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3 Biochar pH, electrical conductivity and liming potential

Balwant Singh, Michaela Mei Dolk, Qinhua Shen and Marta Camps-Arbestain

INTRODUCTION

Biochar pH, electrical conductivity (EC) and liming potential are three chemical properties that are routinely measured for biochar application to soils. Several different procedures have been used for these measurements in the published literature. This chapter reports the pH, EC and liming potential data of the 19 reference biochars and, based on the results, procedures have been proposed that could be used routinely for biochar analysis.

pH

An understanding of biochar pH is important given its likely influence on soil pH and other properties and processes in soils on biochar application. While the effect of biochar on soil pH may be beneficial for ameliorating acid soils, increased pH has been linked to micronutrient deficiencies and yield reductions in some agricultural systems (Kishimoto and Sugiura 1985).

The term pH, first used by the Swedish scientist Sorensen in 1909, describes the intensity of acidity (or alkalinity) of a substance. It is defined as the negative base 10 logarithm of hydrogen ion activity $[H^+]$:

$$pH = -\log[H^+] = \log \frac{1}{[H^+]} \quad [\text{Eqn 1}]$$

Most biochars used for soil amendment are alkaline (Mukherjee and Lal 2014), however, biochar pH values between 3.1 and 12.0 have been reported in the literature (Lehmann 2007; Mukherjee *et al.* 2011). During carbonisation, acidic functional groups are removed and salts of alkali and alkaline earth elements become enriched (Ueno *et al.* 2008; Fuertes *et al.* 2010). These salts include (i) readily soluble salts, (ii) carbonates, (iii) sparingly soluble metal oxides and hydroxides and (iv) silicates, the latter especially when feedstocks contain soil particles (Okuno *et al.* 2005; Singh *et al.* 2010; Vassilev *et al.* 2013b; Wang *et al.* 2014). Most of these salts provide biochars a considerable alkalinity (Vassilev *et al.* 2013b), although this is feedstock- and production process-dependent (Xie *et al.* 2015). Consequently, biochars with low ash content, such as those produced using woody feedstocks, generally have lower pH values than biochars with higher ash content, such as those produced using grass, crop

Table 3.1: Summary of procedures used for biochar pH measurement

Biochar:solution	Solution	Time	References
1:5	DIW	0.5 h shaking	Singh <i>et al.</i> 2010
		Shaking and 1 h equilibration	Gaskin <i>et al.</i> 2008; Yuan <i>et al.</i> 2011
		24 h agitation	Li <i>et al.</i> 2013
1:6.25	DSW	Immediately and successive 1 h periods	Mukherjee <i>et al.</i> 2011
1:10	DIW	1 h equilibration	Lee <i>et al.</i> 2013
	0.01 M CaCl ₂	2 h shaking	Kloss <i>et al.</i> 2012
1:20	DIW	1.5 h shaking	Rajkovich <i>et al.</i> 2012
	DIW and 1 M KCl	1 h intermittent stirring	Cheng <i>et al.</i> 2006; Wu <i>et al.</i> 2012
	1 M KCl	1.5 h shaking	Enders <i>et al.</i> 2012
1:25	DIW	5 min boiling, supernatant cooled	Claoston <i>et al.</i> 2014
1:100	DIW	2 h shaking	Cantrell <i>et al.</i> 2012
1:100	DIW	Water bath at 90°C and stirred for 20 min. Allowed to cool to room temperature before measurement	Ahmedna <i>et al.</i> 1997

DIW = deionised water; DSW = distilled water.

residues or manures (Lehmann *et al.* 2011; Mukherjee *et al.* 2011; Smider and Singh 2014). Biochars produced under high temperatures (>400°C) are likely to have greater pH values than the low temperature (<400°C) biochars from the same feedstock (Lehmann *et al.* 2011; Mukherjee *et al.* 2011; Yuan *et al.* 2011). The pH of biochar may also change post-production depending on the environmental conditions. For example, incubation studies have demonstrated that biochar pH may increase or decrease post-production due to alkaline mineral dissolution or carbon oxidation, respectively (Cheng *et al.* 2006; Nguyen and Lehmann 2009).

Generally, a glass electrode–calomel electrode system is used to measure biochar pH. A more detailed description of electrometric measurement of pH can be found elsewhere (Thomas 1996). A summary of procedures used to measure biochar pH, available in the literature, is presented in Table 3.1. It is evident from this summary that different studies have adopted different procedures. This may present issues if the results from those studies are to be compared, since the procedure used can influence the pH values obtained.

The type of solution used in the analysis can affect the pH value: soil pH measured in 0.01 M CaCl₂ and 1 M KCl solutions generally gives lower pH values than if measured in deionised water (Thomas 1996). Similar effects can be expected in biochars. The ratio of solid to solution can also affect the measured pH, with non-linear increases in observed soil pH values associated with lower ratios (Thomas 1996). Other factors that may affect measured pH include the shaking time and the position of the electrode in relation to the suspension (Thomas 1996).

PROCEDURES FOR pH MEASUREMENT OF REFERENCE BIOCHARS

Biochar pH was measured in 1:5, 1:10 and 1:20 biochar:water (deionised water; DIW) ratio after 1 h shaking, and 1:20 biochar:water ratio after 24 h shaking on a reciprocating shaker at 25°C. After this, samples were allowed to stand for 30 min and then pH was measured using a calomel electrode–glass electrode system. The pH meter was calibrated using buffers of pH 7 and 10. The pH of the reference biochar samples was also measured in 0.01 M CaCl₂ using 1:10 and 1:20 biochar:CaCl₂ ratio after 1 h shaking and 30 min equilibration time as in water. Laboratory A used ~500 mg biochar and 10 mL DIW, whereas Laboratory B used 5.0 g biochar and varying amount of DIW depending on the biochar:water ratio.

The means and standard errors of the pH results for each sample are presented in Table 3.2, and a boxplot of the pH results, grouped by method, is presented in Fig. 3.1. Biochar pH measured in water was significantly ($F = 83.704$, $P < 0.001$) greater than if measured in CaCl_2 . The effects of biochar:solution ratio ($F = 1.123$, $P = 0.3463$) and equilibration time ($F = 0.105$, $P = 0.7571$) were not significant at a 5% level of significance.

Bivariate scatterplots comparing the mean pH for each biochar sample measured using different methods are presented in Fig. 3.2. There are strong positive linear correlations between the pH values measured using the different methods, with the lowest r^2 (0.639) observed for the relationship between pH measured by Laboratory B using 1:5 H_2O and 1:5 CaCl_2 with a 1.5 h equilibration time. The highest r^2 (0.977) occurred for the relationship of the Laboratory B pH measurements using 1:20 and 1:5 in water with 1.5 h equilibration time. The equations of the linear relationships between pH measurements made using the different methods are also presented in Fig. 3.2. These empirical relationships may be used for an approximate comparison of pH values measured using different methods.

Due to the porous nature and high water absorption capacity of biochar, when a biochar:solution ratio of 1:5 was used, many of the samples produced a sludge and there was not enough solution for proper insertion of the electrode. Thus, we recommend the use of 1:10 or 1:20 biochar:water ratio for the measurement of pH.

Electrolyte solutions (e.g. 0.01 M CaCl_2 and 1 M KCl) have been used for soil pH measurements to decrease the pH variability resulting from the presence of varying amounts of soluble salts (Thomas 1996). However, most biochars have a high background level of soluble salts, so the use of a background electrolyte solution may not be necessary for measuring biochar pH values.

Good correlation and slope value close to 1 for the biochar pH data (Laboratory A) using an equilibration time of 1.5 h and 24 h, and the results of the restricted (or residual) maximum likelihood (REML) analysis, suggest that a shaking time of 1.5 h is sufficient to obtain reliable pH values of biochar samples.

Linear mixed models were fitted using REML to evaluate the effects of feedstock and production temperature on biochar pH, adjusting for potential variability associated with solution, equilibration time, biochar:solution ratio and laboratories. Type II Wald F tests indicated that there is a significant interaction between pyrolysis

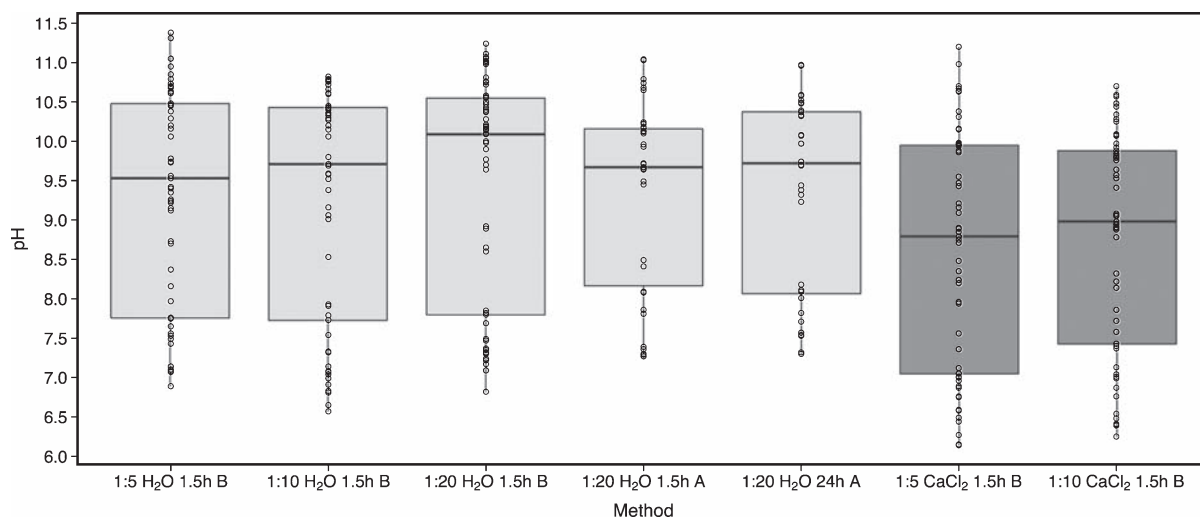


Figure 3.1: Boxplot of pH measurements of 19 reference biochar samples, grouped by method. Upper and lower hinges correspond to 25th and 75th percentiles (1st and 3rd quartiles), respectively. Solid line corresponds to median. Whiskers extend to highest and lowest values within 1.5 times the interquartile range. Individual observations are represented by circles. Light shading signifies use of H_2O as solution; dark shading signifies use of CaCl_2 as solution. In addition to the type of solution, methods differ by solid:solution ratio (1:5, 1:10, 1:20) and equilibration time (1.5 h and 24 h). Analyses were performed by two laboratories (A and B).

Table 3.2: Means and standard errors (SE) of pH measurements of biochar samples

Biochar ID	Name	Laboratory A				Laboratory B									
		Solid:solution ratio													
		1:20		1:5		1:10		1:20							
		1.5 h	24 h	CaCl ₂	H ₂ O	CaCl ₂	H ₂ O	CaCl ₂	H ₂ O	CaCl ₂	H ₂ O				
Mean	SE (n = 2)	Mean	SE (n = 2)	Mean	SE (n = 3)	Mean	SE (n = 3)	Mean	SE (n = 3)	Mean	SE (n = 3)	Mean	SE (n = 3)		
1	Wheat straw 550°C	10.23	0.01	10.38	0.01	10.65	0.01	10.84	0.11	10.12	0.14	10.38	0.05	10.32	0.13
2	Wheat straw 700°C	10.13	0.01	10.33	0.00	10.96	0.14	11.25	0.10	10.55	0.03	10.62	0.02	11.05	0.13
3	Switchgrass 400°C	7.28	0.01	7.55	0.02	6.54	0.05	7.46	0.18	6.43	0.03	7.04	0.03	7.92	0.35
4	Switchgrass 550°C	10.12	0.02	9.97	0.00	8.33	0.38	9.12	0.24	9.01	0.06	9.73	0.03	9.96	0.03
5	Pine chips 400°C	7.38	0.01	7.56	0.02	6.19	0.04	7.02	0.07	6.40	0.08	6.68	0.07	7.33	0.24
6	Pine chips 550°C	8.09	0.00	8.10	0.01	6.89	0.09	7.79	0.19	7.13	0.13	7.23	0.21	7.26	0.03
7	Eucalyptus wood 450°C	7.29	0.02	7.31	0.01	6.95	0.10	7.11	0.02	6.89	0.08	7.10	0.02	7.35	0.01
8	Eucalyptus wood 550°C	9.67	0.00	9.41	0.03	8.78	0.05	9.39	0.02	8.93	0.01	9.35	0.10	9.70	0.04
9	Poultry litter 550°C	9.65	0.00	-	-	8.81	0.02	9.20	0.03	8.85	0.04	9.58	0.00	10.17	0.02
10	Digestate 700°C	10.18	0.00	10.49	0.00	9.92	0.02	10.66	0.04	9.15	0.13	10.72	0.05	10.74	0.01
11	Municipal greenwaste 550°C	7.84	0.03	7.77	0.06	7.14	0.11	8.03	0.18	7.45	0.21	7.81	0.05	7.50	0.34
12	Rice husk 550°C	10.77	0.02	10.50	0.02	8.80	0.24	10.29	0.27	9.99	0.05	10.79	0.01	10.99	0.01
13	Rice husk 700°C	11.04	0.00	10.97	0.00	8.42	0.48	10.62	0.28	10.54	0.08	10.75	0.01	11.05	0.01

14	Miscanthus straw 550°C	10.67	0.01	10.59	0.00	9.99	0.09	10.59	0.09	10.59	0.07	9.58	0.03	10.47	0.13	10.54	0.02
15	Miscanthus straw 700°C	9.95	0.02	10.08	0.00	9.97	0.01	10.46	0.01	10.46	0.01	9.82	0.03	10.35	0.01	10.39	0.06
16	Mixed softwood 550°C	8.45	0.04	8.10	0.09	6.80	0.16	7.57	0.10	7.57	0.10	7.58	0.08	7.39	0.30	7.32	0.09
17	Mixed softwood 700°C	9.47	0.02	9.28	0.04	8.23	0.01	9.24	0.29	9.24	0.29	8.23	0.05	8.87	0.17	8.82	0.09
18	Greenhouse (tomato) waste 550°C	9.65	0.00	9.70	0.00	10.28	0.06	10.22	0.04	10.22	0.04	9.89	0.09	10.25	0.08	10.38	0.01
19	Durian shell 400°C	9.72	0.00	9.74	0.00	9.48	0.04	9.69	0.07	9.69	0.07	10.07	0.16	10.27	0.11	10.09	0.00

Methods differ in solid:solution ratio (1:5, 1:10, 1:20), equilibration time (1.5 h, 24 h) and solution (H₂O, CaCl₂). Analyses were performed by two laboratories (Laboratory A and Laboratory B).

temperature and feedstock ($F = 119.5$, $P < 0.001$). This result suggests that the effect of feedstock on pH differs, depending on the pyrolysis temperature. The significant increase in pH of some biochars with increasing pyrolysis temperature is in agreement with previous studies (Lehmann *et al.* 2011; Mukherjee *et al.* 2011; Yuan *et al.* 2011).

Recommended procedure for biochar pH measurement

Materials

- pH meter with glass–calomel electrodes.
- Deionised water.
- 100 mL centrifuge tubes or bottles.
- Automatic dispenser to deliver 50 mL.
- Standard buffers (pH 4, 7 and 10).
- Reciprocating shaker.

Procedure

- (1) Weigh 5.0 g air-dried biochar sample (ground to <2 mm) into a 100 mL centrifuge tube or bottle.
- (2) Add 50 mL DIW using an automatic dispenser, close the lid and shake well by hand.
- (3) Mechanically shake for 1 h at 25°C.
- (4) Allow the suspension to stand for ~30 min.
- (5) Measure the suspension pH using a pH meter calibrated using pH 7 and pH 10 buffers. If the expected pH of the biochar is <7, then use pH 7 and pH 4 buffers for calibration.
- (6) Record the pH value after stabilisation.
- (7) Rinse electrodes (with DIW) and blot dry between measurements.

ELECTRICAL CONDUCTIVITY

An understanding of the amount of soluble salts in a biochar solution is important since high rates of biochar application to soil may adversely affect salt-sensitive plants (Joseph *et al.* 2009). EC is proportional to the quantity and nature of salts dissolved in solution and is the most widely used soil salinity test (Pansu and Gautheyrou 2006). It is based on the principle that solutions with a higher concentration of salts have a greater ability to conduct an electrical current.

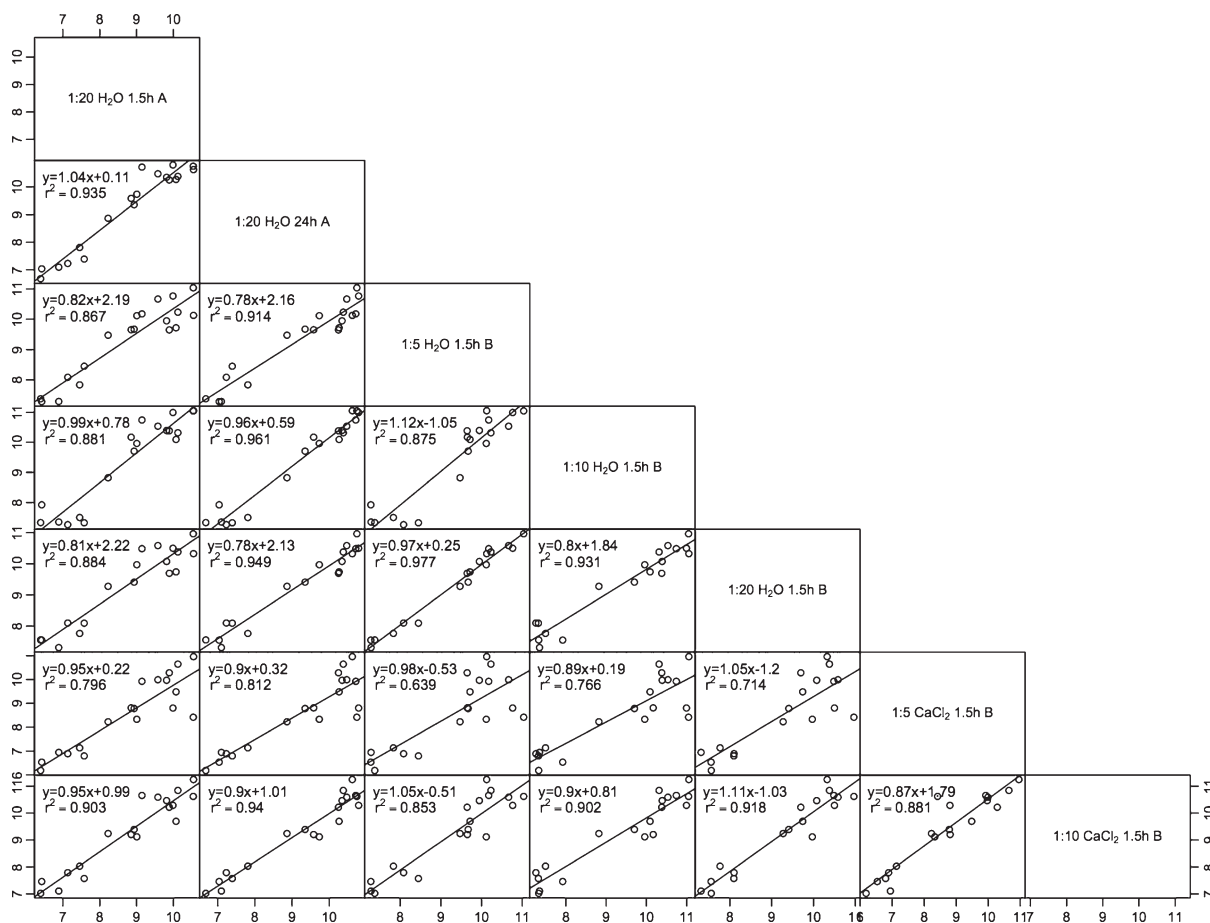


Figure 3.2: Relationship between different pH measurements of 19 reference biochar samples. Methods differ by solid:solution ratio (1:5, 1:10, 1:20), equilibration time (1.5 h, 24 h) and solution (H₂O, CaCl₂). Analyses were performed by two laboratories (A and B). Equations of relationships between results of different methods are displayed, along with r^2 values.

EC is traditionally determined by measuring the resistance (R) of the solution between two flat or cylindrical electrodes separated by a fixed distance. The resistance of conducting material, such as a saline solution, is proportional to its length and inversely proportional to its cross-sectional area (Rhoades 1996). Conductance is the reciprocal of R. The SI unit of EC is Siemens per metre (S m⁻¹). EC is generally reported in deci-Siemens per metre (dS m⁻¹) or milli-Siemens per centimetre (mS cm⁻¹) at 25°C: 1 dS m⁻¹ = 1 mS cm⁻¹ = 1000 μ S cm⁻¹.

Biochar EC values ranging from 0.04 dS m⁻¹ (Rajkovich *et al.* 2012) to 54.2 dS m⁻¹ (Smider and Singh 2014) have been reported in the literature. Similar to pH, the EC of biochar samples is also dependent on the feedstock and the pyrolysis temperature. Biochars produced at higher pyrolysis temperatures generally have higher EC values (Cantrell *et al.* 2012; Claoston *et al.* 2014; Rehrah *et al.* 2014). This effect has been attributed to the increasing concentration of residues or ash caused by the loss of volatile material during pyrolysis (Cantrell *et al.* 2012). Indeed, differences in the EC of biochars produced using different feedstocks have been attributed to differences in their ash contents (Rehrah *et al.* 2014). Wood and paper waste biochars generally have lower EC values than manure biochars (Singh *et al.* 2010; Rajkovich *et al.* 2012); however, differences exist within each of these broad groups. For example, Cantrell *et al.* (2012) found that biochars produced from dairy and feedlot manure had

lower EC values than biochars produced from poultry litter. Additives, such as polyacrylamide (PAM) polymers, used in the manufacturing of some biochars, can also affect EC. For example, a biochar produced from swine solids obtained using a PAM separation system had lower EC than other manure biochars; this was attributed to the inhibition of ionic compound dissociation associated with the pyrolytic degradation of PAM (Cantrell *et al.* 2012).

The ratio of biochar to water in the suspension affects the EC value, with EC values decreasing with increasing dilution. In samples with high soluble salt contents, the equilibration time also affects EC values, with longer equilibration times associated with higher EC values (Singh *et al.* 2010).

PROCEDURES FOR EC MEASUREMENT OF REFERENCE BIOCHARS

EC of 19 reference biochars was measured in 1:10 and 1:20 biochar:water ratio after 1 h shaking, and 1:20 biochar:water ratio after 24 h shaking on a reciprocating shaker at 25°C. After this, samples were allowed to stand for 30 min then EC was measured using a pre-calibrated EC meter. Laboratory A used ~500 mg biochar and 10 mL DIW, whereas Laboratory B used 5.0 g biochar and appropriate volume of DIW depending on the biochar:water ratio.

The means and standard errors of the EC results for each sample are presented in Table 3.3 and a boxplot of EC, grouped by method and displayed on a \log_{10} scale, is presented in Fig. 3.3. The results show that using a 1:10 biochar:water ratio results in greater values of EC than using a 1:20. This is expected due to the effect of dilution on EC. Based on the Laboratory A results (Table 3.3, Fig. 3.3), the EC values measured using an equilibration time of 24 h were significantly higher than EC measured using an equilibration time of 1.5 h ($F = 9.7$, $P = 0.003$). Our results suggest that both biochar:water ratios (1:10 and 1:20) are appropriate for analysis of biochar EC; the values for the two methods are highly correlated ($r^2 = 0.99$) with a slope of close to 1.0 (Fig. 3.4). Furthermore, the good relationship ($r^2 = 0.96$) between results obtained using a 24 h equilibration time and those obtained using a 1.5 h equilibration time suggests that 1.5 h is sufficient to obtain reliable EC values for different types of biochars.

REML methodology was used to fit linear mixed models to explore the effects of feedstock and production temperature on biochar EC, adjusting for potential variability associated with equilibration time, biochar:water ratio and laboratories. EC values were \log_{10} -transformed to satisfy the assumptions of the statistical analysis. Type II Wald F tests indicated that there is a significant interaction between pyrolysis temperature and feedstock ($F = 313.0$, $P < 0.001$, which suggests that the effect of pyrolysis temperature on EC differs, depending on the feedstock. These results are consistent with other published studies (e.g. Cantrell *et al.* 2012; Claoston *et al.* 2014; Rehra *et al.* 2014) that observed increases in EC of biochars with increasing pyrolysis temperature.

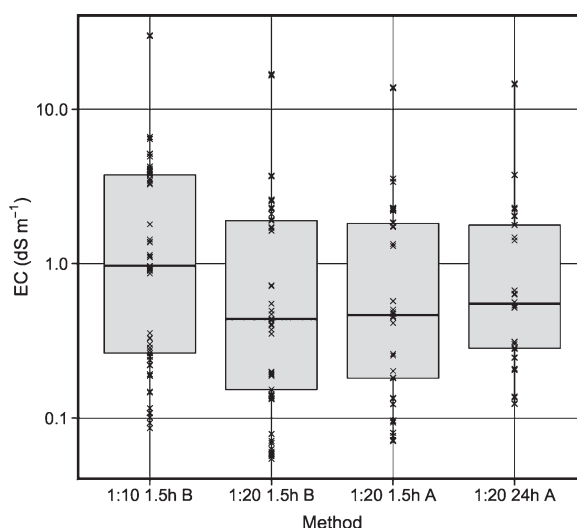


Figure 3.3: Boxplot of EC (dS m^{-1}) measurements of 19 different biochar samples, grouped by method. Upper and lower hinges correspond to 25th and 75th percentiles (1st and 3rd quartiles), respectively. Solid line corresponds to median. Whiskers extend to highest and lowest values within 1.5 times the interquartile range. Individual observations are represented by crosses. Three methods were used (1:10 solid:solution ratio with 1.5 h equilibration time, 1:20 solid:solution ratio with 1.5 h equilibration time, and 1:20 solid:solution ratio with 24 h equilibration time). Analyses were performed by two laboratories (A and B). The y-axis is presented on a log-scale.

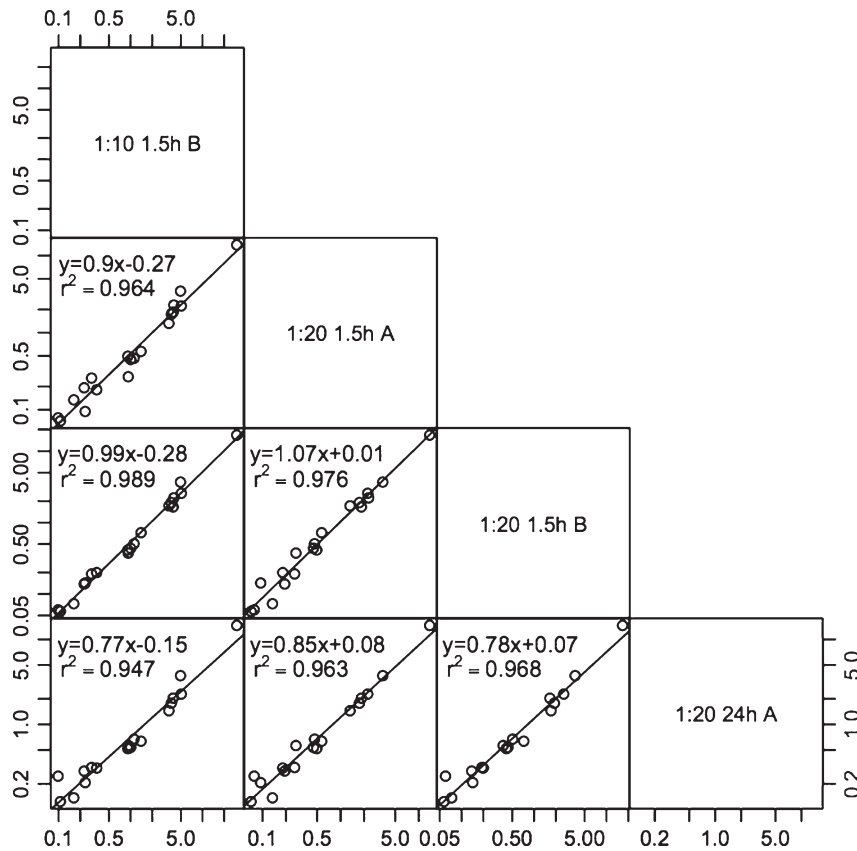


Figure 3.4: Relationship between different EC measurements of 19 biochar samples. Methods differ by solid:solution ratio (1:10, 1:20), equilibration time (1.5 h and 24 h). Analyses were performed by two laboratories (A and B). Equations of relationships between results of different methods are displayed, along with r^2 values.

Recommended procedure for biochar EC measurement

Materials

- Electrical conductivity meter.
- Deionised water.
- 100 mL centrifuge tubes or bottles.
- Automatic dispenser to deliver 50 mL.
- Reference solution for calibration, 0.01 M KCl, this has an EC of 1.413 dS m^{-1} at 25°C .
- Reciprocating shaker.

Procedure

- (1) Weigh 5.0 g air-dried biochar sample (ground to $<2 \text{ mm}$) into a 100 mL centrifuge tube or bottle.
- (2) Add 50 mL DIW using an automatic dispenser, close the lid and shake well by hand.
- (3) Mechanically shake for 1 h at 25°C .
- (4) Allow the suspension to stand for $\sim 30 \text{ min}$.
- (5) Measure the conductivity using a calibrated EC meter following the instructions supplied by the EC manufacturer.
- (6) Record the EC value and units after stabilisation.
- (7) Rinse electrodes (with DIW) and blot dry between measurements.

Table 3.3: Means and standard errors (SE) of EC (dS m⁻¹) measurements of reference biochar samples

Biochar		Laboratory A				Laboratory B			
		Solid:solution ratio							
		1:20				1:10		1:20	
		1.5 h		24 h		1.5 h			
ID	Name	Mean	SE (n = 2)	Mean	SE (n = 2)	Mean	SE (n = 3)	Mean	SE (n = 3)
1	Wheat straw 550°C	1.32	0.02	1.45	0.03	3.41	0.09	1.72	0.01
2	Wheat straw 700°C	2.22	0.02	2.28	0.03	5.07	0.07	2.57	0.02
3	Switchgrass 400°C	0.26	0.00	0.31	0.00	0.29	0.01	0.19	0.00
4	Switchgrass 550°C	0.19	0.01	0.28	0.00	0.23	0.01	0.14	0.00
5	Pine chips 400°C	0.09	0.00	0.21	0.00	0.23	0.02	0.14	0.01
6	Pine chips 550°C	0.07	0.00	0.12	0.00	0.11	0.00	0.06	0.00
7	Eucalyptus wood 450°C	0.46	0.01	0.67	0.00	1.12	0.01	0.51	0.02
8	Eucalyptus wood 550°C	0.27	0.15	0.56	0.00	0.93	0.03	0.37	0.01
9	Poultry litter 550°C	2.29	0.01	–	–	3.99	0.04	2.22	0.06
10	Digestate 700°C	1.85	0.01	2.04	0.00	3.90	0.29	1.66	0.02
11	Municipal greenwaste 550°C	0.08	0.00	0.25	0.00	0.10	0.01	0.06	0.00
12	Rice husk 550°C	0.45	0.00	0.54	0.00	1.00	0.05	0.44	0.00
13	Rice husk 700°C	0.49	0.01	0.52	0.00	0.92	0.01	0.41	0.01
14	Miscanthus straw 550°C	0.57	0.00	0.64	0.00	1.40	0.02	0.72	0.00
15	Miscanthus straw 700°C	1.74	0.02	1.78	0.00	3.69	0.07	1.91	0.01
16	Mixed softwood 550°C	0.13	0.00	0.14	0.00	0.16	0.01	0.07	0.00
17	Mixed softwood 700°C	0.18	0.00	0.31	0.00	0.34	0.01	0.20	0.00
18	Greenhouse (tomato) waste 550°C	13.80	0.10	14.58	0.10	29.93	0.09	16.69	0.11
19	Durian shell 400°C	3.47	0.09	3.75	0.00	4.94	1.57	3.69	0.01

Three methods were used (1:10 solid:solution ratio with 1.5 h equilibration time, 1:20 solid:solution ratio with 1.5 h equilibration time, and 1:20 solid:solution ratio with 24 h equilibration time). Analyses were performed by two laboratories (Laboratory A and Laboratory B) independently.

For improved consistency of EC results, the suspension can be filtered through Whatman no. 1 filter paper (or any equivalent filter paper) immediately after shaking.

BIOCHAR LIMING POTENTIAL

The ash fraction (e.g. alkaline oxides, carbonates) in biochar can provide considerable alkalinity (Vassilev *et al.* 2013a), this being feedstock- and process-dependent (Xie *et al.* 2015). This confers liming properties on biochars and allows their use as liming agents in acidic soils (Novak *et al.* 2009; Yuan and Xu 2011; Chintala *et al.* 2014; Masud *et al.* 2014). Prior to their application, knowledge of the liming potential of the biochar and the pH-buffering capacity (pH-BC) of the soil is needed so that the lime recommendation can be made.

The liming potential of biochar is often assessed following common methodologies intended to measure carbonate content in soil, such as those of Rayment and Higginson (1992), Singh *et al.* (2010) or AOAC 955.01 (Helrich 1990) as suggested by IBI (IBI 2015). These procedures involve treatment of a known mass of biochar

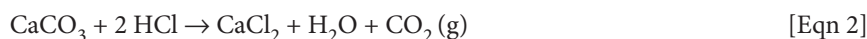
with a known volume of acid and either keeping the mixture overnight (Rayment and Higginson 1992) or boiling the mixture for 5 min (Helrich 1990). The excess acid is back-titrated with a standardised base. The result is reported as an equivalent proportion of the liming effect of pure CaCO_3 (referred to as % CaCO_3 -eq). Based on the observed range of CaCO_3 -eq, biochars have been classified into the following classes: Class 0 (<1% CaCO_3 -eq), Class 1 (1–10% CaCO_3 -eq), Class 2 (10–20% CaCO_3 -eq) and Class 3 (>20% CaCO_3 -eq) (Camps-Arbestain *et al.* 2015). Yuan *et al.* (2011) used an acid-base rapid titration – in which biochar is continually titrated (using an autotitrator) with acid to pH 2.0 while stirring – to estimate the total alkalinity of biochar and reported this as the amount of the acid being consumed by the biochar ($\text{cmol H}^+ \text{ kg}^{-1}$ biochar).

The liming potential of biochars can also be assessed following other common methodologies used for measuring pH buffering capacity (referred to as pH-BC) of soils (Aitken and Moody 1994; Liu *et al.* 2005; Kissel *et al.* 2007; Thompson *et al.* 2010; Xu *et al.* 2012). The soil pH-BC is commonly measured after adding incremental amounts of either a base or an acid – depending on the initial soil pH – to the soil, then letting the soil incubate for a specific period of time (Bloom 2000; Nelson and Su 2010), and establishing a titration curve. This technique is time-demanding (e.g. five days) and involves multiple acid/base additions, and thus is not recommended for a routine characterisation of biochars. Simplified methodologies have been proposed for the determination of soil pH-BC, such as the 2-point titration (before and after a single addition of acid or base) that relies on the fact that the pH-BC curve of most soils is ‘essentially linear’ over the pH range 4.0–6.5 (Magdoff and Bartlett 1985; Aitken *et al.* 1990). More recently, a statistical relationship between the pH-BC of a wide range of soils after a 30 min equilibration with a base ($\text{pH-BC}_{30\text{min}}$) and that obtained after 5 d equilibration ($\text{pH-BC}_{5\text{d}}$) has been established in order to reduce the time required in the measurement of this parameter (Liu *et al.* 2005; Kissel *et al.* 2007, 2012; Thompson *et al.* 2010). These approaches are adequate when the intention is to determine the lime requirement of a soil, as changes in soil pH upon liming will be expected to be in the 4.0–6.5 pH range. However, the applicability of these simplified methods in determining the acid-buffering capacity of biochars is hampered by the fact that changes in biochar pH upon soil amendment may cover a wider range of pH values (<6 to >8), within which the linearity assumption may not apply.

PROCEDURES FOR MEASUREMENT OF BIOCHAR LIMING POTENTIAL: CALCIUM CARBONATE EQUIVALENT

Calcium carbonate equivalent, also referred to as liming equivalence, was determined according to a modified version of the method proposed by Rayment and Higginson (1992) for measuring soil carbonate content. For this, 10.0 mL standardised 1 M HCl solution is added to 0.5 g ground biochar, shaken on an end-over-end shaker for 2 h and left standing overnight (16 h). Then the slurry (without any separation procedure) is titrated using an autotitrator under vigorous stirring with a standardised 0.5 M NaOH solution until a neutral pH (~7.0) is reached. The volume of NaOH solution consumed is recorded (*a* mL). Blank titration (i.e. without biochar) is done by using 10.0 mL standardised 1 M HCl and the volume of NaOH solution consumed is recorded (*b* mL). A reference sample of CaCO_3 powder (previously dried at 105°C for 1 h) is also included in the batch. Liming equivalence (% CaCO_3 -eq) is then calculated using Eqns [2] and [3].

Chemical reaction and calculations



In the above reaction for dissolving 1 mole of CaCO_3 (i.e. 100.09 g of CaCO_3), 2 moles of HCl are consumed. Unreacted H^+ is determined by titration. The amount of H^+ neutralised by the biochar is then calculated by difference between the blank and the biochar sample. The % CaCO_3 -eq is thus determined as follows:

$$\% \text{ CaCO}_3 \text{ equivalent} = \frac{M \times (b-a) \times 10^{-3} \times 100.09 \times 100}{2 \times W} \quad [\text{Eqn 3}]$$

where:

M = standardised molarity of NaOH (mol L⁻¹)

b = volume of NaOH being consumed (mL) by the blank

a = volume of NaOH being consumed (mL) by the biochar sample

10⁻³ = to convert the volume from mL to L

100.09 = molar mass of CaCO₃

100 = multiplier for obtaining % CaCO₃ equivalent

W = mass of biochar (g)

2 = 1 mole of CaCO₃ consumes 2 moles of H⁺.

The mean and standard error of the liming equivalence (% CaCO₃-eq) results for the 19 biochars samples are presented in Table 3.4. A poor correlation ($r^2 = 0.09$, data not shown) between pH of the 19 biochars and the liming equivalence values shows that pH is a poor indicator of the biochar liming potential.

The greatest liming potential was found for the tomato waste biochar (TW550). This was attributed to the large amount of ash (56.4%) (Ch. 2) containing calcite and other carbonate minerals (e.g. magnesite and ankerite) in this biochar (Ch. 21). Biochars made from poultry litter at 550°C (PL550), digestate at 700°C (DB700), durian shell at 400°C (DS400), wheat straw at 550 or 700°C (WS550, WS700), pine and eucalyptus wood carbonised at 550°C (PC550, EW550), and miscanthus carbonised at 700°C (MS700) had a liming equivalence >5% CaCO₃-eq, while the rest of the biochars had a liming equivalence <5% CaCO₃-eq. In general, the liming potential was related to the ash content, as in the biochars for poultry litter (45% ash content) and digestate (33% ash content); however, no relationship was found in the rice husk biochars, as they had an ash content >45% (mostly constituted by silica; Chs 9 and 21) but a low liming potential <1.9% CaCO₃-eq. The chemical composition of the ash therefore has a key role in this regard. It was also observed that biochars produced using the same feedstock but at higher temperature tend to have a greater liming potential than the ones produced at lower temperature (Table 3.4). This was in agreement with the residual concentration of ash caused by the loss of volatile material during pyrolysis (Cantrell *et al.* 2012).

In order to test whether the liming equivalence (% CaCO₃-eq) is a suitable index for estimating the application rate of biochar needed to raise the soil pH to a specific value, a 10 d incubation of two soils amended with different amounts of the 19 biochars was conducted. Two soils with contrasting alkaline pH-buffering capacities were used: an Andic Haplumbrept/Andic Umbrisol, and a Typic Dystrachrept/Haplic Cambisol (IUSS Working Group 2006; Soil Survey Staff 2006) (Table 3.5).

Table 3.4: Means and standard errors (SE) ($n = 2$) of liming equivalence (% CaCO₃-eq) of reference biochar samples

Biochar		Liming equivalence (% CaCO ₃ -eq)	
ID	Name	Mean	SE
1	Wheat straw 550°C	5.7	0.1
2	Wheat straw 700°C	6.5	0.1
3	Switchgrass 400°C	1.9	0.2
4	Switchgrass 550°C	3.0	0.2
5	Pine chips 400°C	3.9	0.1
6	Pine chips 550°C	5.0	0.1
7	Eucalyptus wood 450°C	2.6	0.2
8	Eucalyptus wood 550°C	6.3	0.1
9	Poultry litter 550°C	11.8	0.0
10	Digestate 700°C	10.8	0.4
11	Municipal greenwaste 550°C	1.8	0.5
12	Rice husk 550°C	1.5	0.0
13	Rice husk 700°C	1.9	0.1
14	Miscanthus straw 550°C	3.8	0.1
15	Miscanthus straw 700°C	5.6	0.2
16	Mixed softwood 550°C	1.5	0.1
17	Mixed softwood 700°C	2.3	0.4
18	Greenhouse (tomato) waste 550°C	20.5	0.1
19	Durian shell 400°C	9.3	1.3

Table 3.5: Selected properties of the acidic soils used for incubation

Properties	Units	Andic Haplumbrept	Typic Dystrochrept
pH _{1:2.5 H₂O}		5.3	5.2
CEC	mmol(+) kg ⁻¹	138	88
P retention capacity	%	88	41
Alkaline-pH-BC*	mmol H ⁺ kg ⁻¹ pH ⁻¹	50.8	28.1
Total C	g kg ⁻¹	73	34
Exchangeable acidity	mmol(+) kg ⁻¹	27	34
Exchangeable Al	mmol(+) kg ⁻¹	23	26

All values are expressed on an oven dry weight basis; CEC = cation exchange capacity (Blakemore *et al.* 1987).

* pH buffering capacity (Aitken and Moody 1994).

Subsamples of each of the two soils were separately amended with the 19 biochars under study at two application rates (rate 1 and rate 2) intended to achieve the target pH of 6.5. Rates 1 and 2 were calculated using Eqns [4] and [5] based on the liming equivalence – % CaCO₃-eq (as obtained using Eqn [3]).

$$\text{Rate 1 (g biochar per 100 g soil)} = \frac{\text{pH-BC}_{\text{soil}} \times (\text{pH}_{\text{target}} - \text{pH}_{\text{soil}}) / 2}{\% \text{ CaCO}_3\text{-eq}} \quad [\text{Eqn 4}]$$

$$\text{Rate 2 (g biochar per 100 g soil)} = \frac{\text{pH-BC}_{\text{soil}} \times (\text{pH}_{\text{target}} - \text{pH}_{\text{soil}})}{\% \text{ CaCO}_3\text{-eq}} \quad [\text{Eqn 5}]$$

where:

pH-BC_{soil} is the pH buffering capacity of soil, which is calculated as the inverse of the slope of the titration curve (pH *v.* OH⁻ added) (Thomas and Hargrove 1984; Aitken and Moody 1994), which tends to be linear over the pH range 4.0–6.5 (Magdoff and Bartlett 1985; Aitken *et al.* 1990) and corresponds to the quantity of base required to raise the soil pH by one unit.

pH_{soil} is the pH value of the soil before the addition of the biochar.

pH_{target} is the pH value intended to reach (i.e. 6.5).

These equations differ in the equivalence of moles of hydroxyls generated per mole of dissolved CaCO₃ used: a value of 2 in Eqn [4] and of 1 in Eqn [5]. The reason is that, unless the soil is very acidic, CaCO₃ will dissolve according to reaction [5] instead of reaction [1], in which case the dissolution of 1 mole of CaCO₃ will neutralise only one proton (Bohn *et al.* 1985):



The soils were then thoroughly mixed with the 19 biochars at the calculated rates (rate 1 and rate 2) in duplicates and wetted with DIW to 70% of field capacity. All treatments were incubated in a chamber at a constant room temperature of 20°C for 10 days. Thereafter, the pH was measured.

The pH values of the soils amended with biochar at application rates 1 or 2 (Table 3.6) after a 10 d incubation are plotted in Figs 3.5a and b, respectively. The results indicated that, when the application rates of the amendment were estimated considering an equivalence of 2 (rate 1), 21% of the amended soil pH values fell within ± 0.25 pH units of the target pH 6.5, 55% plotted within ± 0.5 pH units of the target, and the final pH values ranged between 5.6 and 6.5, with a mean pH value of 6.0 (Fig. 3.5a). When the application rates were estimated using an equivalence of 1, the results indicated that 50% of the amended soil pH values fell within ± 0.25 pH units of the target pH 6.5, 89% plotted within ± 0.5 pH units of the target, and the final pH values ranged

between 5.7 and 6.6, with a mean pH value of 6.2 (Fig. 3.5b). Therefore, for the two soils used in this study, pH values of soils amended with rates calculated using an equivalence of 1 were closer to the targeted value than when considering an equivalence of 2. However, as indicated above, the use of 1 or 2 equivalences will depend on the initial pH value of the soil to be limed (Bohn *et al.* 1985). Also, the kinetics of the dissolution reaction will be affected by environmental conditions (i.e. a leaching environment will accelerate the dissolution of carbonate salts), the particle size of the biochar, and the different solubilities of the alkaline salts in the ash of biochar. In this regard, it should be noted that the dissolution of some alkaline salts in soils takes longer than 10 days and longer-term incubations should provide a more realistic response.

Recommended procedure for measurement of biochar liming potential

Materials

- An autotitrator.
- Pure CaCO₃ powder.
- Standardised 1 M HCl solution.
- 35 mL polypropylene tubes.
- Automatic dispenser to deliver 10 mL acid.
- Standardised 0.5 M NaOH.
- Reciprocating shaker.

Procedure

- (1) Weigh 0.5 g air-dried biochar sample (ground to <2 mm) into a 35 mL polypropylene tube.
- (2) Add 10.0 mL of standardised 1 M HCl solution using an automatic dispenser.
- (3) Shake for 2 h at 25°C on a reciprocating shaker and let mixture stand overnight (16 h).
- (4) Titrate the suspension (without any separation procedure) using an autotitrator under vigorous stirring with standardised 0.5 M NaOH until a neutral pH (~7.0) is reached.
- (5) Record the volume of NaOH solution consumed (*a* mL).
- (6) Perform a blank titration (i.e. without biochar) using 10.0 mL standardised 1 M HCl and record the volume of NaOH solution consumed (*b* mL).
- (7) A reference sample of CaCO₃ powder (previously dried at 105°C for 1 h) should be included in the batch.

$$\% \text{CaCO}_3 \text{ equivalent} = \frac{M \times (b-a) \times 10^{-3} \times 100.09 \times 100}{2 \times W} \quad [\text{Eqn 7}]$$

where:

M = standardised molarity of NaOH (mol L⁻¹)

b = volume of NaOH being consumed (mL) by the blank

a = volume of NaOH being consumed (mL) by the biochar sample

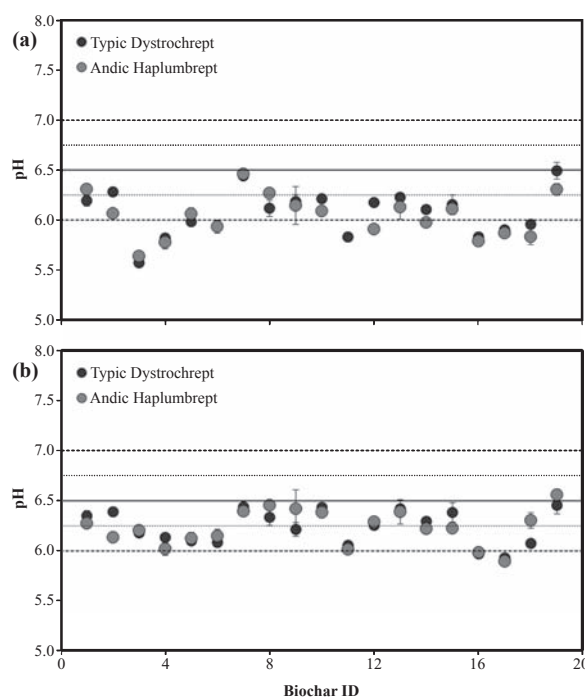


Figure 3.5: The distribution of pH values of an Andic Haplumbrept and a Typic Dystrachrept after a 10 d incubation of samples amended with biochar at application rates (a) 1 and (b) 2 intended to achieve the target soil pH value of 6.5.

Table 3.6: Soils amended with biochar at different application rates

Biochar		Rate 1 (g biochar per 100 g soil)		Rate 2 (g biochar per 100 g soil)	
ID	Name	Andic Haplumbrept	Typic Dystrochrept	Andic Haplumbrept	Typic Dystrochrept
1	Wheat straw 550°C	5.4	3.2	10.8	6.5
2	Wheat straw 700°C	4.7	2.8	9.4	5.6
3	Switchgrass 400°C	16.1	9.6	32.2	19.3
4	Switchgrass 550°C	10.0	6.0	20.1	12.0
5	Pine chips 400°C	7.8	4.7	15.6	9.3
6	Pine chips 550°C	6.1	3.6	12.1	7.3
7	Eucalyptus wood 450°C	11.7	7.0	23.4	14.0
8	Eucalyptus wood 550°C	4.8	2.9	9.6	5.8
9	Poultry litter 550°C	2.6	1.5	5.2	3.1
10	Digestate 700°C	2.8	1.7	5.6	3.4
11	Municipal greenwaste 550°C	16.7	10.0	33.4	20.0
12	Rice husk 550°C	20.9	12.5	41.8	25.1
13	Rice husk 700°C	16.4	9.8	32.9	19.7
14	Miscanthus straw 550°C	8.1	4.9	16.2	9.7
15	Miscanthus straw 700°C	5.4	3.3	10.9	6.5
16	Mixed softwood 550°C	20.6	12.4	41.3	24.7
17	Mixed softwood 700°C	13.2	7.9	26.3	15.8
18	Greenhouse (tomato) waste 550°C	1.5	0.9	3.0	1.8
19	Durian shell 400°C	3.3	2.0	6.6	3.9

The soils were amended with the 19 biochars under study at application rates (x g biochar per 100 g soil) calculated using the liming potential of the biochars estimated by the liming equivalence % $\text{CaCO}_3\text{-eq}$, according to Eqn [4] (Rate 1) or Eqn [5] (Rate 2) intended to target a pH of 6.5.

10^{-3} = to convert the volume from mL to L

100.09 = molar mass of CaCO_3

100 = multiplier for obtaining % CaCO_3 equivalent

W = mass of biochar (g)

2 = 1 mole of CaCO_3 consumes 2 moles of H^+ .

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