Using Biomass Waste in the Remediation of Degraded Land

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Abstract-There has been considerable research into the production of biochar, pyrolysed biomass, which produces a carbon rich material and facilitates long-term CO_2 sequestration. The use of this material in agricultural soils suggests that there may also be productivity benefits to be gained along with atmospheric CO_2 storage. A number of possible reasons why these biochar derived benefits may, or may not, occur have been suggested and include, an additional source of crop nutrition (acting as a fertilizer), as a modifier of the soil physical, chemical and biological environment (acting as soil conditioner) and as possible improver of crop water availability (acting to delay the onset of environmental stress). The apparent capacity of biochar to produce a diverse range of impacts when incorporated into soil appears to depend on a number of factors, these include the feedstock and the protocol used in its pyrolysis. The chemical nature of the biochar produced can be varied, but controllable, given these factors. Importantly, this flexibility suggests that production could enable biochar structure and function to be designed for a specific end use ('Smart Biochar'). This paper examines recent research which supports the notion that biochar products, not only have a supplementary role in agriculture, but also a role in environmental management, by provision of materials which facilitate soil remediation. It will also, more specially, examine the potential to design and produce biochars derived from combinations of various feedstocks and pyrolysis protocols to produce smart biochars to amend degraded and contaminated soils. It can be concluded that the production of biochar from waste biomass can provide a means of sequestering atmospheric CO_2 it also has an important contribution to increasing the function of poor soils with respect to agriculture use and environmental management. Importantly, here there are also opportunities through the selection of feedstocks and the control of the pyrolysis process that has the potential to produce biochars which are designed for a specific purpose, i.e. 'smart biochars' for environmental management.

Keywords – biochar; pyrolysis; smart biochar; degraded land and soils

I. INTRODUCTION

This paper focuses on the studies undertaken on the agricultural aspects of biochar soil incorporation, and to determine how this knowledge can inform its use in soil improvement particularly with respect to amelioration. There is an array of published information regarding the incorporation of soil amendments of various types to improve agricultural performance [1] and this is used to determine the potential of biochar to remediate degraded landscapes and soils. This prospects of using biochar in remediation is relevant beyond the loss soil organic matter (SOM) in agriculture and the decline in fertility, in particular, the release of industrial contaminants and the challenge in remediating soils and sustaining urban and rural environments.

II BIOCHAR - PHYSICAL PROPERTIES AND CHEMISTRY

The physical properties of biochar are key to understanding its function within soil and its potential to act as a route to sequester atmospheric carbon dioxide [2]. Soil incorporation of biochar can influence soil structure, texture, porosity, particle size distribution and density. The importance of biochar surface area in influencing soil fertility (water and nutrient cycling and microbial activity) has also been documented [3, 4]. Biochar is a carbonaceous material which contains polycyclic aromatic hydrocarbons [5]. It is also highly porous and can contain significant amounts of extractable humic and fluvic acids [6]. These hydrocarbons have different numbers of clusters of fused aromatic rings which contain O_2, N_2 and H_2, along with an array of other functional groups [7, 5]. The molecular structure of these biochar's therefore show a high degree of chemical and microbial stability, with a turnover which can be on a timescale of millennia [8, 9]. Biochar does however show that oxidation can take place at the surface of particles and this is related to not only time of exposure, but also mean annual temperatures. This oxidation can impact greatly on soil biogeochemistry and nutrient release and retention [8]. The ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C) are used to describe the state of the material during the biochar production process as these elements are sensitive to temperature conditions during charring [10]. At low temperature pyrolysis these hydrogen and oxygen elemental ratios have a tendency to be higher. The relationship between changes in carbon, oxygen, hydrogen and nitrogen for the charring and pyrolysis of wood at different temperatures has been described [11].

The composition of biochars is heterogenous and their surfaces can be hydrophilic, hydrophobic, acidic and basic and this contributes to their ability to react with other substances in the soil solution. The variability in biochar chemical and physical properties depends extensively on the material used to produce it (feedstock), availability of oxygen and the temperatures achieved during pyrolysis [12, 4]. It is temperature that determines the level of volatilisation and the physical and structural changes in different biochars [2].

A key physical feature of biochar is its porosity which defines its surface area. The presence of pores within biochar particles is important as they enhance the total particle surface area of a soil. Analysis shows that pore size distribution is highly variable and encompasses nano- (<0.9 nm), micro- (<2 nm) to macro-pores (>50 nm) [2]. The larger macro-pores are key to its function in soil, i.e. aeration and hydrology; they also provide a habitat niche for microbes and facilitate root movement through the soil. The smaller sized pores are involved with molecule adsorption and transport. Soil structure varies with soil type and is closely related to its particle size distribution. For example, sandy soils, due to their limited specific surface area (sand 0.01 to 0.1 $m^2\ g^{-1}$), are only able to store relatively small quantities of water or nutrients, while soils containing clay particles have a greater water holding capacity linked to their greater specific surface area (5 to 750 $m^2\ g^{-1}$). The inclusion of black carbon in soils has been shown to enhance specific surface area (x 4.8) compared to adjacent soils [6], while Downe *et al*. [2] quoted biochar sources that had specific surface areas significantly greater than those of clay (>1500 $m^2\ g^{-1}$).

The porous nature of biochar is also important as it can provide refugia for some beneficial organisms such as mycorrhizae and bacteria [13, 14]. The porosity and surface area of a biochar is also important as it can influence nutrient retention capacity [15]. The presence of carbon particles in the soil has been shown to influence cation and anion surface the binding [6]. Ion retention depends on biochar cation and anion exchange capacities. Increases in pyrolysis temperature are known to increase biochar CEC [16]. CEC increases when biochars are exposed to oxygen in the presence of water, and through partial degradation by microbial activity [9].

III BIOCHAR – NUTRIENTS

Products produced from organic biomass (manures, compost and biochar) would be expected to contain large amounts of carbon and macro- and micro-nutrients see [15]. Incorporation of biochar has been shown to enhance the availability of key macro-nutrients such as N and P, as well as some metal ions [12], but can also induce a decline in N availability [3]. Both feedstock and pyrolysis conditions influence the amount and distribution of biochar minerals see [4]. Biochars produced from a coniferous source at 350ºC were shown to have lower absorptive capacity (CEC), but a greater amount of available nutrients than those produced at 800ºC [12]. The amounts of key elements present in biochar can be shown to be dependent on the concentrations of these components in the feedstock [17, 18]. There is some evidence from the study of nitrogen levels that at higher pyrolysis temperatures its concentration within the biochar can decline, while for P, considerably more can be retained in the biochar relative to nitrogen, given the optimum pyrolysis temperature [19].

Nitrogen and P availability are particularly important with respect to plant growth and even with some biochars high in total N content (e.g. sewage sludge), mineral nitrogen (ammonium-N and nitrate-N) levels and available phosphorus can be very low [19]. The ratio of carbon to nitrogen (C/N) with biochar is also highly variable, and is cited as a means of inferring mineralisation and release of inorganic nitrogen to the soil. Given the high C/N ratios for biochar the expectant nitrogen immobilisation, inducing plant nitrogen deficiency, is limited because of the recalcitrant nature of the carbon [15].

Biochar incorporation has been shown to induce soil alkalisation which can indirectly increase soil nitrification [18]. But increases in soil nitrification rates can be achieved in the absence of soil pH changes [20]. The formation of 'smart biochars' has potential [21]. For example, biochar on reaction with ammonia, produced NH_4HCO_3-biochar, which acted as a slow-release nitrogen fertiliser. This approach can also reduce the release of biochar-nitrate that may contaminate ground water [15].

IV EFFECTS OF BIOCHAR ON SOIL CHEMISTRY

Biochar soil incorporation can be shown to change soil pH, electrical conductivity (EC), cation exchange capacity (CEC) and nutrient concentrations [6, 12, 22, 4]. Liang *et al*. [6] showed that as a consequence of the oxidation of black carbon particles and the adsorption of organic matter to its surface, the charge density (CEC per unit surface area) in some soils could increase. The surface positive charge will, however, decrease in response to the rate at which the biochar oxidises [9]. While in highly weathered tropical soils, with little available P, and the low pH induced release of Al and Fe, binds it further [23, 24]. Greenhouse experiments show that ammonium leaching was reduced by biochar (by 60%), along with N_2O emissions [3, 25]. Biochar derived from bamboo added to sewage sludge during composting reduced N-leaching and the mobility of heavy metals (Cu and Zn) from the material [26]. Biochar can reduce the concentration of soluble compounds in the soil solution, e.g. phenols [12]. The presence of some elements that are known to be toxic to plant growth, particularly at low pH, such as Al, Cu and Mn, have also been shown decline in the presence of charcoal [23, 24, 27]. Availability of other elements can increase where biochar induced increases in soil pH enhance solubility e.g. N, P, Ca, Mg and Mo.

V EFFECTS OF BIOCHAR ON SOIL PHYSICAL PROPERTIES

There is less data regarding the effects of incorporation of biochar on soil physical properties, see review [28]. Factors such as its mobility within the soil profile are important, particularly with respect to how it may benefit plant production and the movement of surface and ground waters [29]. Limited evidence, from long-term (35 years) sugar cane waste production burning, shows that semi-natural biochar moves into the subsoil [30, 29]. More recent evidence shows, that biochar's highly condensed carbon movement into the subsoil can be tracked over 100 of years [31]. This may be linked to changes in biochar particle size which appears to decline with age in the soil [32]. Biochar soil incorporation has been shown to reduce 'soil strength' (soil mechanical impedance). The ease with which plant roots penetrate the soil impacts on growth and yields [33]. Soils, particularly when dry, which limit root penetration have been shown to be improved through biochar application [34].

VI EFFECTS OF BIOCHAR ON SOIL BIOTA

The structure and function of biological communities within soils are complex. Soil inhabitants include algae, archaea, arthropods, bacteria, fungi, nematodes, protozoa and other invertebrates. The presence and abundance of these groups of organisms have a profound effect on soil function, 'health' and productivity. Soil type and its physical management, e.g. the application of biochar will impact on soil biota and performance. Soil biota composition has limited use in understanding soil function, particularly when also considering soils highly spatial and temporal heterogeneity. Application of biochar to soil is known to alter carbon utilisation profiles, microbial population structures, and cause respiration rates to increase [14, 35].

Diazotrophs are a specialised group of bacteria which contain the enzyme nitrogenase which reduces atmospheric N (N_2) to ammonia (NH_3). This NH_3 can be nitrified (NO_3^-) prior to plant uptake and utilisation in the synthesis of amino acids etc. Despite their ubiquitous presence these free-living N-fixing bacteria have been insufficiently studied with respect to the influence of biochar on their N_2-fixing capacity [18]. Ammonification of organic complexes containing N, is driven by heterotrophic bacteria and some fungi. Nitrification occurs in the presence of autotrophic organisms such as bacteria and archaea [18]. Biochars have been shown to increase net nitrification in forest soils [20, 18]. This may not be true in grassland or agricultural soils which have existing functional nitrifying communities [3, 36]. Biochars are generally low in inorganic N and this may provide diazotrophs with a competitive advantage in colonising the large surface area of biochars. This combined with biochar's potential for NH_4^+ exchange with soil solution can modify soil N availability to plants and stimulate nodulation and fixation.

Little is known about the impacts of biochar on N immobilisation and denitrification [18]. The reducing of NO_3^- to N_2 in the absence of oxygen is achieved *via* several intermediates (NO_2^-, NO, N_2O) which can be released to the atmosphere. Biochar may have the potential to catalyse the reduction of N_2O to N_2, reducing the emission of a key greenhouse gas [37]. It should be stressed that despite biochar application reducing, in particular, N_2O emissions supporting long-term evidence is limited [37]. Evidence shows that increasing biochar application rates to soil can increase the proportion of N derived from fixation, which increased *Phaseolus vulgaris* yield [36]. The beneficial effects of this were linked to increased Mo and B availability and increased soil pH. Rhizobia functionality increase in pH neutral soils, so increasing alkalinity in acidic soil can enhance nodulation and N fixation.

Saprophytic fungi can modify the persistence of soil biochar, through its decomposition. Their hyphal invasive growth and extracellular enzymatic capability enable them to colonise biochar pores. Knowledge of the effects of biochar on soil pathogens and population structure and function is limited [38]. Evidence shows biochar incorporation influences mycorrhizal fungi (MF) [39]. Arbuscular mycorrhizae have been shown to increase root colonisation sites in the presence of biochar [39, 22]. Biochar additions can also increase the extent of endomycorrhizal plant associations, enhancing the availability of P [40, 22]. Biochar presence in the soil provides a physical niche for mycorrhiza and bacteria which can be devoid of fungal grazers [13, 14]. Measurements of biochar porosity support the notion that soil grazers in the size range of Collembola and protozoans (>1.6 mm) would be excluded from pores of this size.

VII EFFECTS OF BIOCHAR ON CROP PRODUCTION

It is well established that biochar applications to soil can increase agricultural productivity [3, 42]. Lehmann and Rondon [42] report that, depending on the amount of biochar added, improvements in plant productivity range from 20 to 220%. It is, however, still not clear under what conditions (soil and climatic) such increases in crop yield might be seen. Recent work questions biochar improvements in high quality soils [43]. Generally soils and climates where biochar work has been carried out include South America and South-East Asia where soils are highly weathered (show a high degree of leaching, and have a low nutrient content), acidic (elemental toxicity) with little clay and are low in nutrition.

VIII EFFECTS OF BIOCHAR ON CROP WATER RELATIONS

Increasing SOM content frequently enhances soil moisture retention and crop water availability which is a key factor in determining crop productivity [44]. Glaser *et al.* [45] compared an Amazonian 'dark earth' soil (high in biochar) and the local native ferralsols with the former having a 15% increase in 'field capacity', from this it was concluded that the agricultural benefits from a soil high in biochar was at least in part due to an improved crop water supply, as may be case elsewhere [46]. Recent reports on biochar benefits generally provide little critical data to support the notion of biochar induced changes in soil water content [3, 32, 2]. Speculation implies that it is through increases in SOM that improvements in aggregation and porosity that crop water availability is influenced, particularly in soils with coarse structures [3, 25]. This notion has limited support, while the effects of changes in soil structure on crop water availability can only be determined from measurements of soil 'matric potential' as this provides a true measures of the work required by the plant to utilise the soils full water content. Despite the lack of data to support the idea that increased plant growth with biochar was due to improvements in plant-soil water relations, this does not mean that the pyrolysed organic carbon incorporated into soil, as biochar, will not increase its water holding capacity [47, 48]. Biochar, is highly porous with an ability for chemical adsorption and the retention of gases, in proportion to its pore geometry and size [49, 50, 51], but less is apparent about its water holding capacity [52]. Evidence of the impact of biochar incorporation in temperate soils is not extensive but, work with North American forest soils shows that charcoal soil increases 'available moisture' (increased by 18%) and reduces evaporation [53]. However these differences were only detectable in sandy soils, and when incorporation rates were high (45% by volume, ~70 t ha^{-1}). Incorporation rates, at a high level, are unlikely to be achievable for several reasons, beyond the availability of sufficient feedstock to produce the biochar. Chan *et al.* [34] suggests that biochar improves soil water holding capacity with applications in excess of 50 t ha^{-1}. They however only provide measurements made at field capacity, so despite a possible increase in soil water content this is not a measure of plant water availability. Soil moisture conservation may be enhanced but if not availability to the plant crop performance will not increase, particularly under water restricted conditions. A number of studies similar to those of Chan *et al.* [34] imply biochar improved soil water status. Conversely, few studies show beneficial biochar responses in the absence of suggestions that crop and soil water relations have improved; Graber *et al.* [54] shows a positive biochar effects but no change in soil water status. While Uzoma *et al.* [55] suggests that water use efficiency was increased by biochar application; the improvement was not due to less water being used just an increased yield in the absence of a direct link with water use or its availability. More recent work also suggests the notion that increased soil available water, due to biochar incorporation, is restricted to sandy soils [56, 57, 55, 58]. The work of Baronti *et al.* [59] is rare in that it provides links between crop physiological behaviour and the appropriate soil and plant water analyses and methodology to do this. In conclusion the evidence for biochar enhancing in soil water availability is not well supported but there may be opportunities to develop a biochar's characteristics, providing they translate into physical changes in for example, soil hydrology and field capacity, to produce smart biochars [60, 21]. Pyrolysis temperature and feedstock are candidates to alter these characteristics, e.g. hydrophobicity [61, 62, 63, 64, 52, 65].

IX EFFECTS OF BIOCHAR ON CROP NUTRITION

Soil mineral nutrition is a limiting factor in maximising crop yield, with nitrogen the most limiting factor. It is well established that post-fire soils show elevated N-cycling with increased N-availability [66, 12]. Biochar applications to forest from different geographic regions have been shown to stimulate N transformation in these phenol-rich soils [12]. There is evidence to show that soil nutrient dynamics are influenced by black carbon [67, 3]. Three key elements N, P and Ca are known for their capacity to influence nutrient dynamics and the fertility of most types of soils [68]. Soil N exists primarily in organic complexes, which are subsequently ammonified (NH_4^+) then nitrified (NO_3^-), before plant uptake. As yet there is no evidence that free-living N-fixing bacteria are influenced by biochar application. However, excessive soluble forms of N in the soil solution do reduce N-fixation [69], while available P stimulates nitrogen fixation, and therefore its presence in a soluble form, could increase bacterial N_2-fixation [3].

Evidence from black carbon studies shows that despite the expected loss of labile N volatilised on burning (70-90%), charcoal residues can contain considerable amounts of N [70, 71]. They showed that the amounts of N in the black carbon ranged from 21-370 mg kg dw^{-1}. However, the effects of biochar on soil N dynamics are not fully understood. Pot experiments with *Raphanus sativus* show that green waste biochar, despite not directly enhancing cropping, did show a positive interaction when N fertiliser was incorporated with the biochar [34], while nitrogen fixation, with respect to beans and non-free living symbionts (e.g. *Rhizobia* spp.) were shown to be enhanced [42, 36]. Savanna-type grassland studies show N accumulation with burning which was suggested to occur indirectly due to P stimulated N fixation by cyanobacteria or the stimulation of N_2 fixation when root nodule forming species were present [72].

The bioavailability and plant uptake of P, K, Ca, Zn and Cu increases in response to charcoal application, while N leaching declines [3, 18]. Phosphorus is often considered the primary limiting nutrient in soils that are highly weathered in the humid tropics [35] Availability of P is highly pH-dependent; in acid soils (<pH 4) insoluble Fe and aluminium phosphates form, while on alkaline soils (>8.5 pH) insoluble calcium phosphates dominate. Abiotic stress events like drought are known to decrease P availability. While complex reactions with clay and organic matter are apparent, it remains unclear what the mechanistic explanation is for changes in fluxes between insoluble and soluble P which are linked with biochar. Explanations include biochar acting as a source of soluble P salts and exchangeable P, as a modifier of soil pH (ameliorating P complexing metals) and as an enhancer of microbial activity and mineraliser of P [18].

Plant tissues when heated lose carbon by volatilisation at the relatively low temperature of 100ºC, while for P volatilisation requires 700ºC. This therefore enhances the availability of P relative to biochar carbon [73]. Biochar generally, irrespective of production temperature, is known to increase soil extractable P (PO_4^{3-}). The ion exchange capacity of a biochar can alter P availability directly through its anion exchange capacity, or by changing availability of cations which P interacts with. Phosphorus precipitation can also influences the solubility of P and the amount available to the plant. The effectiveness (strength of the ionic bond) with which phosphorus combines and forms insoluble compounds with various cations (Ca^{2+}, Al^{3+} and Fe^{2+3+}), and subsequently precipitates, depends on pH. By altering soil solution pH biochar can alter the bonding as well as absorbing of metal cations, avoiding their precipitation with P. Increasing pH can increase alkaline metal (Mg^{2+}, Ca^{2+} and K^{+}) oxides. This reduces soluble forms of Al which is an important response of biochar on P solubility [18]. In soils that are already alkaline or neutral; adding alkaline metals would potentially enhance Ca bonding with P.

Biochar can also have indirect effects on P availability and uptake by changes in the soil environment with respect to the function of microorganisms. Symbiotic soil fungi are enhancers of the efficiency of plant P uptake, particularly in low P soils. Under these conditions biochar can increase the yields of maize and peanut by changes in phosphorus availability [74]. The presence of beneficial symbiotic fungi, such as mycorrhizae, and their enhancement due to biochar, may how low rates of crop applied nutrients can be effective. This has been suggested to be achieved is *via* mycorrhizal hyphae enhancing the interception of minerals that would potentially be lost as leachates [75].

It can be generally concluded that most agricultural production benefits are most often achieved when ‘fertilisers’, mineral or organic, have been included with the application of biochar [41].

X EFFECTS OF BIOCHAR ON SOIL REMEDIATION

Evidence already exist to suggest that biochar application to soil has benefits via reducing the leaching of nutrients from the soil [76]. Biochars physical structure particularly with respect to porosity is suggested as key determinant. It is the process of pyrolysis that importantly increased the surface area of the biochar. Given what is known about the capacity of activated carbon in soil remediation, it is perhaps surprising that the ability of biochar to absorb inorganic and organic molecules, particularly those which are toxic, has yet to be heavily explored or exploited, see Table 1 in both [77, 78]. A meta-analysis of mine responses to biochar application has been undertaken by [79]. We have the opportunity to combine our knowledge of carbon rich compounds to act as chemical absorbents with that of the biochar pyrolysis process and the feedstock to influence over the chemical and physical structure of the resultant biochar. From this insight it becomes possible to acquire biochar with a functional specificity. The capacity to determine a biochar’s specification will enable the concept of smart biochars to be exploited for specific contaminants and soil types. The work of Uchimiya *et al*. [80] demonstrates the different adsorption characteristic of soils with contrasting capacities to retain Cu, in the presence of biochar. They conclude that the sorption characteristic of a metal are linked to cation exchange capacity and presence of surface functional groups on the biochar.

Beesley and Marmiroli [81] provide experimental evidence of capability of biochar (mixed European wood species) to lower the concentrations of some heavy metals, particularly Cd, in water soluble soil sediment leachates. Again, specific solutions for particular problems may well be necessary As contamination will be more challenging to deal with in a soil with a biochar that increases soil pH [77]. While the adsorption of a metal appears to be sensitive to the type of biochar used [82]. Beesley and Marmiroli [81 also found that once sorption of the metal pollutant to the biochar had taken place is was not immediately reversible (reduced mobility). The fate of such contaminants, once sorption to biochar has taken place (reduced bioavailability), needs to be considered carefully, but again the microbial recalcitrant nature of biochar may be a beneficial trait.

To determine the potential of biochar to enable mine tailings (contaminated with Pb and Zn) to be revegetated various samples were removed from the mine environment and subject to laboratory analysis in which they were combined with different quantities of biochar (*Prunus* spp.) with showed potential for phytostabilisation linked to a decrease in the bioavailability of these contaminants [83].

XI CONCLUSIONS

The benefits of the application of biochar to agriculturally degraded soils are likely to be highly dependent on soil type and climate. Application of biochar will have its greatest impact to soils which are either structurally poor, or nutritionally weak, or both. Biochar application to non-agricultural soils, which have been degraded via industrial activities, also appear to provide benefits with respect to remediation. The extent to which remediation is required will vary and could require large quantities of biomass to produce biochar. No attempt has been made here to determine the cost benefit of such applications which clearly will be expensive if large areas of degradation require treatment. More specifically evidence is now being generated which supports the notion that biochar can provide a means to remove contaminants from soils. The emerging science indicates that specific pollutant can be managed by an improved understanding of biochar action in the soil. The opportunity to manipulate biochar chemistry and its structure through selection of feedstock and the control of the pyrolysis process suggests that ‘smart biochar’ can be developed for tackling specific remediation tasks. The exploitation of biomass waste streams, rather than utilising specific biomass grown for biocharing, also provides an important contribution to avoiding conflicts with food crops and provides potential added value to biomass chains where waste is produced and may in some circumstances not have recycling

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