Characterization of biochars to evaluate recalcitrance and agronomic performance

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ABSTRACT

Biochars (n = 94) were found to have ash contents from 0.4% to 88.2%, volatile matter from 13.2% to 70.0%, and fixed carbon from 0% to 77.4% (w/w). Greater pyrolysis temperature for low-ash biochars increased fixed carbon, but decreased it for biochars with more than 20% ash. Nitrogen recovery varied depending on feedstock used to a greater extent (12–68%) than organic (25–45%) or total C (41–76%) at a pyrolysis temperature of 600 °C. Fixed carbon production ranged from no enrichment in poultry biochar to a 10-fold increase in corn biochar (at 600 °C). Prediction of biochar stability was improved by a combination of volatile matter and H:C ratios corrected for inorganic C. In contrast to stability, agronomic utility of biochars is not an absolute value, as it needs to meet local soil constraints. Woody feedstock demonstrated the greatest versatility with pH values ranging from 4 to 9.

1. Introduction

Biochar, the solid product of biomass carbonization intended as a soil amendment, has attracted attention due to its ability for long term improvements in soil physical and chemical properties, with potentially important effects on soil biota. Specifically, biochar may improve water infiltration (Ayodele et al., 2009), soil water retention, ion exchange capacity and nutrient retention (Laird et al., 2010; Lehmann et al., 2003), pH (Van Zwieten et al., 2010a), and improve N use efficiency (Van Zwieten et al., 2010b). The substantial changes in bulk soil properties and around biochar particles have shown to influence soil biological processes with significant implications for soil biogeochemistry (Lehmann et al., 2011).

Thermochemical conversion during pyrolysis alters constituent carbon compounds to yield materials that are depleted of H and O (Küçükbayrak and Kadioğlu, 1989) and possesses a greater proportion of aromatic C in comparison with the biomass feedstock (Baldock and Smernik, 2002). These materials offer greater chemical recalcitrance and resistance to biological decomposition (Baldock and Smernik, 2002; Zimmerman, 2010), thereby ensuring that any beneficial effects of biochar endure. On one extreme, naturally occurring black C is able to persist for millennia (Lehmann et al., 2008; Skjemstad et al., 1996). This has promoted interest in biochar as a carbon sequestration tool (Lehmann et al., 2006).

Biochar yield (Williams and Besler, 1996), physical (Wildman and Derbyshire, 1991), and chemical properties (Shafidazeh, 1982) depend on the conditions during pyrolysis as well as the composition of the feedstock biomass. Furthermore, different soil constraints require different biochar properties by also recognizing the different crop needs for example of legume or cereal crops (Van Zwieten et al., 2010b). As a result, not all biochars have demonstrated improved crop yield in all instances (Deenik et al., 2010; Gaskin et al., 2010; Van Zwieten et al., 2010a), and there are significant differences in stability between biochars (Spokas, 2010; Zimmerman, 2010). In addition, biochar properties change over time in soil and these changes may also be affected by the initial properties of the biochars (Joseph et al., 2010). Therefore, the differences between biochar properties have to be well understood as a function of production conditions and feedstock type, in order to match soil needs with the appropriate biochar type.

Agricultural application of biochar would benefit from a characterization framework to identify which biochars produce increases in short and long term yields and improvements in soil health for a given crop and soil. From an agronomic standpoint it is important to determine if the biochar causes toxic effects, alters soil physical attributes at a specific application rate, improves nutrient availability and use efficiency, or changes the population and density of microorganisms and fauna. To date biochar characterization has mainly utilized tests developed for the power industry and for soils. For example, the so-called "proximate analysis" according to ASTM D1762-84 determines moisture, volatiles, and ash content of wood charcoal with regard to its use as a fuel. The volatile content may to some extent be informative to understand the stability of the material (Zimmerman, 2010) and effects on N availability

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and plant growth (Deenik et al., 2010). However, for biochars that frequently have high ash contents, the volatilization of metals (Dean, 1999) at the high temperatures used by the ASTM method may pose a significant problem. In addition, the relationship between feedstock or production conditions and biochar properties designed to improve soil properties (Chan and Xu, 2009) and to be recalcitrant against microbial decomposition (Spokas, 2010) is still insufficiently known.

Therefore, the purpose of this study was to examine how feedstock and pyrolysis temperature affect the final composition of the biochar with respect to the most commonly used analytical protocols to evaluate biochar agronomic value and stability properties using a large set of samples.

2. Methods

2.1. Biochar feedstock

The following feedstocks were collected in Wisconsin from local suppliers: bull manure with sawdust (Bull Manure), corn stover (Corn), dairy manure with rice hulls (Dairy Manure), hazelnut shells (Hazelnut), oak wood (Oak), pine wood (Pine), and poultry manure with sawdust (Poultry Manure).

An additional manure biochar series was produced with feedstocks originating from a single source of dairy cow manure subjected to various pretreatments prior to pyrolysis (AA Dairy, Candor, NY). Raw dairy manure biochar (Raw Dairy Manure) did not receive pretreatment. Anaerobically digested dairy manure biochar (Digested Dairy Manure) was derived from dairy manure that had been anaerobically digested, after which the liquid fraction was removed via a screw press. Composted dairy manure biochar (Composted Dairy Manure) was produced by composting the screw pressed solid product of anaerobic digestion in windrows. The composted manure was also mixed in a 1:1 ratio (w/w) with chipped wood waste just prior to pyrolysis to produce composted dairy manure with wood waste biochar (Composted Dairy Manure + Wood).

Grass Clippings, leaves, and brush were collected in Ithaca, NY in the summer, fall, and winter, respectively, and pyrolyzed to produce summer yard waste (Grass Clippings), fall yard waste (Leaves), and winter yard waste (Brush) biochars.

Food waste (Food) was collected from Cornell University dining hall waste, including discards from food preparation (identifiable were fruit and vegetable peels, beans, lettuce, bread, egg shells, etc.), unconsumed prepared foods (identifiable were French fries, chicken bones, meat, olives, fruit residues such as orange peels, bread, and pasta), as well as paper plates and napkins. Approximately 1 week of material from across campus was subsampled from freshly deposited material.

White paper mill sludge was collected to produce paper mill waste biochars (Paper) (Mohawk Fine Papers Inc., Cohoes, NY).

2.2. Biochar production

Biochars were produced from the above feedstocks by Best Energies Inc. using the Daisy Reactor, pyrolyzing the feedstocks in 50 °C increments from 300 to 600 °C (Cashton, WI, USA). All feedstocks were dried at 60 °C to ca. 10% moisture (w/w) prior to pyrolysis. Approximately 3 kg of feedstock were manually placed into a main chamber, which was thoroughly purged with N_2 while the mixer was running. The pre-dried material was pyrolyzed in a uniformly heated chamber for 80–90 min. This time includes both raising the temperature from ambient to target at less than 10 °C per minute, and holding at the target temperature for 15–20 min. After completion of the pyrolysis, the furnace was turned off and the main chamber was allowed to cool before unloading the biochar under N_2 purge to reduce rapid oxidation and auto-ignition (leading to a more homogeneous product).

2.3. Biochar from different producers and literature values

A number of other biochars were utilized to broaden the range of thermochemical production conditions studied. These include updraft carbonized, auger fed intermediate rate pyrolysis, fixed and fluidized bed fast pyrolysis, as well as pressurized flash pyrolysis biochars at varying temperatures. Feedstocks included annual crop residue, soft and hardwoods, nut shells, as well as poultry manure and processing waste used at unknown moisture contents (Supplementary Table S1). In addition, we compared our data to values already published in the literature (Supplementary Table S2).

2.4. Physical and chemical analyses

Unless otherwise noted, air-dry biochars were ground with mortar and pestle and sieved prior to analyses to achieve a particle size range of 149–850 μm. Proximate analysis methods were conducted using ASTM D1762-84 Chemical Analysis of Wood Charcoal after modification to accommodate biochar reactivity. In addition, a low temperature (LT) method was developed to facilitate volatiles determination deemed to be more relevant to biochars (Joseph et al., 2009) (see Supplementary online material for detailed description of the adapted proximate analyses used here). All proximate analyses were performed in duplicate.

For elemental (ultimate) analyses, sieved biochars were ball milled to achieve a homogenous fine powder using a Retsch MM 301 (Retsch GmbH, Haan, Germany). Total C (C_{tot}) and N were determined by Dumas combustion using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Organic C (C_{org}) was derived by pretreating weighed samples in silver capsules in two stages. Initial decomposition of carbonates was achieved by fuming HCl to prevent sputtering and physical loss of sample. Sample tins were held upright in a porcelain spot plate (#60430, CoorsTek, Inc., Golden, CO) placed atop a digestion block preheated to 80 °C and covered with an inverted glass dish. A 25 by 150-mm borosilicate tube (#9825-25, Corning Life Sciences, Corning, NY) was filled with 40 mL of 38% HCl and was placed into the block under the cover. Samples were retrieved the next day after all HCl had vaporized. Carbonate decomposition was completed by dropwise addition of 9.5% (v/v) HCl followed by drying at 80 °C prior to crimping the capsules for analysis. Hydrogen was determined by combustion using a Hekatech HT Oxygen Analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Total O was derived by subtraction according to the ASTM method as follows:

$$O (\%w/w) = 100 - ash (\%w/w) - C (\%w/w) - N (\%w/w) - H (\%w/w)$$

The majority of carbonates in biochar, specifically calcium and potassium carbonates, resist decomposition at 750 °C (Dean, 1999), the temperature prescribed by ASTM for quantification of the ash content. It is therefore assumed that O bound to carbonate is accounted for in the ash content, as per the equation above. Separate correction for carbonate O via inorganic C would therefore count the inorganic O twice. Elemental analyses were done in duplicate.

For the determination of total metals, biochars were weighed to 200.0 ± 5.0 mg and transferred to 25 by 150-mm borosilicate glass tubes. Samples were ashed in a muffle furnace for 8 h at 500 °C (Fisher Isotemp Model 126, Thermo Fisher Scientific, Waltham,

MA). Subsequently, 5.0 mL HNO_3 were added to each vessel and the mixture heated to 120 °C on a digestion block to dryness (Martin Machine Co., Ivesdale, IL). Samples were cooled to ambient before adding 1.0 mL HNO_3 and 4.0 mL 30% H_2O_2, and then heated at 120 °C to incipient dryness. After cooling, 1.43 mL concentrated HNO_3 was added and samples were vortexed to dissolve the ash residue prior to adding 18.57 mL deionized water, thereby achieving the 5% acid concentration required for further elemental analysis. Samples were analyzed using an axially viewed ICP trace analyzer emission spectrometer (model ICAP 61E trace analyzer, Thermo Electron, Waltham, MA). Transfer optics were replaced with a short depth of field transfer optics to reduce matrix effects. Total metal analyses were performed in triplicate.

For measurements of pH values, biochars were weighed to 1.0 ± 0.01 g directly into 60-mL screw-top glass vials. Vials were filled with 20 mL of 1 M KCl prepared with deionized water and then agitated on an orbital shaker table for 1.5 h. The slurry was continually mixed with a stir bar while pH was measured. Analyses were performed in duplicate.

2.5. Statistical analyses

Analysis of variance (ANOVA) was carried out using JMP 9.0 (SAS, Cary, NC). Significant differences were calculated by post hoc tests across all methods for all materials using Tukey's HSD at $P < 0.05$. Methodological precision was evaluated with percent relative standard deviation (%RSD), defined as the following:

$$\%\text{RSD} = \frac{\text{standard deviation}}{\text{average}} \times 100 \qquad (1)$$

3. Results

3.1. Proximate analyses

The low-temperature (LT) adaptation of the proximate analysis tested here for quantification of volatile contents correlated well with the ASTM standard methodology (Supplementary Fig. S1). The volatile matter showed a narrower and lower range using the LT tests (5–50%) than the ASTM tests (15–70%).

The ash content quantified by the ASTM method varied mostly between different feedstock materials (1–60%; $P < 0.0001$) and less between pyrolysis temperatures (less than 10% points within any given feedstock) with typically increasing ($P < 0.0001$) ash content as production temperature increased (Fig. 1). Largest proportions of ash were found in the animal manure (Bull Manure, Poultry Manure, Digested Dairy Manure) and waste biochars (Food, Paper) and the lowest proportions in the woody biochars (Hazelnut, Oak, Pine). When pyrolyzed at 500 °C, Raw Dairy Manure biochar possessed higher ash content (32%) than Digested Dairy Manure, due to dewatering following anaerobic digestion (15%), but lower than Composted Dairy Manure (50%; Supplementary Table S2), presumably due to passive accumulation of mineral elements during decomposition of organic C, O and H. For yard waste biochars produced at 500 °C, Brush biochar possessed the lowest ash content (2%) in comparison to Leaves biochars (14%) or Grass Clippings biochar (25%).

In contrast to ash, volatile matter per unit ash free mass depended less on feedstock ($P = 0.0241$) than on temperature ($P < 0.0001$) (Fig. 1). Biochars made from woody materials (Hazelnut, Oak, Pine) had the largest variation in volatile matter (e.g., 28–61% for Oak), whereas biochars made from animal manures (Bull Manure, Dairy Manure, Poultry Manure, Digested Dairy Manure) and wastes (Food, Paper) demonstrated the smallest variation (e.g., 97–100% for Paper).
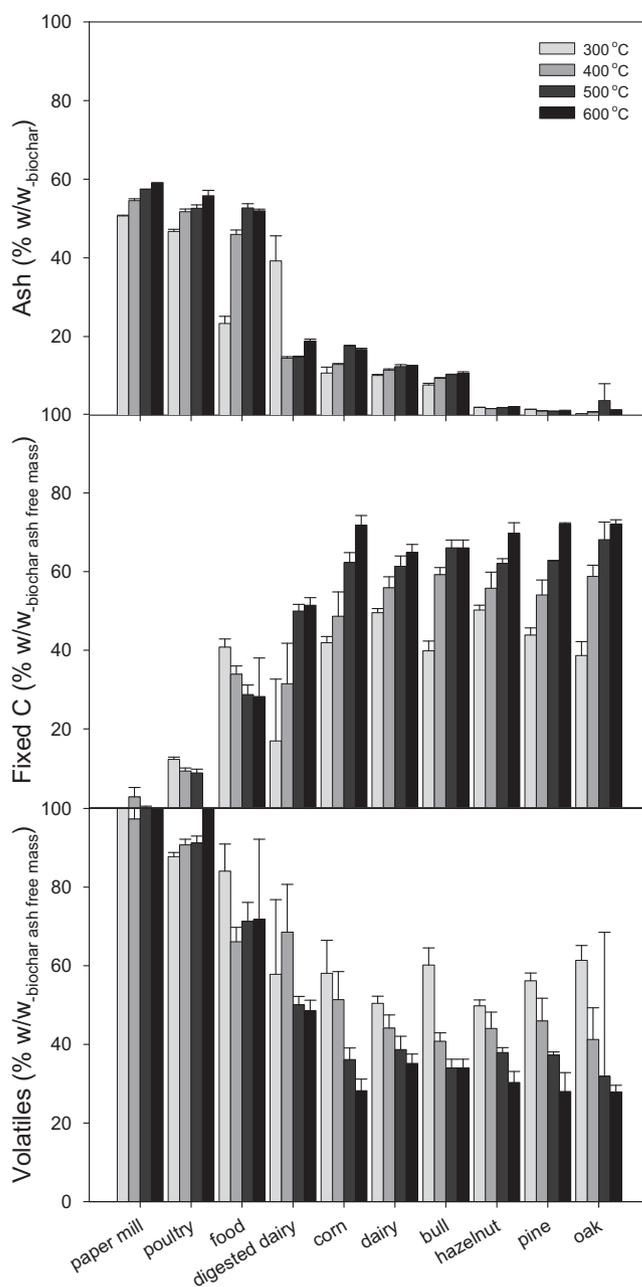

Fig. 1. Ash, volatile and fixed carbon contents (w/w) of biochars generated from different feedstocks at varying temperatures ($n = 2$).

Volatile contents for the full set of biochars (Supplementary Table S1) per unit dry weight ranged from 13% to 70%, with the majority between 20% and 60%. Fast pyrolysis biochars ranged from 28% to 57% volatile matter.

Fixed carbon contents for the full set of biochars ranged (refer to Supplementary Table S1) from 0% to 77% per unit dry weight, and 27% to 63% for the subset of fast pyrolysis biochars. Paper biochars contained less than 1% fixed carbon, and Poultry Manure biochars less than 7%. Fixed carbon content of biochars significantly increased with increasing pyrolysis temperature. Within the set of slow pyrolysis biochars, Pine and Oak pyrolyzed at 600 °C demonstrated the highest fixed carbon contents, both 71%.

3.2. Carbon, oxygen, hydrogen

Total C contents increased while total H and O decreased with increasing temperature during pyrolysis (Supplementary

Table S3). Total C contents of biomass feedstocks (Corn, Hazelnut, Oak, Pine) were similar between 43% and 49%, whereas C contents of biochars derived from those feedstocks varied more widely from 60% to 91%, with greater variation due to pyrolysis temperature (maximum increase by 24%) than due to feedstock (maximum increase by 19%). The correction for inorganic C bound in carbonates decreased C values for the biochars made from high-ash feedstocks such as poultry manure or paper waste by as much as 24%, but had negligible effect of less than 0.7% on biochars made from woody or grass feedstocks. This suggests that a large percentage of the ash in high-ash feedstocks is comprised of carbonates (Supplementary Table S3).

The H:C_{org} molar ratios for most biochars (Bull Manure, Corn, Dairy Manure, Hazelnut, Oak, Pine) are reliably 2.5 times the O:C_{org} molar ratios ($r^2 = 0.9024$), with the exception of high-ash Poultry Manure and Paper biochars (Fig. 2a). Both the O:C_{org} and H:C_{org} molar ratios are highly correlated with volatile contents per unit ash free mass, again with the exception of Poultry Manure and Paper biochars (Fig. 2b). Correlation between volatile contents per unit ash free mass and H:C for these high-ash biochars showed negligible improvement (r^2 from 0.1362 to 0.1416) when correction for carbonate-C was applied. The analogous correlation to

O:C even decreased slightly (r^2 from 0.1720 to 0.1621) when correction for carbonate-C was applied.

3.3. Mass and elemental recovery

The average mass recovery of biochars produced at 600 °C (Bull Manure, Corn, Dairy Manure, Hazelnut, Oak, Pine, Poultry Manure, Food, Paper) converged at 23%, if the ash content of the biochars lay below 50% (Fig. 3). Poultry Manure and Paper feedstocks showed mass yields of more than 50% at 600 °C. The average total C recovery for the same set of biochars was 45%, decreasing on average only slightly to 43% if expressed as organic C (Fig. 3). With increasing pyrolysis temperature, the fixed carbon content changed differently depending on feedstock type and particularly its ash content. Generally, fixed carbon content of biochar relative to fixed carbon content of feedstock increased with increasing pyrolysis temperature, by over 500% in several instances. However, this effect diminished with increasing ash content to the point of complete disappearance of fixed carbon in the case of Poultry Manure. Furthermore, these variations in fixed carbon recovery were much greater than for total or organic C. Nitrogen recovery (Fig. 3) varied
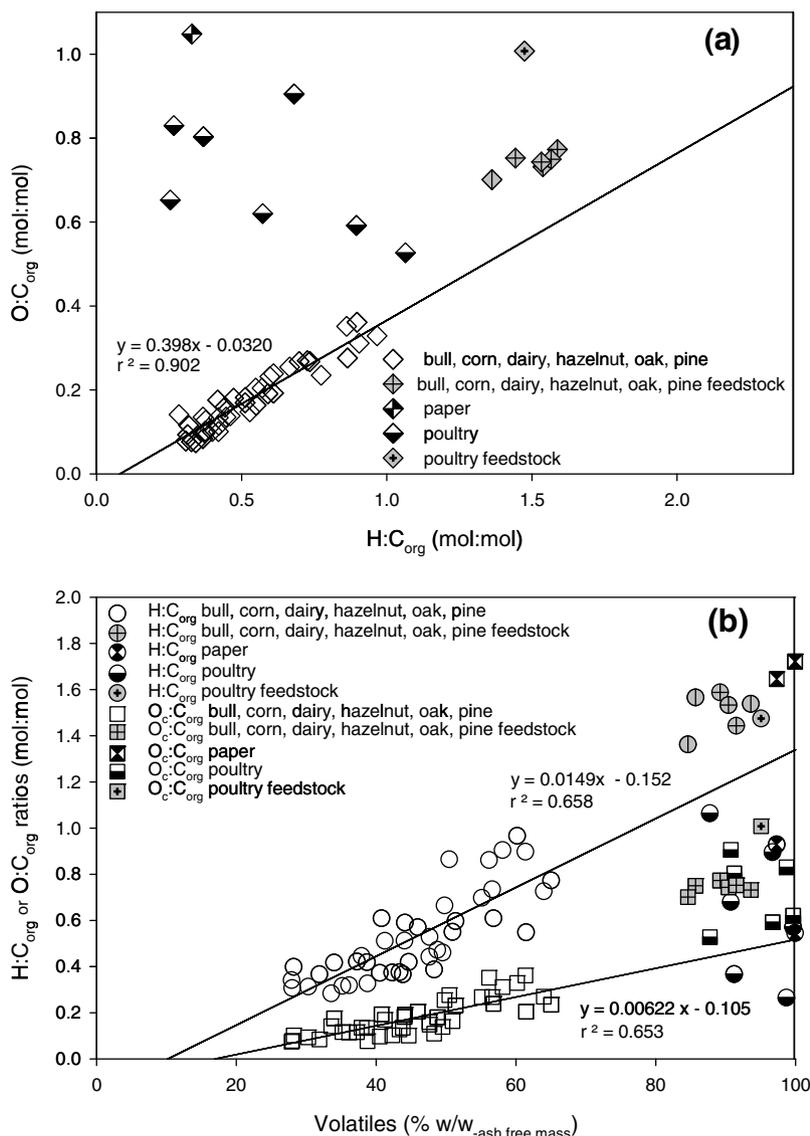
Fig. 2. Relationship between O:C_{org} and H:C_{org} (a) and to volatile matter (b) for different biochars and their feedstocks ($n = 2$).
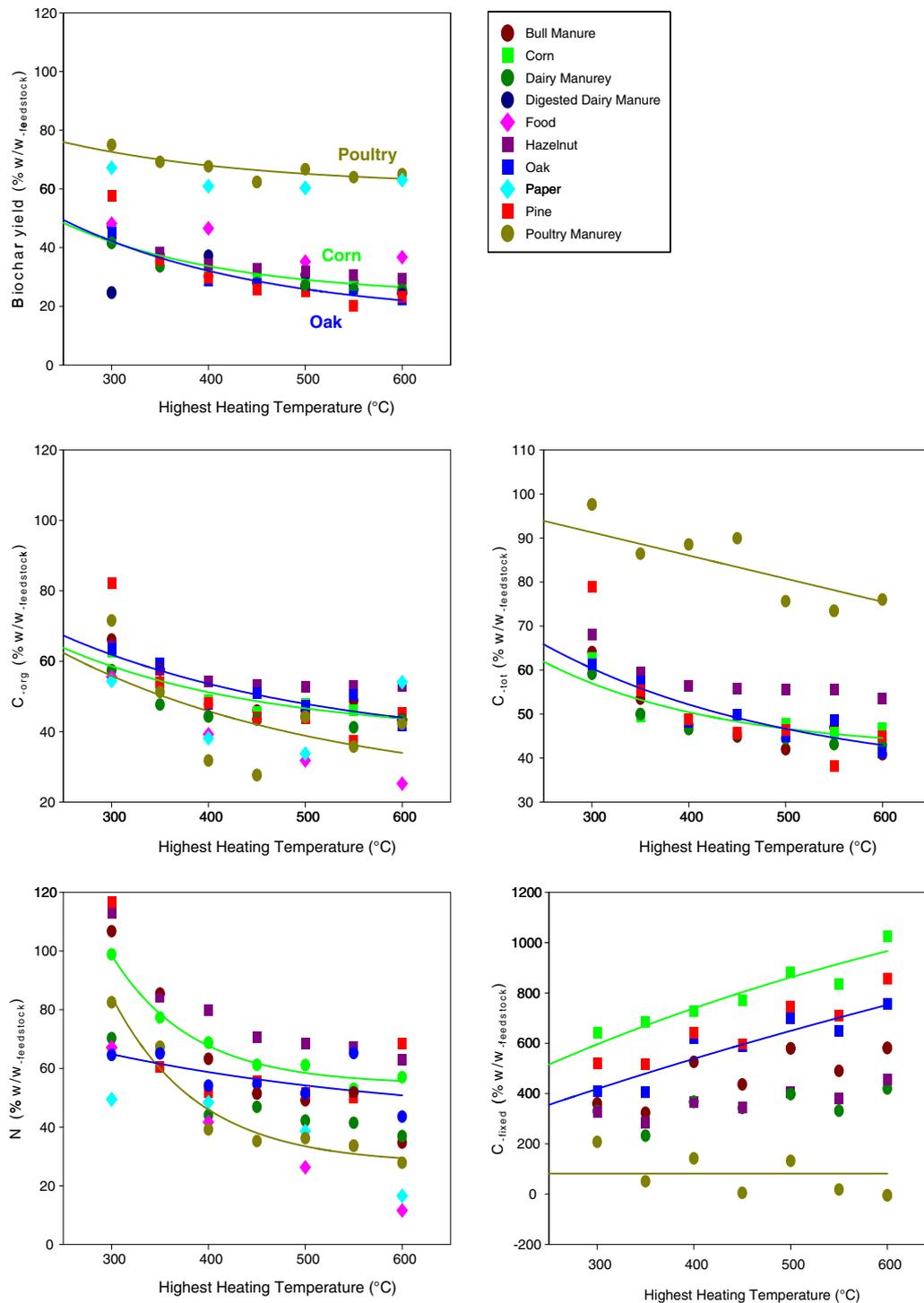
Fig. 3. Recovery of mass, total and organic C, total N and fixed carbon per unit weight of the same parameter in the feedstock with increasing pyrolysis temperature using slow pyrolysis (*n* = 2 for elemental contents, *n* = 1 for mass; regressions with two-parameter exponential equations to improve clarity; regressions through feedstock except for N).

to a greater extent (12–68%) than organic (25–45%) or total C (41–76%) at 600 °C.

The total P, N, Ca, Mg, K and Na concentrations of biochars varied greatly and mainly depended on feedstock elemental contents (Supplementary Table S4). Pyrolysis temperature also influenced total nutrient contents, but to a much smaller extent. The N changes were the most complex (similar for S) with Hazelnut and Pine feedstock showing enrichment when heated to 300 °C, whereas a few feedstocks showed little change or even a decrease as for Paper (Fig. 3). Upon further heating from 300 to 600 °C, Oak

and Pine biochars showed N enrichment, whereas Poultry Manure biochars showed volatilization (Fig. 4). All other nutrients and Na were enriched with increasing pyrolysis temperature, more for Corn, Hazelnut, Oak, and Pine than for those made from manures and waste feedstocks (Bull Manure, Dairy Manure, Poultry Manure, Food, Paper). The exception is P in pine, which showed large error due to low absolute concentrations. Only the N and K recovery at 600 °C is well correlated with the concentration of that nutrient in the feedstock (Supplementary Fig. S2), but not those of other nutrients in this study.
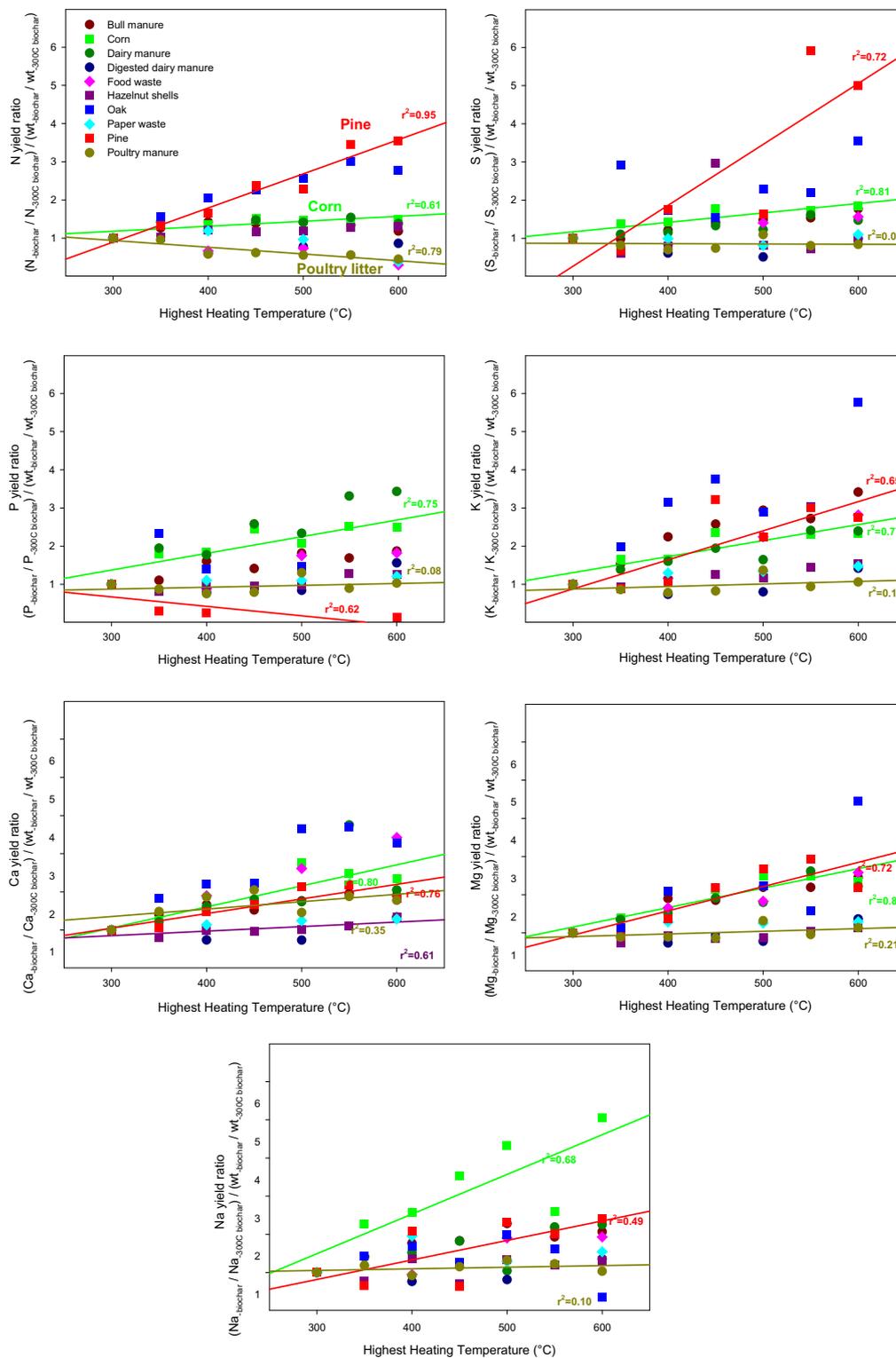
Fig. 4. Enrichment of N, S, P, K, Ca, Mg, and Na in biochars with increasing pyrolysis temperature in comparison to 300 °C ($n = 3$; linear correlations including 300 °C).

3.4. pH values

Biochar pH values ranged from 4.48 for Oak at 300 °C to 11.62 for Paper at 600 °C (Fig. 5a; Supplementary Table S5). All biochars with less than 8% ash were below pH 8.6, and pH values below 7.5 were only observed for biochars made from woody biomass that had an ash content of less than 1.5% (Hazelnut, Oak, Pine) (Fig. 5a). Conversely, all biochars made from animal manures (Bull Manure, Dairy Manure, Poultry Manure, Raw Dairy Manure, Di-

gested Dairy Manure, Composted Dairy Manure, Composted Dairy Manure), annual crop residues (Corn, Grass Clippings, Leaves) or waste (Food, Paper) had pH values above 7.5. All biochars with pH values above 10 had more than 32% ash. Biochar pH correlated well with the natural log of both ASTM ash content ($r^2 = 0.645$; $n = 53$; $P < 0.0001$) and the sum of K, Ca, Mg, and Na ($r^2 = 0.613$; $n = 53$; $P < 0.0001$). However, individual concentration of P, S, K, Ca, Mg, Na, Mn, and Zn had no discernable effect on pH for the set of biochars studied here (data not shown). Increasing the pyro-
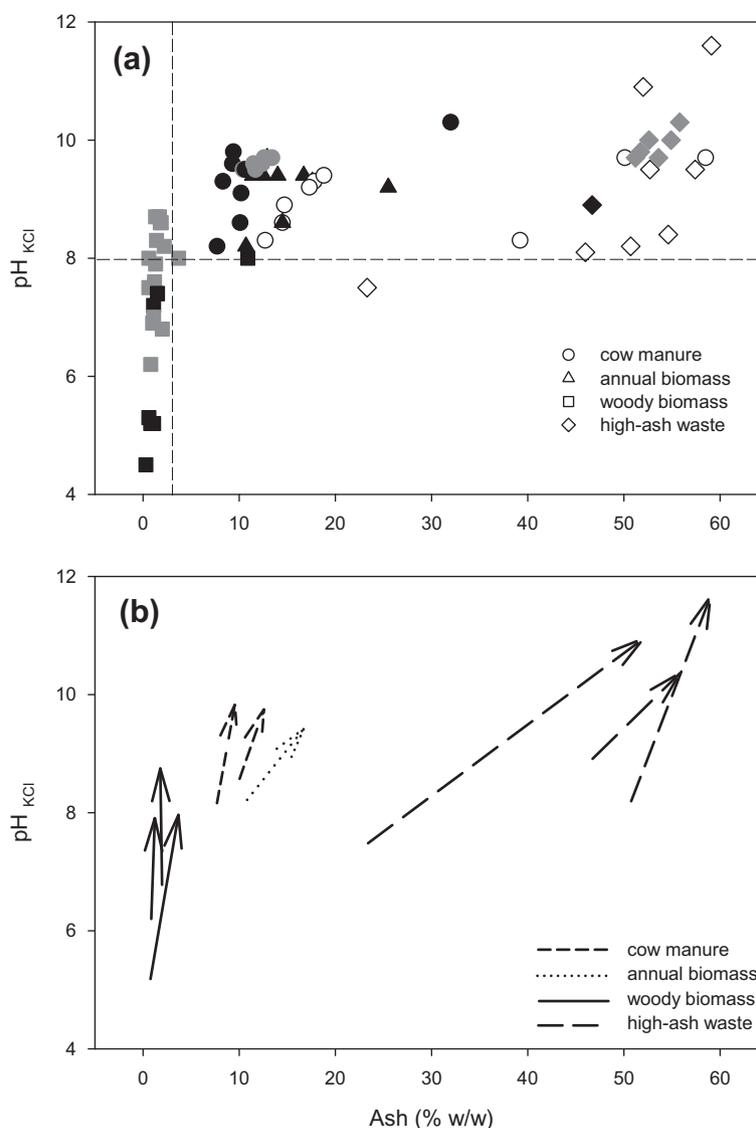
Fig. 5. Relationship between ash content and pH values (black symbols indicate CEC greater and gray symbols those lower than the median value of 265 mmol kg^{-1}; no CEC data available for biochars shown with open symbols) (a), and the effect of increasing pyrolysis temperature (b) ($n = 2$; arrows connect biochars of the same feedstock pyrolyzed at 300 and 600 °C).

lysis temperature had the greatest effect on proton activity for the low-ash biochars made from woody biomass which increased from pH 4–5 to pH 7–9 without significant increases in ash content (Fig. 5b), likely due to decreases in acid functional groups with greater pyrolysis temperature as indicated by the higher CEC (indicative of carboxyl groups) of low-pH woody biochars (Fig. 5a). In contrast, high-ash biochars made from wastes showed pH increases with a concomitant increase in ash contents. Biochars made from annual crop residues demonstrated lower increases in pH values than those made from wastes.

4. Discussion

4.1. Methodological limitations of proximate analysis

Ashing as per ASTM D1762-84 requires high temperatures for an extended period of time. This is beneficial to ensure the complete decomposition of recalcitrant pyrolytic materials. However, certain elements are known to volatilize at temperatures as low as 500 °C, notably P, K, and S (Ali et al., 1988) or a fraction of carbonates (Dean,

1999) that are present in high amounts in animal manures and annual crop residues (Supplementary Table S4). It is therefore likely that ashing at 750 °C for 6 h underestimates the ash content of biochars by volatilizing certain elements, with resulting increases in calculated values for fixed carbon as well as oxygen.

The high (950 °C) temperatures required by ASTM for determination of volatiles was also problematic for replicability. Furnace reheating after sample introduction was impacted by heat loss resulting from opening the furnace door and the thermal mass introduced by the crucibles. It is likely that reheating rates will vary between different furnaces and with different thermal masses. Anoxic conditions were not maintained by the crucible covers, as traces of white ash were visible on the surface of a number of samples. It is possible this occurred during the time necessary to cool the samples after they were removed from the furnace. Furthermore, heating, especially radiative heating, of the crucibles would vary according to placement within a batch. Nonetheless, the ASTM volatiles correlated well with the O:C$_{org}$ and H:C$_{org}$ ratios and decreased systematically with greater production temperature for the biochars made from woody biomass and annual crop residues, indicating that for low-ash biochars the ASTM

volatile matter may be a reflection of a meaningful material property relevant to soil biogeochemical cycles. However, biochars made from biomass that are rich in ash were not well characterized by the ASTM volatile method as seen from the lack of difference with increasing production temperature and lack of correlation with $O:C_{org}$ and $H:C_{org}$ ratios.

The LT methods (Joseph et al., 2009) were devised to enhance replicability between laboratories by standardizing heating rates during volatiles determination. Unfortunately, the LT volatile method demonstrated a higher variability between replicates than the ASTM volatiles method. Average %RSD across all biochars for the LT method was 12.9%, compared to 6.3% for ASTM. Additionally, pyrolytic decomposition of lignin continues up to 497 °C under the heating rates employed during slow pyrolysis (Demirbaş and Arin, 2002; Supplementary Table S6), therefore some portion of lignin may persist following the LT volatile method which includes heating to 350 °C. Indeed the difference between LT and ASTM volatiles values was greater for materials that were high in lignin than those rich in cellulose as suggested by the curvilinear regression between the two methods ($r^2 = 0.671$).

4.2. Thermal properties of biochars

The high volatiles content of Oak biochar produced at 300 °C and large difference compared with that at 600 °C is explained by the recalcitrance of lignin that resists pyrolytic decomposition at 300 °C, but not 950 °C used for quantifying volatiles with the ASTM test (Demirbaş and Arin, 2002). The low volatiles content of biochar made from corn stover at 600 °C is likely due to complete decomposition of the predominantly cellulosic feedstock at lower temperatures coupled with a relatively longer period of devolatilization during pyrolysis (Antal and Grønli, 2003).

The combination of ash, fixed carbon and volatile matter can be mapped on a triangle using a compilation of data from this study (Fig. 6a) and the literature (Fig. 6c). Areas of the triangle remain unpopulated despite the large number of biochars included. Specifically, fixed carbon contents of biochars with greater than 35% ash were limited to below 30%. In addition, fixed carbon contents increased with increasing pyrolysis temperatures when they contained less than 20% ash, but decreased for biochars above 20% ash (Fig. 6b). This likely results from interactions between organic and inorganic feedstock constituents during pyrolysis. Ash contents per unit dry mass also correlated well with contents of volatile matter per unit ash free mass ($r^2 = 0.675$; $n = 110$ analyzed in our study including those made by varying producers from Supplementary Table S1), while maintaining mathematical independence. Nearly all of the organic matter in Poultry Manure and Paper biochars was volatile according to proximate analysis. Furthermore, the Poultry Manure biochars were found to possess high levels of K, Ca, Mg, and Na, and the paper waste biochars very high levels of Ca. It has been documented that inorganic constituents of biomass have a strong influence on pyrolysis and gasification chemistry (Fahmi et al., 2007; Raveendran et al., 1995; Shafidazeh, 1982). Mineral matter generally increases biochar yield from cellulosic feedstocks, however K and Zn decrease biochar yield from lignocellulosic feedstocks (Raveendran et al., 1995). Alkali carbonates are but a subset of the inorganic compounds documented as gasification catalysts in steam environments (Takarada et al., 1986). Alkalis are also used as activating agents in the production of activated carbon (Adinata et al., 2007).

4.3. Elemental recovery in biochar

An improvement of the correlation between volatile values and H:C or O:C values through correction for carbonates was expected for the biochars made from poultry litter and paper waste as they may contain large proportions of C and O that are not in organic form. The failure to align those O:C ratios with the global correlation shown for low-ash biochars (Fig. 2) is likely due to inflated O values resulting from volatilization of inorganic species during ash determination (Supplementary Table S7). This may possibly be avoided by utilizing an O-rich environment to decompose biochars at temperatures below 550 °C. In contrast, calcium and potassium carbonates resist decomposition at these temperatures (Dean, 1999; Supplementary Table S7). Decomposition or loss of ash species also inflates fixed carbon values as they are derived by subtraction. These results question the universal applicability of the proximate analysis (including fixed carbon and volatiles) designed to estimate the fuel quality of wood charcoals that are typically low in ash, to biochars that may have often high ash contents.

The wide variation in N and S recovery can be explained by the fact that both elements can be volatilized in gaseous form even at low temperature (Supplementary Table S7), whereas the other elements can only be driven off in particulate form or at high temperatures. Despite the existence of gaseous N and S species, N and S were also greatly retained in biochars made from woody feedstocks, likely due to the formation of heterocyclic N such as pyridones or pyrrols (Yu et al., 2007) and biochar-complexed S resulting from devolatilization of inorganic S species (Knudsen et al., 2004). The high-N-containing feedstocks such as poultry manure lose N to a greater extent than C, possibly due to the negligible formation of aromatic C forms as shown by the lack of fixed carbon at high pyrolysis temperatures. The relatively large retention of metals such as Na in corn biochar despite similar or greater concentrations may be related to the Si structure frequently found in grass biochars (Wornat et al., 1995) (see Supplementary online material for elemental composition).

4.4. Biochar properties and stability

The volatile content was hypothesized to be a proxy for stability and indeed was shown for certain data sets to correlate with decomposition rates (Zimmerman, 2010). Conceptually, the volatile fraction does not equate to a labile component in identical proportions, as biochars with about 40% volatile matter showed a calculated decomposition over 100 years of less than 10% (Zimmerman, 2010). O:C ratios were better correlated with stability than volatiles (Spokas, 2010). However, also the O:C ratios do not distinguish well between the rapid decomposition of high-ash biochars such as those produced from poultry manure compared to woody biochars (Spokas, 2010), even when the O:C ratios are corrected for carbonates (Whitman, unpublished data). The $H:C_{org}$ ratio distinguishes better between the different temperatures at which high-ash feedstocks such as poultry manure or paper waste are pyrolyzed, and are less prone to errors as H is directly analyzed whereas O is in most cases calculated by difference as done in our study. However, even the $H:C_{org}$ ratio ranks Poultry Manure and Paper biochars produced above 500 °C similar to woody biochars that were found to be much more stable (Whitman, 2011). Only the analysis of volatile matter separates these high-ash biochars characterized by rapid decomposition from crop residue and woody biochars (Fig. 2b). Therefore, we propose to use a combination of volatile matter, and $O:C_{org}$ or $H:C_{org}$ ratios to classify the stability of biochars (expanding the concept by Spokas (2010)), until a better method is available. A volatile matter above 80% (w/$w_{biochar\ ash-free\ mass}$) may indicate biochars with no C sequestration value; a volatile matter below 80% (w/$w_{biochar\ ash-free\ mass}$) and an $O:C_{org}$ ratio above 0.2 (Spokas, 2010) or $H:C_{org}$ above 0.4 may indicate moderate sequestration ability; and a volatile matter below 80% (w/$w_{biochar\ ash-free\ mass}$) and an $O:C_{org}$ ratio below 0.2 or $H:C_{org}$ below 0.4 may indicate high C sequestration potential. Further refinements in classifying biochar stability may be achieved by using
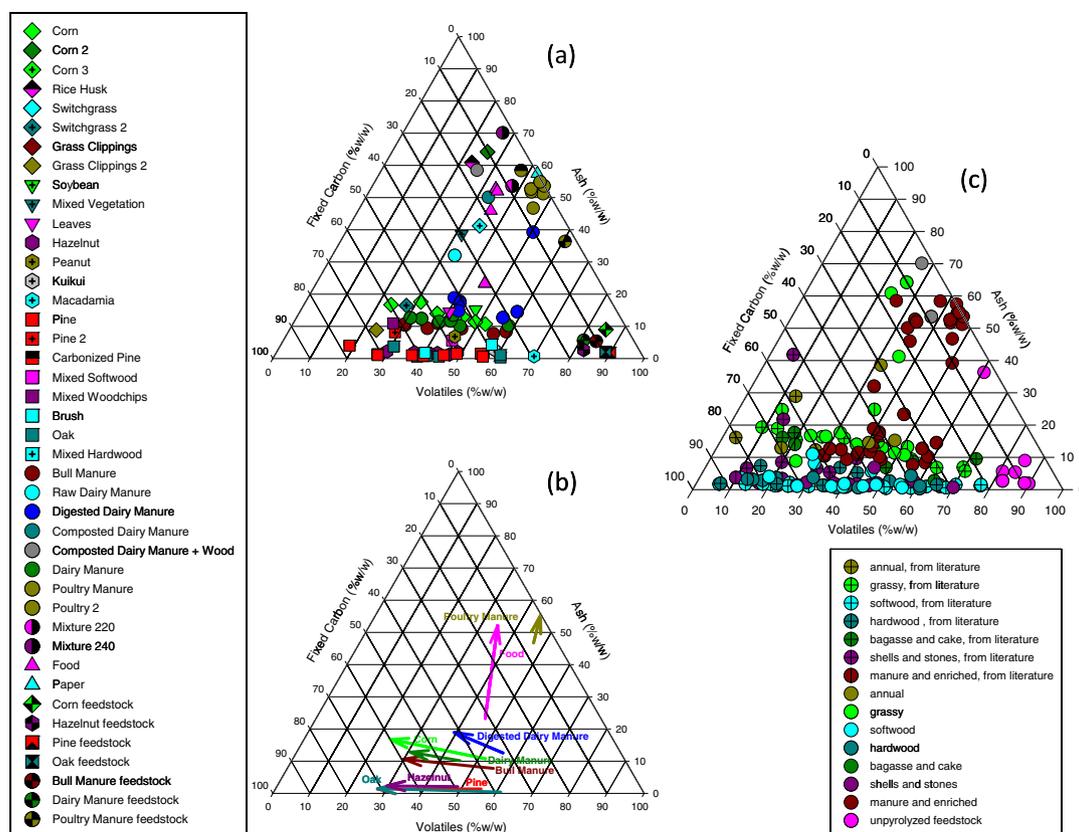
Fig. 6. Triangle plots of ash, volatile matter and fixed carbon contents (a) (sources listed in Supplementary Table S1); the effect of pyrolysis temperature (b) (n = 2; arrows connect biochars of the same feedstock pyrolyzed at 300 and 600 °C); and a comparison between data from this study to literature data (c). Literature values listed in Supplementary Table S2.

Fourier transform infrared transmission spectroscopy (Whitman, 2011) capitalizing on the ability to combine aspects of bond quality between C and O that are not apparent through the molar ratio of the amount and nature of mineral admixture.

The amount of stable biochar in a biochar system is not only a material property but also depends on the conversion efficiency during pyrolysis, similar to total C. Fixed carbon content in biochar relative to that in feedstock increased with rising pyrolysis temperature for those feedstocks that generated the highest fixed carbon concentrations such as woody biomass (Fig. 3). Furthermore, the fixed carbon content of biochar consistently increased with increasing pyrolysis temperature for low ash feedstocks, but decreased for high ash feedstocks (Fig. 1). The reason may be that high ash contents hinder formation of aromatic C forms, supported by the negative correlation between fixed carbon yield and ash contents of biochars produced between 300 and 600 °C (r^2 = −0.749; n = 70; P < 0.0001). However, when expressed per unit mass of feedstock, there is little difference in the amount of fixed carbon generated by pyrolysis at 300 versus 600 °C for each feedstock. The exception is Pine, which when pyrolyzed at 300 °C converts 24% of feedstock mass into fixed carbon, but only 16% at 400 °C.

4.5. Biochar properties and agronomic effects

The evaluation and quantification of biochar properties conducive to improving crop productivity is more difficult to evaluate than those for characterizing stability in biochars. The reason is that different soil constraints may require different biochar properties as seen for different soil pH (Van Zwieten et al., 2010a). The pH can vary widely and is a function of both the ash content as well as

the pyrolysis temperature (Fig. 4) and therefore offers ample opportunity to tailor biochars to specific soil pH constraints.

In addition, biochars have combinations of properties that escape simple classification even for choosing the appropriate biochar for a single soil. Therefore, mapping plant growth of corn from a short-term greenhouse experiment (data from Rajkovich et al., 2012) onto the parameter space that volatile matter, fixed carbon and ash capture, does not identify unique properties that allow us to distinguish biochars that increase or decrease growth (Supplementary Fig. S3). Even on the studied fertile Alfisol, corn growth significantly increased with greater P, K, and Mg contents in the biochar, but decreased with Na contents especially at high application rates of 7% by weight (Rajkovich et al., 2012). Therefore, in this particular case, mineral contents of biochar played an important role for agronomic responses even on a fertile soil. In addition responses of different crops with the same soil–biochar combination may differ (Van Zwieten et al., 2010a). Therefore, the most effective approach to predicting agronomic performance of biochars is to first define the predominant limiting factors of a particular soil–crop-climate situation and apply biochars likely to address growth constraints according to a library of characterization data. Such a library would include but is not limited to pH (or liming equivalence and buffering capacity not examined here) and element contents.

However, some properties of biochars may be positive or negative in all soils. For example, greater biochar stability is not only useful from a climate mitigation point of view, but also for maintaining possible positive agronomic effects over longer periods of time. On the other hand, phytotoxicity of certain elements such as Na is likely detrimental across different soils and crops. Universal growth-stimulating properties of biochars have not been identified in our study.

5. Conclusions

Biochars have widely varying properties that escape characterization using simple parameters such as those provided by proximate analysis. Thermal degradation does, however, remain a useful tool to quickly approximate biochar stability. Standardizable thermogravimetric analyses could add much needed replicability to quantification of biochar thermal devolatilization. Elemental contents are currently the most accessible approach for evaluating recalcitrance and together with pH also plant responses. A combination of methods may be needed as even elemental contents such as $H:C_{org}$ are not sufficient on their own to predict behavior of biochars in soils. Future characterization efforts should combine information of elemental contents and functional group chemistry.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2012.03.022.

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