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Materials and Methods

Biochars were produced using BEST Energies continuous slow pyrolysis process. Chicken litter (CL) was pyrolysed with a highest temperature of treatment (HTT) of 450°C and held at this temperature for 30 min. Greenwaste (GW) and paper mill sludge (PM) were both pyrolysed with a HTT of 550°C and residence time of 60 min. The CL feedstock also included sawdust, whereas the PM feedstock had woodchip as secondary constituent. Therefore, all feedstocks had 20–30% of woody material. The three fresh biochars differed in some key chemical characteristics in that (i) the PM biochar had a very high acid neutralizing capacity (29% $CaCO_3$ equivalence compared with 14% for the CL biochar and 0.5% for the GW biochar), and (ii) the CL biochar had a high P and N content compared with the other two biochars. These biochars were incorporated in a Ferrosol in a sub-tropical environment at the Wollongbar Research Station (Industry and Investment NSW, Australia; 28°50′S, 153°25′E)). A summer sweet corn, winter pulse rotation was established at the site.

Soil samples (*ca*. 1 kg) were taken after the first and the second year of biochar incorporation from three sites at each experimental plot to a depth of 10 cm and then pooled. The fresh wet soil was dispersed by agitation in ten volumes of demineralised water (1:10). The soil/biochar mix was sieved using a 750 µm sieve. Biochar pieces were manually removed from the sieve surface using a jeweler forceps. Light biochar pieces were recovered from the supernatant by centrifugation at 2000 x G. Samples where then washed 3 times with demineralised water in a

beaker with slight agitation from a magnetic stirrer, dried and then stored dry in an airtight container at 4^{o}C.

Biochar samples were mounted on aluminum stubs and carbon coated prior to the analysis using scanning electron microscopy (SEM), energy X-ray dispersive spectrometry (EDS) and transmission electron microscopy (TEM). Samples were examined in a Hitachi 3400 SEM (Japan) to which EDS facilities were attached. Electron transparent sections for TEM specimens were prepared using a focused ion beam (FIB) (FEI Nova Nanolab 200 dual beam FIB). More details of the sectioning technique are found in Giannuzzi (2005). All TEM specimens were examined using a Philips CM200 field emission gun TEM. Scanning TEM mode (STEM) was used to perform EDS mapping and line scans (individual points were taken at 1 nm intervals) in the region of interest.

The atomic concentrations of elements at the surface of biochars, as well as their chemical bonding, were investigated by X-ray photoelectron spectroscopy (XPS) (ESCALAB-220i-XL, VG Scientific, UK) with a monochromatic Al Kα X-ray source ($h\nu$ = 1486.6eV) induced by 10 kV, 15 mA Al Kα radiation with a spot size approximately 1 mm in diameter. The pass energy for survey scans was 100eV with a scan step of 1eV, and for region scans, 20eV with a scan step of 0.1eV was used. Neutralization was applied by using a 4eV electron flood source to avoid surface charging. A peak shift was performed using the C1s peak at 285eV as a reference. Photoelectrons were collected at a take-off angle of 90°. XPS spectra were analyzed and deconvoluted using the Gaussian-Lorentzian sum function with a different % Gaussian-Lorentzian value to optimize the spectra. A Shirley background correction was carried out to remove background noise. For non-metal elements, the quantitative measurement error is around 1–5%, but can be minimized to 0.5–1% by increasing region scan times.

Solid state ^{13}C magic angle spinning (MAS) NMR spectra were obtained at a frequency of 50.3 MHz using a Varian (Palo Alto, CA) Unity200 spectrometer. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end caps and spun at the ‘‘magic angle” (54.7) at 5000 ± 100 Hz in a Doty Scientific (Columbia, SC) MAS probe. Free induction decays (FIDs) were acquired with a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms. All spectra were zero-filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.010 s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. Cross polarisation (CP) spectra represent the accumulation of 4000 scans and were acquired using a 90°Hz pulse of 5–6 μs duration, a 1 ms contact time and a 1s recycle delay. Direct polarisation (DP) spectra represent the accumulation of 500–1000 scans and were acquired using a 90° ^{13}C pulse of 5–10 μs duration and a 90s recycle delay. Spin counting was carried out using the method of Smernik and Oades (2000). Briefly, spin counting experiments involve comparison of the ^{13}C NMR integrated signal intensity of a sample with that of a standard with a known mass and carbon content. Glycine (AR grade, Ajax Chemicals) was used as external reference material. Aliquots of each heat-treated material (200 mg) were placed in 2 ml glass vials with PTFE-lined screw caps. Neat ^{13}C-labelled sorbates (ca. 10 μl) were added using a micropipette and the samples were shaken for ca. 1 min and stored at room temperature until analysis using NMR.

Giannuzzi LA, Stevie FA (2005) ‘Introduction to Focused Ion Beams Instrumentation, Theory, Techniques and Practice’, Springer, New York.

Smernik RJ, Oades JM (2000) The use of spin counting for determining quantitation in solid state ^{13}C NMR spectra of natural organic matter 1. Model systems and the effects of paramagnetic impurities. *Geoderma* **96,** 101–129.