SUPPORTING INFORMATION

Differentiating Inorganics in Biochars Produced at Commercial Scale Using Principal Component Analysis

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1. Acid neutralization potential

The neutralization potential (NP) equation was developed for wood ash to estimate potential contribution to alkalinity based on total Ca, Mg, and K concentrations (MDDEFP, 2012). The NP of an amendment estimates its ability to consume acid. For biochars produced from similar feedstock, using similar pyrolysis conditions at two different temperatures, those produced at lower temperatures were more acidic. Airex 1 and BassWd 400, which were pyrolyzed at lower temperatures, had slightly acidic pH, lower NP, and significantly more volatile matter compared to Airex 2 and BassWd 450 (Tables 3 and S1, Figure 2). The NP of Willow, SGrass, and Poultry litter biochars pyrolyzed at 450 °C was also lower than those pyrolyzed at 500 °C (Table S1). This trend was similar to those reported by Singh et al. (2010) who estimated CaCO$_3$ equivalents using a titration method, and found that the majority of biochars produced at 400 °C were more acidic than those produced at 550 °C.

Poultry litter had the highest NP, followed by WdAsh and Willow biochars (Table S1). Identification of sylvite by X-ray diffraction (XRD), and the relative intensities of K and Cl in the Poultry litter 450 energy dispersive X-ray (EDX) spectra indicate that KCl was the dominant K-containing mineral in Poultry litter biochars (Figures 5, 7g). KCl is not expected to consume protons, unlike carbonate and silicate minerals (Blowes et al., 2014), and the acid neutralizing potential of Poultry litter biochars may have been over-estimated. Still, Poultry litter, Willow biochars, and WdAsh A had the highest total inorganic C values (Table 3), and likely contain higher carbonate concentrations than the other samples. The high NP of Poultry litter biochars is also consistent with greater CaCO$_3$ equivalents in manure- compared to wood-derived biochars that were determined using titration methods (Singh et al., 2010). Signals attributed to Ca-oxalate (whewellite) were identified in Willow 450, whereas Ca-carbonate was more common in
the other biochars and WdAsh (Figure 5). The pKa of oxalate are 1.27 and 4.28, whereas those of carbonate are 6.4, and 10.3 (Goldberg et al., 2002). Despite similar NPs of Willow 450 and WdAsh B (Table S1), differences in the type of Ca-containing minerals may translate to differences in buffering and acid neutralizing behaviour and NP may not sufficiently reflect the buffering behaviour of biochars and WdAsh. Site properties must also be considered when estimating the ability of amendments to change the pH of a site. Experiments that applied 1–30 wt.% biochar and wood ash showed that the extent of pH change also depended on the type of receiving material at the site (Beauchemin et al., 2015; Fellet et al., 2011; Kelly et al., 2014; Ohno and Erich, 1990). The pH of a site is influenced by organic matter concentration and composition, biological activity, as well as the types and particle size of minerals, and these properties may also limit the efficacy of amendments to change the site pH (Fellet et al., 2011; Ohno and Erich, 1990).

2. Elements of Interest

Selected elements, which at high concentrations may result in adverse environmental effects, and their threshold values in soil amendments as defined by the International Biochar Initiative (IBI), European Biochar Certificate (EBC), and 2 Canadian provinces are listed in Table S2. For all samples, concentrations for Co were <41 mg kg\(^{-1}\), which is below the lower limit set by the IBI, Ontario, and Quebec and are not shown (IBI, 2013; MOE/OMAFRA, 1996; MDDEFP, 2012). From Table S2, SGrass and Poultry litter biochars exceeded the maximum allowable Mo concentrations of 20 mg kg\(^{-1}\) set by the IBI and Quebec. In addition, SGrass had high Fe, Cr, and Ni concentrations, with a 200-fold increase in Fe compared to its feedstock (Tables 2 and S1, Figure 1). Magnetic Fe-oxide, with XRD diffraction patterns similar to
magnetite, were observed in BassWd, SGrass, and Poultry litter biochars (Figure 5). As well, SEM-EDX analysis of these biochars revealed discrete particles with intense Fe signals (Figures 7c, f, g). The parent material of these biochars, along with Willow were pyrolyzed using steel pellets as heat carriers. Abrasion of steel pellets during pyrolysis likely provided additional Fe, Cr, Mo, and Ni (that reacted and were transformed during pyrolysis) to BassWd, SGrass, Poultry litter, and to a lesser extent Willow. A previous study reported unusually high enrichment of Cr, Fe, and Ni (82.8%, 207.2%, and 226.0% respectively) in biochars, and eroded steel has been considered a possible source of contamination during biochar production (Buss et al., 2016; EBC, 2015). In this study, abrasion of the pellets may have been exacerbated by the higher Si content of SGrass (Figure 3). WdAsh A exceeded the maximum allowable As concentration of 41 mg kg\(^{-1}\) in Quebec (Table S2). Yet, these concentrations are within the 6–62 mg kg\(^{-1}\) range reported for bottom ash residues from incinerated household, wood, fuel, and industrial waste (Saqib and Bäckström, 2016).

The guidelines set by the EBC, IBI, and various jurisdictions encompass the application of amendments such as biochars and WdAsh in agriculture, forestry, horticulture, and urban development (EBC, 2015; IBI, 2013; MOE/OMAFRA, 1996; MDDEFP, 2012). However, there is also interest in using these materials in contaminated sites that may already contain elements (e.g. As, Cd, Cu, Ni, Pb, Zn) at levels that exceed the recommended threshold values (Beauchemin et al., 2015; Kelly et al., 2014). In these cases, application rates of biochar and WdAsh may be indirectly governed by other regulations, such as environmental regulations for metal discharges at mine sites that may restrict the input rate of amendments (MMER, 2015).
3. Loadings Plots

The loadings plots generated after PCA of chemical, XRD, and EDX data are displayed in Figures S1, S2, and S3. R v.3.1.1 with the hyperSpec package was used to process the data (R core team, 2014; Baleites and Sergo 2015). Along with vectors plotted in Figures 4, 6, and 8, the loadings plot illustrate the relationship between the calculated principal components (PC) and measured variables. Variables below the horizontal are negatively correlated, and those above are positively correlated to the PC. The vectors correspond to the loadings plot. For example, the loadings plot for the EDX spectra shows that Ca was highly negatively correlated to PC1 and slightly negatively correlated to PC2. Similarly, the corresponding vectors plot in Figure 8a shows that Ca plots more negatively along the x (PC1) compared to the y (PC2) axis.

4. Individual scores plot for PCA of EDX

Figure S4 displays scores plots for the 11 materials analyzed by SEM-EDX individually to better visualize the data distribution. R v.3.1.1 with the hyperSpec package were used to process the data (R core team, 2014; Baleites and Sergo 2015). The same data points are also displayed in Figure 8. Particles containing [Al, Si] were not observed in BassWd 400 (Figure S4g), but were found in the BassWd 450 scores plot (Figure S4i). Otherwise, biochars produced from similar feedstock (Airex 1 and Airex 2, Willow 450 and Willow 500) produced similar data distributions. The aluminosilicate particles in BassWd 450, not observed in BassWd 400 may help explain the greater discrepancy in pH between the two materials compared to other feedstock pyrolyzed with a difference of 50 °C. Additional experiments are needed to validate this hypothesis.
Tables and Figures
Table S1. Seven of the main elements detected after digestion with *aqua regia*, total organic carbon (OC)/N ratio of biochars and WdAsh. Neutralization potential (NP) was estimated using the following equation developed for WdAsh (MDDEFP, 2012): NP (% CaCO\(_3\) equivalent) = (% Ca x 2.5) + (% Mg x 4.17) + (% K x 1.2). Standard error (S.E.) of duplicates are shown.

|                | Al  | Ca    | Fe  | Mg  | Na  | S    | Si   | Total OC/N | OC/N | NP     | % dry weight (S.E.) |
|----------------|-----|-------|-----|-----|-----|------|------|-------------|------|--------|---------------------|
|                | mg kg\(^{-1}\) dry weight (S.E.) |       |      |     |     |      |      |             |      |        |                     |
| Airex 1        | 64.2 (11.0) | 1878.2 (125.2) | 520.7 (17.7) | 327.1 (5.7) | 88.2 (5.7) | <620 | <300 | 300 | 0.7 (0.0) |                     |
| Airex 2        | 40.7 (24.3) | 2983.2 (486.6) | 84.1 (7.9) | 277.7 (96.8) | 36.5 (0.5) | <620 | <300 | 362 | 1.0 (0.2) |                     |
| Pyrovac        | 705.5 (18.8) | 19022.7 (1776.9) | 2372.6 (606.2) | 774.5 (79.4) | 205.4 (6.8) | <620 | 1103 (109) | 118 | 5.4 (0.5) |                     |
| BassWd 400     | 81.0 (4.2) | 8246.5 (166.2) | 12722.9 (51.9) | 889.0 (9.4) | 76.9 (1.0) | <620 | <300 | 165 | 2.9 (0.0) |                     |
| BassWd 450     | 69.6 (1.0) | 10291.5 (93.5) | 7544.7 (264.8) | 1121.6 (10.4) | 72.7 (1.0) | <620 | <300 | 144 | 3.6 (0.0) |                     |
| Willow 450     | 338.4 (49.7) | 53725.4 (1692.1) | 2432.5 (116.3) | 1263.8 (47.6) | 153.9 (47.1) | <620 | 642 (103) | 91 | 15.2 (0.4) |                     |
| Willow 500     | 446.2 (19.6) | 61643.8 (1369.9) | 4088.5 (168.6) | 1480.5 (36.9) | 123.8 (12.1) | <620 | 888 (61) | 88 | 17.4 (0.4) |                     |
| BasquesC       | 2269.6 (746.2) | 32592.4 (6891.6) | 2725.5 (766.9) | 2932.8 (756.5) | 146.1 (31.1) | <620 | 3140 (1492) | 77 | 10.4 (2.3) |                     |
| BasquesF       | 3118.6 (320.1) | 37691.0 (309.8) | 5049.6 (134.2) | 3727.8 (62.0) | 171.9 (17.0) | 668 | 2928 (449) | 75 | 12.1 (0.1) |                     |
| SGrass 450     | 1567.2 (68.6) | 17044.0 (158.3) | 63057.4 (52.8) | 4126.4 (52.8) | 445.9 (17.4) | 890 | 5562 (21) | 99 | 6.6 (0.0) |                     |
| SGrass 500     | 1687.0 (42.4) | 17718.8 (212.2) | 65305.0 (159.2) | 4880.6 (53.0) | 702.4 (30.8) | 915 | 6796 (38) | 90 | 7.3 (0.1) |                     |
| Poultry litter 450 | 1051.7 (6.4) | 66127.1 (1481.3) | 14971.2 (899.3) | 18727.2 (317.4) | 13225.4 (211.6) | 10136 (106) | 1534 (11) | 24 | 32.3 (0.6) |                     |
| Poultry litter 500 | 1110.4 (21.2) | 79790.6 (370.1) | 21626.5 (1110.4) | 18982.7 (52.9) | 13166.2 (52.9) | 10470 (63) | 1851 (42) | 21 | 35.8 (0.0) |                     |
| WdAsh A        | 4817.9 (781.4) | 74209.5 (2587.5) | 4010.6 (543.4) | 5956.4 (439.9) | 4905.9 (82.8) | 1584 | 5092 (21) | 54 | 22.5 (0.8) |                     |
| WdAsh B        | 7318.8 (451.8) | 49589.0 (1328.8) | 7286.9 (366.7) | 6994.5 (127.6) | 2976.4 (85.0) | <620 | 5942 (74) | 74 | 16.3 (0.3) |                     |
Table S2. Concentrations of selected elements with the standard error of duplicates (S.E.), and threshold concentrations defined by 2 Canadian provinces – Ontario (ON) and Quebec (QC), the International Biochar Initiative (IBI), and European Biochar Certificate (EBC).

|                | As  | Cd  | Cr  | Cu  | Mo  | Ni  | Pb  | Se  | Zn  |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                | mg kg\(^{-1}\) dry weight (S.E.) |     |     |     |     |     |     |     |     |
| Airex 1        | <1.0 | <1.0 | <17 | >4.2 | <1.1 | 1.4 | 2.5 | <1.0 | 62.1 |
| Airex 2        | 0.2 (0.1) | <0.1 | <17 | 2.1 (0.0) | 0.1 (*) | <0.1 (0.1) | 2.5 (0.8) | <0.1 | 24.3 |
| Pyrovac        | 0.6 (0.1) | 0.4 (0.0) | 254.9 (91.0) | 13.1 (2.6) | 4.8 (2.7) | 130.0 (42.9) | 3.8 (0.1) | <0.1 (7.8) |
| BassWd 400     | <1.0 | <1.0 | 143.3 (0.5) | 27.5 (0.1) | 7.4 (0.8) | 67.4 (0.8) | <1.0 (*) | <1.0 (7.8) |
| BassWd 450     | <1.0 | <1.0 | 127.7 (0.2) | 20.3 (0.5) | 4.3 (0.7) | 61.9 (0.7) | <1.0 (0.3) | <1.0 (7.8) |
| Willow 450     | 0.4 (0.6) | 4.1 (0.3) | 83.6 (7.4) | 22.7 (0.5) | 1.2 (0.3) | 40.0 (4.2) | 1.4 (0.3) | 0.3 (15.3) |
| Willow 500     | 0.2 (0.5) | 3.1 (0.1) | 121.7 (26.9) | 29.5 (1.1) | 2.0 (0.3) | 64.4 (11.5) | 1.2 (0.2) | 1.0 (5.3) |
| BasquesC       | 0.8 (0.3) | 1.4 (0.5) | <17 (2.1) | 10.4 (<0.1) | 0.002 (2.2) | 6.8 (0.3) | 1.5 (0.3) | <0.1 (20.2) |
| BasquesF       | 0.4 (0.4) | 1.9 (0.2) | <17 (2.6) | 17.0 (0.6) | 0.1 (0.0) | 11.9 (0.0) | 2.7 (0.2) | <0.1 (6.7) |
| SGrass 450     | 4.6 (0.7) | 0.3 (0.1) | 328.7 (6.9) | 209.5 (12.1) | 32.7 (1.1) | 222.4 (17.8) | 2.8 (0.2) | 1.1 (4.2) |
| SGrass 500     | 6.8 (0.5) | 0.2 (0.0) | 594.2 (1.1) | 191.0 (3.2) | 41.3 (0.4) | 380.0 (4.8) | 7.0 (0.4) | 1.4 (2.7) |
| Poultry litter 450 | 0.1 (0.5) | 0.6 (0.0) | 46.0 (1.6) | 272.4 (3.7) | 24.0 (0.6) | 35.4 (0.4) | 2.3 (0.4) | 1.2 (15.9) |
| Poultry litter 500 | 1.8 (0.6) | 0.8 (0.0) | 65.6 (4.8) | 310.4 (0.5) | 25.8 (0.5) | 88.3 (36.3) | 2.7 (0.1) | 1.9 (21.2) |
| WdAsh A        | 52.1 (1.9) | 3.2 (0.4) | 71.4 (1.0) | 157.3 (4.0) | 5.1 (0.5) | 7.6 (0.8) | 65.6 (<0.1) | <1.0 (210.6) |
| WdAsh B        | 32.4 (2.0) | 1.4 (0.2) | 48.4 (3.7) | 83.5 (1.6) | 4.0 (0.1) | 10.6 (0.5) | 9.3 (0.5) | <1.0 (4.3) |
| ON             | 13-170 | 3-34 | 210-2800 | 100-1700 | 5-94 | 62-420 | 150-1100 | 2-34 | 500-4200 |
| QC             | 13-41 | 3-10 | 210-1000 | 400-1000 | 5-20 | 62-180 | 150-300 | 2-14 | 700-1850 |
| IBI            | 12-100 | 1.4-39 | 64-1200 | 53-1500 | 5-20 | 47-600 | 70-500 | 1-100 | 200-2800 |
| EBC            | <1.5 | <90 | <100 | <50 | <150 | <400 |

(*) = duplicate was below detection limit.
Figure S1. Loadings plots of the pseudo-total element concentrations of biochars and WdAsh, with % of variance explained by each principal component (PC). IC refers to total inorganic C. Scores and vector plots are shown in Figure 4.
Figure S2. Loadings plots of XRD patterns with % of variance explained by each principal component (PC). Multiple signals attributed to the same mineral are numbered (m1, m2, m3 for magnetite/maghemite; s1 and s2 for sylvite). Because the organic regions were broad, vectors in Figure 6 were plotted based on $^\circ \theta$ values labelled with * for cellulose and ◊ for turbostratic crystalline carbon. Scores and vector plots are shown in Figure 6.

Figure S3. Loadings plots of EDX spectra with % of variance explained by each principal component (PC). Scores and vector plots are shown in Figure 8.
**Figure S4.** Individual scores plots from Figure 8 in the main text. Principal component analysis of scanning electron microscopy-energy dispersive X-ray spectra of 10 biochars and WdAsh A. PC1 represents 38.7% of the variance, PC2 represents 23.0% of the variance, and PC3 represents 15.5% of the variance. EDX spectra were filtered using PC3 to plot data that did not contain signals from Cl, K, Mg, Na, and P at PC5 = 0, and the resulting Filtered PC5 vs. PC2 scores plot illustrates the distribution of Cl, K, Mg, P, and S in the samples. The vector direction and main correlated elements are labelled in the scores plots of Airex 1, but arrow lengths are meaningless (a, b, b.1). Each row shows scores plots for the 10 biochars and WdAsh A: a), b), b.1) Airex 1; c), d), d.1) Airex 2; e), f), f.1) Pyrovac; g), h), h.1) BassWd 400; i), j), j.1) BassWd 450; k), l), l.1) Willow 450; m), n), n.1) Willow 500; o), p), p.1) Basques C; q), r), r.1) SGrass 450; s), t), t.1) Poultry 450 (derived from poultry litter), and u), v), v.1) WdAsh A. The same PC combinations are plotted along columns: a), c), e), g), i), k), m), o), q), s), u) are the PC1 vs. PC2 scores plots for 10 biochars and WdAsh A; b), d), f), h), j), l), n), p), r), t), v) are the PC3 vs. PC2 scores plots for 10 biochars and WdAsh A; and b.1), d.1), f.1), h.1), j.1), l.1), n.1), p.1), r.1), t.1), v.1) are the Filtered PC5 vs. PC2 scores plots for 10 biochars and WdAsh A.
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