evidence to improve precision of predictions of BC_{+100} (Lehmann et al., 2009; Zimmerman et al., 2012), likely increasing the stable carbon component calculated, since the current proposed method is highly conservative. The known long-term incubations experiments will continue and a revised future methodology will reflect improvements based on longer periods of observation. Only a few long-term field experiments have been published beyond a few years (Major et al., 2010), but are expected to be available for up to 10 year-periods in the coming years. However, pitfalls of field experiments are that these often do not distinguish between mineralization and physical loss by erosion and leaching, and the capabilities to estimate these differential losses over long periods of time are typically low. Therefore, these experiments often give at best a minimum mean residence time. A third approach is the use of aged biochars as proxies for biochar that has weathered in soil for long periods of time. Examples are biochar-type materials from Terra Preta (Liang et al., 2008), from charcoal storage sites (Cheng et al., 2010) or possibly archaeological deposits. The challenge using this approach is to develop adequate proxies for the starting material to assess its properties.

Gamma: Great progress has been made over the past years in understanding the change in the chemical form of fused aromatic carbons beyond aromaticity. Advancement in this area may come from NMR studies (Mao et al., 2012), measurements of adsorbed C-13-benzene (McBeath et al., 2012) and wet chemical methods such as BPCA (Glaser et al., 1998; Brodowski et al., 2005; Schneider et al., 2010). To improve predictability of biochar decomposition, next steps may include systematically relating structural information to improved Alpha-type methods, as defined in this document

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6. Conclusions

One of the most important properties of biochar – if not the most important one – is its stability, as it allows all other ancillary environmental benefits, especially in the agronomic field (i.e. soil amelioration), to persist in time. Mainly, the stability of the carbon component in biochar makes it particularly useful as a long-term climate change mitigation strategy, and thus having a scientifically valid methodology for the quantification of stable carbon will allow unlocking the potential benefits of biochar. That is what makes this effort, oriented by an Expert Panel, ground-breaking, and as such can contribute to the development of policies and programs that promote the deployment of biochar systems.

Given that this is the first such methodology to be developed, and that the science is rapidly evolving, the Panel necessarily devised a conservative methodology that is likely to underestimate the amount of stable carbon in biochar to a period of 100 years. But with continued research and development, some of which is described herein, we are confident that the test methodology will grow more robust and more rigorous over time, allowing for a more complete and precise estimation of stable carbon in biochar.

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Supplementary Information Section 1

Priming of SOC mineralization by black carbon

Priming can be defined as any change (positive or negative, persistent or ephemeral) in the turnover rate of soil organic matter caused by the addition of a new substrate (Woolf and Lehmann 2012). Increased or decreased turnover rates are defined as positive or negative priming, respectively. Only positive priming is considered in this assessment protocol, because this is a risk factor that might reduce the net C sequestration of biochar systems. Negative priming is not considered here due to application of the precautionary principle, whereby detrimental feedbacks should be included in the assessment protocol if there exists a non-negligible probability that they may be realised, whereas beneficial feedbacks should not be included unless they are unequivocal.

Addition of biochar to soils has been shown to alter the mineralization rate of non-pyrogenic SOC (npSOC). Positive priming of npSOC has been reported by Abiven and Andreoli (2010); Cross and Sohi (2011); Hamer et al. (2004); Jones et al. (2011); Keith et al. (2011); Liang et al. (2010); Luo et al. (2011); Novak et al. (2010); Spokas and Reicosky (2009); Wardle et al. (2008); Zimmerman et al. (2011). Negative priming of npSOC mineralization has been reported by Keith et al. (2011); Kuzyakov et al. (2009); Liang et al. (2010); Spokas and Reicosky (2009); and Zimmerman et al. (2011). Zimmerman et al. (2011) found that initial positive priming gave way to net negative priming over time. Where it has been possible to discriminate between labile- and stable-SOC decomposition, either no priming of stable SOC (Cross and Sohi 2011; Jones et al. 2011) or an increase in the stabilized SOC fraction (i.e. negative priming; Liang et al. 2010) was observed.

Only a few studies have allowed discrimination between priming of labile- or stable-npSOC decomposition. Where it has been possible to discriminate between labile- and stable-npSOC decomposition, either zero or negative priming of stable npSOC has been reported. Liang et al. (2010) added organic matter (AOM) with a distinct ^{13}C isotopic signature (from a C_4 plant) to BC-rich Anthrosols and BC-poor adjacent soils. They found a 19–340% increase in AOM-carbon in the organo-mineral fraction (assumed to indicate an increase in C stabilised by mineral associations) after 1.5 yr in BC-rich relative to adjacent soils. Cross and Sohi (2011) compared the priming effect in a silty-clay loam from Rothamsted Research, U.K., where three different management practices had been maintained for >60 years: (1) bare fallow (soil kept completely bare with regular cultivation), (2) continuous arable (wheat) and (3) managed grassland. The fallow soil was assumed to contain only stable npSOC due to the long period without organic matter inputs. Slight (no p statistic given, may not be significant) negative priming was observed from additions of BC to the fallow soil. Jones et al. (2011) found negative priming of a ^{14}C label that had been applied to the soil (Ah horizon, Typic Dystrochrept) 6 years prior to addition of BC in an incubation study. Due to the long interval between applying the radiocarbon label and the subsequent incubation trial, the ^{14}C was assumed to be present only in stable npSOC.

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Wardle et al. (2008) conducted a 10 year litterbag study with charcoal in a boreal-forest litter-layer in which positive priming was observed only during the first year. Other studies have observed positive priming over a period of a few weeks to months in short-term incubations (Luo et al. 2011; Keith et al. 2011; Zimmerman et al. 2011). Nonetheless, the precautionary principle suggests that we should consider the possibility that priming effects might persist long term. Woolf and Lehmann (2012) modeled the impact of biochar on priming over 100 years in a system designed to probe the upper bounds of priming impacts on npSOC. Specifically, they assumed[17]:

1. priming effects up to and including the largest that have been measured in any published short-term study;

2. that priming effects persist long-term;

3. that BC stocks accumulate in soil at a high rate (because they are produced from the abundant residues from a high-NPP crop; the BC is produced in an engineered pyrolysis system that gives high yields of BC per unit biomass feedstock; and the BC is produced under controlled conditions which ensure that it decomposes only slowly).

Under this set of highly conservative assumptions, Woolf and Lehmann (2012) found that no more than 3 to 4% of initial npSOC might be mineralised due to priming by BC over 100 years. In absolute quantities, this loss of npSOC was greatest in soils with the highest initial stocks of npSOC. Biochar production was also positively correlated with initial npSOC, due to the greater production of crop residues for feedstock on more fertile soils. Table S1 shows the initial npSOC ($npSOC_0$), potential loss of npSOC due to positive priming over 100 yrs ($\Delta npSOC_{p+}$), BC remaining in soil after 100 years (BC_{+100}), and $\Delta npSOC_{p+}$ expressed as a percentage of BC_{+100}, (denoted as RPL = Relative Priming Loss) for each of the locations studied in Woolf and Lehmann (2012).

Table S1. **Loss of soil carbon over 100 yr due to positive priming caused by BC at three study locations.** Source: Woolf and Lehmann, 2012

Site	$npSOC_0$ (kg C m^{-2}, in top 0.15m of soil profile)	$\Delta npSOC_{p+}$ (kg C m^{-2})	BC_{+100} (kg C m^{-2})	RPL
Colombia	0.94	0.037	3.31	1.1%
Kenya	1.56	0.05	3.29	1.5%
Iowa	6.29	0.26	5.95	4.4%

A linear regression of RPL versus $npSOC_0$ yields the relationship

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[17] In this paper, biochar is added gradually over 100 years and not in one large treatment in year zero. However, the model has been run using initial large application of biochar to soil and priming results were similar in magnitude.

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$$RPL = 0.0062 \text{ npSOC}_0 + 0.0053 \quad (R^2 = 0.99992)$$

From which it follows that the maximum npSOC_0 for which RPL is less than 5% is 7.2 kg C m^{-2} in the top 0.15m of the soil profile. I.e. for soils starting with less that 7.2 kg npSOC m^{-2}, cumulative priming losses will be less than 5% of the BC remaining after 100 years. If a 5% threshold for positive priming enhancement due to the addition of biochar to soil would be defined as a condition to disregard the effect of priming for biochar carbon stability estimations, biochar should not be applied to soils with more than 7.2 kg npSOC m^{-2}. However, soils with such concentrations are rarely found within agricultural soils, and are more frequent in forestland or peat soils (Davidson and Ackerman, 1993), where biochar would not likely be applied. In the case that biochar were applied to soils with concentrations higher than 7.2 kg npSOC m^{-2} it could lead to positive priming, which is factored into the calculations of stable carbon, with a discount factor of 5%, although – as stated – it would be rare to find soils with organic carbon content higher than the stated limit, in order to maintain a conservative approach to stability estimations. Additionally, it would not make much sense to apply a carbonaceous-rich material to a carbon-rich soil, if agronomic and environmental benefits are sought from biochar use.

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Supplementary Information Section 2

Selection process of the test method

Twenty-eight test methodologies were identified through an assessment of the peer-reviewed literature of existing techniques to determine biochar carbon stability in soil (shown in Table S2). These were grouped into five categories related to characterization approaches for physical-chemical properties of biochar, as defined in the scope of work.

Table S2. Test methods available for characterization of physical-chemical properties of biochar related to stability

Category	Test	Source
Microbial Incubations	Short-term Incubation (<50 d)	Suggested by Expert Panel
	Long-term Incubation (>1 y)	Liang et al 2008, Hammes et al 2008, Singh and Cowie 2008, Kuzyakov et al 2009, Zimmerman 2010, Singh 2012
	Incubation data modeled with 2 component model	DeGryze et al 2010
	Incubation data modeled with Power model	Zimmerman 2010
Volatile matter / stable carbon	Proximate analysis (ASTM D1762-84)	Major et al 2010, Lehmann et al 2011, Schmimmelpfennig and Glaser 2012
	Modified Proximate Analysis (e.g. Wang et al 2011)	Wang et al 2011, Enders et al 2012
	Ultimate analysis (resident carbon)	DeGryze et al 2010
	Modified Ultimate Analysis (e.g. DeGryze et al 2010)	McLaughlin et al 2009
	Lower temperature volatile matter measurement (e.g. Enders et al., 2012)	Enders et al 2012

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	NMR Relaxation (mobility of labile components)	Suggested by Expert Panel (multiple citations)
	NMR Cryoporometry (pore size distribution and volumes)	Suggested by Expert Panel (multiple citations)
	Thermogravimetric analysis (TGA) including R50 approach	Hammes et al 2007, Calvelo Pereira et al 2011
C functional group chemistry (aromaticity)	Scanning Transmission X-ray Microscopy (STXM)	Liang et al 2008
	Near-Edge X-ray Fine Structure Spectroscopy (NEXAFS)	Lehmann et al 2005, Liang et al 2008
	X-ray photoelectron spectroscopy	Nishimaya et al 1998, Schneider et al 201,
	Soil density fractionation	Sohi et al 2001, Liang et al 2008
	Alkyl-to-aromatic ratio (13C NMR)	Miknis et al 1981, Liang et al 2008, Brewer et al 2009
	Cyclic voltammetry	Joseph et al, 2010
	Dichromate oxidation	Hammes et al 2008, Rumpel et al 2009, Manning and Lopez-Capel 2010
	Infrared diffuse reflectance spectroscopy in the near- or mid-infrared spectral range (NIRS/MIRS)	Bellon-Maurel and McBratney 2011
	Benzene ring-current or benzenepolycarboxylic acids	Glaser et al 1998, Brodowski et al 2005, Schneider et al 2010, McBeath et al 2011, Schimmelpfennig and Glaser 2012

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Elemental ratios	H/C_{org} O/C_{org} ratios, Van Krevelen diagram	Baldock and Smernik 2002, Hammes et al 2007, Spokas 2010, Schimmelpfennig and Glaser 2012, Harvey et al 2012; Enders et al., 2012
Other	Soluble C fraction	Zimmerman et al 2012
	Electrochemical Impedance Spectroscopy	Suggested by Expert Panel
	Microscopic examination	Suggested by Expert Panel
	Molecular fin/gerprints by py-GC/MS	Kaal et al 2012

In order to quantitatively evaluate these methods, an evaluation matrix was completed by the experts. Eight of the experts evaluated the methodologies on the basis of seven criteria, on a scale from 1 to 5, with 5 being the highest value for each criterion. When referring to cost, the "highest" score equates to "least expensive" (e.g. a score of 5 for this criterion means that it is very inexpensive). The 7 criteria were given the same relative weight (1/7 or 14% each). The results are provided in Table S3.

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Table S3. Ranking of test methods based on scoring by experts.

Category	Method / procedure	Cost [1]	Availability [2]	Calibration against stability [3]	Repeatability [4]	Reflection of material property [5]	Publications - impact [6]	Robustness [7]	AVERAGE	Votes casted	Highest	Lowest
Elemental ratios	C,H,N Van Krevelen diagram	4.00	3.75	4.75	4.50	4.75	3.50	4.50	4.25	5	5 [1,3,4,5,6,7]	1 [1]
Elemental ratios	H/Corg (ratio)	4.14	3.67	4.33	4.67	3.83	3.17	4.00	3.97	7	5 [1,3,4,5,7]	1 [6]
Elemental ratios	O/Corg (ratio)	4.00	3.67	4.17	4.17	3.83	3.33	4.00	3.88	7	5 [1,2,3,4,5,6]	2 [5,6]
Microbial Incubations	Incubation data modeled with 2 component model	3.67	3.67	4.00	4.00	3.67	3.50	3.50	3.71	6	5 [1,2,3,4,5,6]	1 [1,2,3,6]
C functional group chemistry (aromaticity)	Infrared diffuse reflectance spectroscopy in the near- or mid-infrared spectral range (NIRS/MIRS)	4.40	3.40	3.00	4.00	4.40	3.00	3.60	3.69	5	5 [1,2,3,4,5,6,7]	1 [3,6]
Volatile matter / stable carbon	Modified Ultimate Analysis (e.g. DeGryze et al 2010)	3.67	3.33	3.33	4.00	3.67	3.67	3.67	3.62	3	5 [1,2,4,5,6]	1 [2]
Microbial Incubations	Incubation data modeled with Power model	3.50	3.50	3.83	3.83	3.83	3.33	3.50	3.62	6	5 [1,2,3,4,5,6,7]	1 [1,2,6,7]
Volatile matter / stable carbon	Ultimate analysis (resident carbon)	4.20	4.20	3.00	3.60	3.40	3.20	3.40	3.57	5	5 [1,2,4,5,6]	2 [3,4,5,6]
Volatile matter / stable carbon	Lower temperature volatile matter mreasurment (e.g. Enders et al., 2012)	4.20	3.80	3.40	3.80	3.40	2.60	3.40	3.51	5	5 [1,2,4]	1 [2,6]
Volatile matter / stable carbon	Proximate analysis (ASTM D1762-84)	4.43	4.17	3.33	3.33	3.17	3.17	3.00	3.51	7	5 [1,2]	1 [5]
Volatile matter / stable carbon	Thermogravimetric analysis (TGA) including R50 approach	3.43	2.57	3.86	3.86	3.71	3.14	3.86	3.49	7	5 [1,7]	1 [2,6]
C functional group chemistry (aromaticity)	Alkyl-to-aromatic ratio (13C CP/DP NMR)	2.20	2.20	4.00	3.60	4.40	3.60	4.20	3.46	5	5 [3,5,6,7]	1 [2]
Microbial Incubations	Long-term Incubation (>1 y)	2.29	3.14	4.00	3.00	3.57	4.14	3.71	3.41	7	5 [1,2,3,6,7]	1 [2,5]
C functional group chemistry (aromaticity)	Benzene ring-current	3.00	2.25	4.00	3.50	4.00	3.00	4.00	3.39	5	5 [1,2,3,5,7]	1 [2]
Volatile matter / stable carbon	Modified Proximate Analysis (e.g. Wang et al 2011)	4.33	3.67	3.17	3.67	3.17	2.67	3.00	3.38	6	5 [2]	1 [1,5]
C functional group chemistry (aromaticity)	Dichromate oxidation	3.83	3.83	3.17	3.50	2.83	3.00	2.83	3.29	6	5 [2]	1 [1,6,7]
Microbial Incubations	Short-term Incubation (<50 d)	3.57	3.43	2.43	3.29	2.86	3.57	3.29	3.20	7	5 [1,2,6]	1 [3,5,7]
Volatile matter / stable carbon	NMRC	1.86	1.83	3.33	3.67	4.33	2.83	3.50	3.05	7	5 [1,3,4,5,7]	1 [1,2,6]
Volatile matter / stable carbon	NMRR	2.14	2.00	3.17	3.50	4.17	2.67	3.50	3.02	7	5 [1,3,5,7]	1 [1,2,6]
C functional group chemistry (aromaticity)	Cyclic voltammetry	2.67	2.33	2.67	3.33	3.33	3.00	2.67	2.86	3	3 [all]	1 [6,7]
Other	Soluble C fraction	4.20	3.60	2.40	3.00	2.20	1.80	2.40	2.80	5	5 [2]	1 [1,3,5,7]
Other	Pyrolysis GC/MS	2.25	1.80	2.80	3.20	3.60	2.60	3.00	2.75	6	5 [1,5]	1 [2,3,6]
C functional group chemistry (aromaticity)	X-ray photoelectron spectroscopy	1.71	1.33	2.67	3.33	3.83	2.67	2.67	2.60	7	5 [1]	1 [2,3,6]
C functional group chemistry (aromaticity)	STXM	1.80	1.75	2.50	2.75	3.50	2.50	3.00	2.54	5	5 [1]	1 [2,6]
C functional group chemistry (aromaticity)	NEXAFS	1.33	1.20	2.80	2.40	4.20	2.60	3.00	2.50	6	5 [1,3]	1 [1,2,6]
C functional group chemistry (aromaticity)	Soil density fractionation	2.00	2.25	1.75	2.50	3.25	3.00	2.75	2.50	4	4 [1]	1 [3,6,7]
Other	Microscopic examination	2.40	2.75	2.00	2.75	2.25	1.75	2.00	2.27	5	5 [2]	1 [2,3,6,7]
Other	Electrochemical Impedance Spectroscopy	2.00	2.00	2.00	3.00	2.00	1.50	1.50	2.00	2	5 [1]	1 [2,3,6,7]

Color labels:

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3.5-5	Green
2-3.5	Yellow
0-2	Red

Criteria besides cost [1] include: [2] availability, referred to how common it is to find a laboratory that can perform the analyzed test; [3] calibration against stability, for those methods that have been correlated with other types of direct measurements of stability in published literature; [4] repeatability, as in the ability of the test to be performed periodically while maintaining precision without demanding extensive resources; [5] reflection of material property, or how well a test represents what is being measured; [6] publications – impact, as to the frequency with which the test can be found in published literature; and [7] robustness, meaning the precision, consistency and flexibility of the test.

Out of the twenty-eight methods evaluated (including three elemental ratios), ten obtained an overall score above 3.5 (green label), seventeen between 2 and 3.5 (yellow label) and only one below 2 (red label). The top 10 scored methods were further analyzed. A detail of the rankings for this sub-group is provided in table S4.

Table S4. Frequency of scores of the top 10 test methods.

#	Method	[1] 5	4	3	2	1	[2] 5	4	3	2	1	[3] 5	4	3	2	1	[4] 5	4	3	2	1	[5] 5	4	3	2	1	[6] 5	4	3	2	1	[7] 5	4	3	2	1	Votes	Avg value	Highest	Lowest
1	C,H,N Van Krevelen diagram	1	3	1				3	1			3	1				3		1			3	1				1	2			1	2	2				5	4.25	5 [1,3,4,5,6,7]	1 [6]
2	H/C$_{org}$ (ratio)	2	4	1				4	2			2	4				4		2			2	2	1	1		4		1		1	1	4	1			7	3.97	5 [1,3,4,5,7]	1 [6]
3	O/C$_{org}$ (ratio)	1	5	1				3	3			2	3	1			3	1		2		2	2	1	1		3	2	1			1	4	1			7	3.88	5 [1,2,3,4,5,6]	2 [5,6]
4	Incubation data modeled with 2 component model	3	1		1	1	4					2	3	2			3		2	1		1	3	1	1		2	1	2		1		4	1	1	1	6	3.71	5 [1,2,3,4,5,6]	1 [1,2,3,6]
5	Infrared diffuse reflectance spectroscopy in the near- or mid-infrared spectral range (NIRS/MIRS)	4			1		2		1		2	1	1	1	1	1	1	3	1			3	1	1			2			2		2	1	1	3		5	3.69	5 [1,2,3,4,5,6,7]	1 [3,6]
6	Modified Ultimate Analysis (e.g. DeGryze et al 2010)	1		2			1	1			1	2		1			1	1	1			1		2			1			2	1						3	3.62	5 [1,2,4,5,6]	1 [2]
7	Incubation data modeled with Power model	2	2		1	1	3	1			2	2	2	1	1		3		2	1		2	2	1	1		2	1	1	1	1	1	3	1		1	6	3.60	5 [1,2,3,4,5,6,7]	1 [1,2,6,7]
8	Ultimate analysis (resident carbon)	2	2	1			2	2	1			2	2	1			1	2	1	1		1	1	2	1			3	1				2	3			5	3.57	5 [1,2,4,5,6]	2 [3,4,5,6]
9	Lower temperature volatile matter mreasurment (e.g. Enders et al., 2012)	3		2			2	2				3	1	1			1	2	2				2	3					4		1		2	3			5	3.51	5 [1,2,4]	1 [2,6]
10	Proximate analysis (ASTM D1762-84)	4	2	1			2	3	1			3	2	1			3	2	1			3	2		1		2	3	1			1	4	1			7	3.51	5 [1,2]	1 [5]

Although further processing of the data was performed and presented to the Expert Panel with concrete proposals of test methods to be used for biochar C stability measurements, it was considered by the experts that this approach was useful only to frame the discussion and to discard some test methods, but that it was not the most appropriate path to officially select the final test method(s) to be used to calculate BC$_{+100}$. An in-depth analysis of the top-scoring methods was carried out in order to reduce the list to less than five suitable methods.

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Among the five highest scoring methods, the NIRS/MIRS method was discarded since, although there are scientific publications about its use to characterize other biogenic material and soils, currently there are no references that directly relate it with biochar C stability. It was included in the list of methods as a suggestion by the Expert Panel, and seems to be promising according to its overall score, but in order to comply with the premise of conservativeness, it was discarded.

The described analysis resulted in the conclusion that methods related to elemental composition –either elemental ratios or measurements of volatile and fixed matter- were to be considered as suitable Alpha methods. These are: (modified) proximate and ultimate analyses, and H/C_{org}.

Among proximate and ultimate analysis, the first measures moisture content, volatile matter, fixed carbon and ash; whereas the second determines the amount of carbon, hydrogen, oxygen, nitrogen and sulfur. Since there are more publications relating proximate analysis with biochar stability (e.g. Spokas 2010, Enders et al 2012) than relating ultimate analysis with biochar stability, it was considered that proximate analysis would be more suitable as a proposed method, and that it would allow for calibration to be performed more swiftly. Thus, ultimate analysis was discarded.

Among elemental ratios, as shown in figure 2, $H/_{Corg}$ and O/C_{org} are correlated. Since O is usually calculated by subtracting C, N and H from the full weight of a sample (i.e. it is derived rather than measured), H/C_{org} was considered simpler and more robust than O/C_{org}, which thus was discarded. A Van Krevelen diagram requires a calculation of O/C_{org} to plot it against H/C_{org}, and therefore was discarded as well.

This analysis led to the following preliminary conclusion: either proximate analysis, H/C_{org} or a combination of both would be best used as the method to determine BC_{+100}. A modification of the proximate analysis was considered feasible, as the one proposed by Enders et al. (2012). The quantification of H and C would be realized with the use of an elemental analyzer, and the threshold for a material qualifying as biochar to determine recalcitrance would be the threshold indicated in the IBI Standards (<0.7). The remaining question was whether the definitive test methodology should use one or a combination of these test methods.

In order to provide an answer to this question, a key input was the analysis of pyrolyzed material containing a high proportion of ash. Through the experience of the experts, the H/C_{org} was considered to provide flawed results when analyzing high-ash biochar, by yielding values under the defined threshold for H/C_{org} (<0.7) but which were actually not stable. Thus, an additional test was deemed necessary to eliminate this possible source of error, and proximate analysis was the preferred option, as it reports the ash content in biochar. A maximum value of 80% of ash content was proposed by the experts.

A combination of H/C_{org} and proximate analysis was then considered robust enough for an Alpha method to determine BC_{+100}. However, in order to simplify the proposed test method without sacrificing

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precision, it was stated that by restricting biochars to "Class 1" as defined in the IBI Standards (organic carbon content above 60%), a similar level of correlation between H/C_{org} and BC_{+100} could be yielded. Through this logic, it was agreed that H/C_{org} would be the sole measure of biochar stability.

The proposed Alpha method can and should be further improved as the science of biochar continues to accumulate, as this is a first attempt at estimating BC_{+100}. For that, it is suggested that information from observations of incubation experiments with laboratory-produced biochars and with charcoal from archaeological sites be made available, in order to establish parameters to calibrate this alpha-type test method to a beta-type. The beta method will not necessarily be used by biochar producers; rather, it should be performed in laboratories to propose amendments and modular updates to the alpha method, which is devised to be used by producers.

The Beta method to which the selected Alpha method is calibrated is the use of recorded measurements of biochar degradation from incubation experiments, combined with modeling to predict BC_{+100}. Given an observed behavior of biochar degradation across experiments (Kuzyakov et al 2009, etc., Cheng et al., 2008, Liang et al., 2008, Major et al., 2010), a two-component double exponential model was deemed appropriate to estimate the amount of carbon likely to be degraded in a time horizon of 100 years. The second possible model was the Power model (Zimmerman, 2010), which was considered by the Expert Panel as more appropriate from a biophysical standpoint (it better reflects the physical and chemical composition of biochar) and which actually yielded higher results for predicted stable carbon (ranging 80-97% vs 60-80% for the two-component model). However the Power model was discarded in favor of the more conservative double exponential model.

The two-component model was selected since it is a minimum adaptation to the concept of multiple pools, and is likely to underestimate BC_{+100}, as explained previously. The two pools are simplified to represent two main components of biochar – a relatively stable and a more labile fraction – which have different turnover rates.

Correlation between the chosen alpha and beta methods was performed using data from from two incubation experiments led by two members of the Expert Panel (Singh et al., 2012; Zimmerman, 2010, as extended in Zimmerman and Gao, 2013) on a range of laboratory-produced biochars conducted over 3 to 5 years under conditions that favor decomposition (e.g. adequate temperature conditions[18]). In vitro experiments may also inhibit decomposition over time by, e.g. not allowing influx of new nutrients or removal of microbial metabolites.

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[18] Singh et al. (2012) incubated at 22°C and Zimmerman (2010) incubated at 32°C

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