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# Characterization of an enriched biochar

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ABSTRACT

Carbonized materials are responsible for maintaining a high level of fertility and soil organic matter in soils such as the Amazonian Dark Earths, also known as Terra Preta. It is hypothesized that an enriched biochar, which will have long term stability similar to Terra Preta, can be synthesized by mixing biochars with manures, minerals and clays and heating the mixture at low temperatures. This treatment will promote bonding between the mineral and the organic phases, which may occur naturally after several years of aging in soil. This paper describes the characterization of an enriched biochar by a range of analytical methods. Examination of the enriched biochar showed that it has high concentrations of exchangeable cations, available phosphorus and high acid neutralizing capacity. Structural analysis of the enriched biochar reveals a microstructure that suggests that bonding has indeed occurred between the biochar and mineral phases. Using natural $^{13}C$ abundance and a two-pool exponential model, the half-life of enriched biochar-C was estimated to be 104 years in a clayey soil.



## 1. Introduction

Biochar is a carbon-rich solid material produced by heating biomass in an oxygen-limited environment. It may be added to soils where, potentially, it can act as a means to sequester carbon (C) and to maintain or improve soil and agronomic functions [1,2]. Biochar can form a highly stable pool of C, promote plant growth and potentially mitigate greenhouse gas emissions from soil [3–5]. Research has shown that carbonized materials are responsible for maintaining a high level of soil organic matter (SOM) in ancient soils such as Amazonian Dark Earths (ADE), which is likely due to its high stability in soil [6]. Recent studies using 11 different types of biochars (*Eucalyptus saligna* wood and leaves, papermill sludge, poultry litter, cow manure, etc.) pyrolyzed at 2 different temperatures has shown that the estimated mean residence time (MRT) of C in biochars varied between 90 and 1600 years [7]. However, even though it is apparent that application of biochars to soil will increase SOM over a long period of time, little is known about the reactions that takes place between biochars and soil.

Cheng and Lehmann [8] showed an increase in oxygenated functional groups, acidity and negative charge at the surface of oak biochar particles aged for 12 months in a controlled aerobic incubation experiment. These findings are supported by results from Joseph et al. [9], who examined aged biochar particles extracted from field trials, and reported an increase in negative surface charge and oxygenated functional groups as compared with freshly produced biochar particles. It has been suggested that changes in the surface properties of biochars may promote the aggregation of organo-mineral complexes at biochar surfaces [9]. This is supported by research into ADE, where it was deduced that slow oxidation at the edges of the aromatic backbone of black C-generated carboxylic groups, resulted in increased cation exchange capacity (CEC) and the formation of organo-mineral complexes [10].

Studies of the structure and chemistry of ADE have revealed that these soils are composed of micro-aggregates that may have been formed by the interaction of thermally treated organic matter, charcoal and ash from fires, residual fired clay, and fragments of bones [11–13]. Liang et al. [14] found that ADE has a higher water holding capacity (WHC), higher CEC and higher fertility compared to adjacent soils. Chia et al. [15] demonstrated, through analytical electron microscopy, that ADE particles consisted of a mixture of black C (possibly arising from the breakdown of biochar), clays and other minerals, including titanium dioxide, manganese oxides, iron hydroxides, calcium phosphate and calcium carbonate. Dünisch et al. [16] showed that by mixing charcoal with ashes or by impregnating wood residues with nutrients such as N, P, and K, slow-release N- and K-fertilizers can be produced. It was hypothesized that an organo-mineral complex that may have similar properties to ADE could be produced by mixing manures/sludge, woody materials, clays, and other minerals, and heating these at

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**Table 1**
Raw materials used to synthesize the enriched biochar.

| Component | % dw |
|---|---|
| Air dried kaolinitic clay (sourced from Geraldton brick works, Western Australia) | 36.0 |
| Chicken manure | 23.0 |
| *A. saligna* biochar (produced at 380 °C for 6 h and reacted with phosphoric acid) | 30.0 |
| Calcium carbonate, rock phosphate, ilmenite, manganese sulfate. Exact formulation is confidential | 11.0 |
| Total | 100 |

low temperatures (up to 240 °C) [17]. It was further hypothesized that the reactions between the manure, woody materials and minerals during heating would result in the formation of redox-active phases that would have variable charge, along with a range of oxygenated labile organic C and N-containing compounds, some of which would be intercalated into the mineral phases [18].

In a further step, this study introduces a biochar-enriched organo-mineral complex (enriched biochar, EB). The EB was produced by coating biochar particles in clay, manure, and minerals and then heating at 200–240 °C. Adding biochar to the organo-mineral complex, described in an earlier study [17], was hypothesized not only to increase the aromatic C content of the final product, but also to increase the content of oxygenated functional groups and Lewis acid and base sites that may adsorb more of the organic matter from the breakdown of the manure. As a result, the physical and chemical structures of EB may be much closer to that described for ADE by Liang et al. [14]. It was also hypothesized that the EB would have a longer half-life than that of the organo-mineral complex lacking biochar. A half-life greater than 100 years is an important quality for biochar, and the high stability of EB will ensure sustained translation of its beneficial effects to soil especially through the evolving cation retention property on EB surfaces. An earlier study performed by Lin et al. [19] showed that by torrefying a Jarrah-based biochar (produced at 600 °C) together with chicken manure, clay and minerals, a higher concentration of plant available P was found with minimal N lost from the original feedstock after torrefaction. The clay, minerals and manure were incorporated into the biochar structure and a higher concentration of dissolved organic carbon was found [20].

The objectives of this paper are to present the methods used to synthesize EB, characterize the chemical, morphological and surface properties of EB, and estimate its C stability in soil through an incubation experiment. This paper also explains the interaction that occurs when reacting biochars with clay and minerals, which simulates the reaction that occurs between biochar and soils. Details of the results of field trials with this EB are reported in a separate paper [21].

## 2. Materials and methods

The EB was manufactured by Anthroterra Pty Ltd using its patented formulation (PCTI/AU2010/000534). The raw materials used to produce the EB are listed in Table 1. Biochar produced from *Acacia saligna* wood at 380 °C in a batch reactor was pre-treated with 10% phosphoric acid solution (at a 1:1 solution: biochar ratio), drained and then held for 24 h prior to mixing with the remaining raw materials. The purpose of the acid treatment was to oxidize the surface, to enhance the stability of the carbonyl groups and to promote the loss of hydrogen from the biochar's surface [22]. Six kilograms of rainwater was added to a 20 kg mixture of raw materials to ensure that the materials coagulate, after which the mixture was homogenized using a commercial cement mixer. The resulting slurry was dried in 25 mm deep trays at 80 °C for 24 h in a ventilated oven before being mechanically broken into <15 mm fragments with a garden mulcher. The mixture was then placed into a rotating torrefaction kiln and heated at 5–7 °C $min^{-1}$ up to 220 °C. The oxygen content in the torrefaction chamber was maintained at approximately 4% by purging with the exhaust gas from a gas-powered electricity generator (Honda; 5 kW). The materials were heated for 1hr at 220 °C and the final product was cooled under atmospheric conditions to room temperature.

Ultimate, proximate, and ash analyses were performed by Bureau Veritas International Trade Pty Ltd in Sydney, NSW, Australia according to the relevant Australian standards (AS1038.3, AS1038.6.1 and AS1038.6.2) respectively. Agronomic analyses (CEC, available phosphorus, extractable nitrate ($NO_3^-$) and extractable ammonium ($NH_4^+$) concentrations) were performed by New South Wales Industry and Investment, Wollongbar, NSW, Australia, using methods described by van Zwieten et al. [4]. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific ESCALAB250Xi using a 500 micron diameter beam of monochromatic Al Kα radiation (photon energy = 1486.6 eV) at a pass energy of 20 eV. The core level binding energies (BEs) were aligned with respect to the C1s BE of 285.0 eV.

Low molecular weight organic molecules in the *A. saligna* biochar and EB were extracted by boiling 5 g of sample for 1 h in 40 mL of solvent using an automated Soxhlet apparatus (VELP, Italy), rinsed for 1 h in the condensed solvent vapors, and then reduced to 10 mL. The solvent system was dichloromethane (DCM):MeOH 95:5 (v/v), following Graber et al. [23]. A portion of the extract was evaporated to dryness and derivatized using 0.5 mL of N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) and 1 mL acetonitrile for 15 min at 60 °C. A blank (no biochar) was carried through the whole process. Analysis was performed by GC/MS (Agilent, Santa Clara, USA; model number 6890N/5973N) in scan mode using temperature programming (oven 60 °C, initial hold 5 min, ramp to 275 °C at 5 °C $min^{-1}$, final hold 2 min; inlet 250 °C; split ratio 2; transfer line 280 °C) and a 30 m long capillary column with a (5%-phenyl)-methylpolysiloxane phase, 0.25 mm inner diameter, and 0.25 μm film thickness. Total ion chromatograms (TIC) were compared with the NIST08 mass spectral library (Fig. 1, Table 5).

An incubation experiment, where the total amount of added EB-C that was mineralized and the mean residence time of the EB-C in a clayey soil (Vertisol) were estimated, was performed using the methods described by Singh et al. [7]. Briefly, air-dried soil (equivalent to 612 g, oven dry; <2 mm sieved), adjusted to ~67% of water holding capacity using a nutrient solution containing $NH_4NO_3$ (50 mg N $kg^{-1}$ dry soil), and inoculated with a microbial inoculum, was placed in plastic jars. The microbial inoculum was prepared by mixing soils collected from native eucalyptus forests, pine plantation, maize cropping and grazed pastures, to introduce a diverse range of microbial communities to the soil [7,24]. Each soil jar was inoculated with ~1 g of microbial inoculums [7]. These jars were then placed in sealed 5 L buckets and preincubated for 12 days in the dark at 22 ± 1 °C. After pre-incubation, a nutrient solution (6 mL) that contained ($kg^{-1}$ soil) ca. 500 mg N, 80 mg P, 200 mg K, 30 mg S, and trace elements was uniformly mixed with the soil [6]. The EB (<2 mm sieved; $\delta^{13}C$ −24.0‰; 29.1%C; pH 6.3) was mixed at 0.82% (wt/wt) with the soil containing $C_4$ organic matter ($\delta^{13}C$ −14.2‰; 0.42%C; pH 8.2) [7], and adjusted to the bulk density of 1.2 g $cm^{-3}$. A control soil (without the EB) was also included. The EB-soil mixture and the control soil ($n = 3$) were then incubated at 22 °C for 630 days. The $CO_2$ evolved from the soil was trapped in 30 ml of 2 M NaOH. The trap was periodically removed at 3, 9, 20, 126, 192, 287, 364, 462 and 630 days and analyzed for total $CO_2$-C and associated $\delta^{13}C$ [7]. The proportion of added EB-C in the total $CO_2$-C evolved was determined by a two-pool $^{13}C$ isotopic mixing