

Biochar and Remediation of Disturbed Lands and Water

A Review of the Effects of Biochar on Reducing Contaminant Concentrations in Disturbed Soils and Water

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Table of Contents

1.0 Introduction	1
2.0 Biochar Reduces Heavy Metals Concentrations	2
3.0 Biochar reduces Concentrations of Organic Contaminants (including PAHs, petroleum hydrocarbons, legacy pesticides)	6
4.0 Biochar reduces Concentrations at Multi-Contaminated Sites	9
5.0 Carbon Sequestration and Credits	10
6.0 Biochar Improves Soil Quality	11
7.0 Biochar Reduces Bioavailability of Contaminants	12
8.0 Summary	13
9.0 References	13

Biochar and Remediation of Disturbed Lands and Water

1.0 Introduction

Healthy ecosystems provide valuable goods and services, including soil erosion control, production of commodities and biodiversity, water supply, carbon sequestration, recreation, and many more. Many ecosystems across the globe have been disturbed which in turn causes a reduction in ecosystem services. Soil remediation and land reclamation aim to restore the value of disturbed areas, and successfully reclaimed areas can return up to 93% of native land benefits within one decade (Dodds et. al. 2008).

Disturbed lands represent significant acreage across the US. Colorado, alone, has 23,000 mines that require remediation, and EPA estimates that there are 450,000 Brownfields in the US. Disturbed lands often have contaminated soils and decreased soil quality. Frequently, heavy metals, organic compounds, increased compaction, reduced CEC, reduced organic content, and altered pHs are found at many disturbed locations. In addition to ecological and human health concerns, these attributes often make the soil toxic to plants and thus, restoration of the landscape very difficult, if not impossible.

Disturbed lands can be improved with the addition of biochar. Biochar is a premium biochar made from clean waste wood is an effective remediation tool for soils for three basic reasons:

- 1) it adsorbs and holds metals and organic compounds thereby removing the material from contact with plants, animals and humans;
- 2) it supports systemic resistance to disease in plants and fosters the introduction of beneficial microbes which also promote remediation; and
- 3) it improves the overall soil quality and results in overall increased plant production. Specifically, increased vegetative cover and seed emergence, faster shoot emergence and length, and greater biomass.

See Appendix 1 for a matrix summarizing the utility of biochar to clean land and water.

The characteristics of biochar, listed below, improve soil quality and make it ideal for remediation and improving ecosystem functions:

- high Cation Exchange Capacity (CEC)
- high adsorption capacity
- high mechanical strength
- high carbon content
- high organic content
- very long half-life (>100 yrs)
- high water-holding capacity
- high nutrient retention capacity
- high pesticide retention capacity

An added bonus to biochar is that it sequesters carbon and reduces greenhouse gas emissions (Please See Section 7.0)

2.0 Biochar Reduces Heavy Metals Concentrations

Biochar has been shown to be very effective in adsorbing and sequestering a number of heavy metals and trace elements including arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc, thus making it well suited to remediate soils contaminated by heavy metals (Wingate et al. 2009).

Sequestering the heavy metals means that the metals are no longer biologically available to plants, animals or humans, and that they are not available for transport offsite in water or air. Biochar thus reduces exposure potential to animals and plants. Reducing phytotoxicity allows soils that were once contaminated to support diverse and healthy vegetation, which is critical to restoring ecological services.

A study to determine the utility of biochar as a soil amendment on mine impacted sites was conducted in Colorado (Peltz 2011). By testing the effect of biochar on plant cover, above ground biomass, and seed emergence the researchers were able to determine the effect of biochar on three aspects of plant growth, e.g., sprouting, growth, and vigor, as well as water holding capacity of the mine tailings and the study results are summarized as follows:

1) when compared to seeding alone, the addition of a 30% by volume biochar soil amendment increased vegetation cover on acid affected soils by 240%.

2) Seed emergence was faster with more emergence and longer sprouts (350% - 670% increase in length) at 120 hours for treatments that

contained biochar when compared to soil.

3) Shoot emergence was faster, with more shoots and greater heights of those shoots at 120 hours.

4) Above ground biomass was positively affected by biochar additions, with acid mine sites showing a 192% increase in biomass.

5) The addition of a 30% by volume amount of biochar increases soil water holding capacity in field settings by >100% relative to no biochar.

6) Biochar treatments increased water holding capacity in all soils by 90% - 180%.

7) The volumetric water content (VWC) measurements strongly suggest that biochar improves the water holding capacity of degraded mine soils.

8) In container trials biochar increases both VWC and above ground biomass by >100% and >66% respectively ($p < 0.001$).

A number of studies have examined the effect of biochar on heavy metals in soils and they are summarized below. The studies quantify the positive effects that biochar has on reducing concentrations and bioavailability of heavy metals.

Park et al. (2011) examined the effect of biochar on the bioavailability and phytotoxicity of cadmium, copper and lead

from contaminated soils. Application of biochar significantly reduced NH_4NO_3 extractable Cd, Cu and Pb concentrations of soils, indicating the immobilization of these metals. Chicken manure-derived biochar increased plant dry biomass by 353% and 572% for shoot and root, respectively with 1% by weight of biochar addition. This was attributed to reduced toxicity of metals and increased availability of nutrients such as P and K. Both chicken manure and green-waste biochars significantly reduced Cd, Cu and Pb accumulation by Indian mustard (*Brassica juncea*), and the reduction increased with increasing amount of biochar application except Cu concentration. Metal sequential fractionation data indicated that biochar treatments substantially modified the partitioning of Cd, Cu and Pb from the easily exchangeable phase to the less bioavailable organic bound fraction.

The authors concluded the following:

“This study clearly has shown that biochar application to metal contaminated soil has the potential of *in situ* remediation by immobilizing metals, thereby reducing metal availability to the plants. In addition, biochar improves agronomic properties by increasing nutrient availability and microbial activity”.

Regemi et al. (2009) conducted column studies of the ability of biochar to remove metals from solution. They treated Cu, Cd, and Pb with 0.5, 1 and 2 g biochar/L and tested the result at time intervals over two days. Lead concentrations were reduced by 98% within 30 min at all concentrations. With 2 g biochar/L, copper concentrations were effectively zero within 6 hrs, 98 % of

the lead was removed in 1 hr and cadmium concentrations were essentially zero after 24 hrs. Copper concentrations were similarly reduced with biochar concentrations of 0.5 and 1 g/L, but times to achieve reductions were longer, 48 hr and 6 hr, respectively. Cadmium concentrations were highly dependent on biochar concentrations. With 2 g biochar/L cadmium concentrations were essentially zero after 24 hrs. However, with 1 g Biochar/L cadmium concentrations were reduced by 35% and with 0.5 g biochar/L concentrations were reduced by less than 15%.

Beesley et al. (2010) determined that biochar applied to soils resulted in a 10-fold decrease in Cd in the soil and resultant reduction in phytotoxicity to plants.

The capability of biochar to immobilize and retain arsenic (As), cadmium (Cd) and zinc (Zn) from a multi-element contaminated sediment-derived soil was explored by Beesley et al. (2011) using a column leaching experiment and scanning electron microanalysis. Sorption of Cd and Zn to biochar's surfaces resulted in a 300 and 45-fold reduction in their leachate concentrations, respectively. Retention of both metals was not affected by considerable leaching of water-soluble carbon from biochar, and could not be reversed following subsequent leaching of the sorbant biochar with water at pH 5.5. Weakly water-soluble As was also retained on biochar's surface but leachate concentrations did not duly decline. It is concluded that biochar can rapidly reduce the mobility of selected contaminants in this polluted soil system, with especially encouraging results for Cd.

Cui et al. (2011) examined rice growth in a rice paddy that had been contaminated by a metallurgy plant. They found that biochar significantly reduced soil concentrations of Cd by an average of 35% and reduced rice plant uptake of Cd by an average of 37%.

Uchimaya et al. (2010) determined that biochar effectively sequestered copper, cadmium and nickel in contaminated soils.

Uchimaya et al. (2010a) studied poultry litter char in an effort to understand the mechanisms by which biochar immobilizes heavy metals. They found that both in water and in soil, pH increase by the addition of basic char enhanced the immobilization of heavy metals. Heavy metal immobilization resulted in nonstoichiometric release of protons, that is, several orders of magnitude greater total metal concentration was immobilized than protons released. The results suggest that with higher carbonized fractions and loading of chars, heavy metal immobilization by cation exchange becomes increasingly outweighed by other controlling factors such as the coordination by π electrons (C=C) of carbon and precipitation.

In additional studies to elucidate mechanisms of heavy metal inactivation, Uchimaya et al. (2011) examined a San Joaquin soil that was alkaline and a heavy clay and was enriched with metals. They noted that copper retention was enhanced by biochar and likely resulted from the following mechanisms: electrostatic interactions between copper and negatively charged soil and biochar surfaces, sorption on mineral (ash) components, complexation of copper by surface functional groups and

delocalized π electrons of carbonaceous materials, and precipitation.

Uchimaya et al. (2011a) conducted a study to fingerprint the principal components responsible for the stabilization of heavy metals (Cu, Ni, Cd, Pb) in soils. Surface ligands including oxygen-containing carboxyl, hydroxyl, and phenolic surface functional groups of soil organic and mineral components play central roles in binding metal ions, and biochar amendment can provide means of increasing these surface ligands in soil. The analysis indicated that effective heavy metal stabilization occurred concurrently with the release of Na, Ca, S, K, and Mg originating from soil and biochar, resulting in as much as an order of magnitude or greater equilibrium concentrations relative to the soil-only control. In weathered acidic soil, the heavy metal (especially Pb and Cu) stabilization ability of biochar directly correlated with the amount of oxygen functional groups. Equilibrium speciation calculation showed minor influence of hydrolysis on the total soluble metal concentration, further suggested the importance of binding by surface ligands of biochar that is likely to be promoted by biochar-induced pH increase.

Namgay et al. (2010) studied the interaction of maize and As and Cd in a pot study. Addition of biochar to soil was found to reduce shoot concentrations of As and Cd in the maize. They concluded that the application of wood biochar to soil possesses the potential to reduce the availability of As and Cd to plants.

Namgay et al. (2010a) conducted a pot experiment to investigate the influence of biochar on the availability of As, Cd, Cu, Pb,

and Zn to maize (*Zea mays* L.). An activated wood biochar, pyrolysed at 550°C, was applied at 3 rates (0, 5, and 15 g/kg) in factorial combinations with 3 rates (0, 10, and 50 mg/kg) each of As, Cd, Cu, Pb, and Zn separately to a sandy soil. After 10 weeks of growth, plants were harvested, shoot dry matter yield was measured, and concentration of trace elements in shoots was analysed. Sorption of trace elements on biochar with initial loadings up to 200 µmol at pH 7 occurred in the order: Pb > Cu > Cd > Zn > As. The results show that biochar application can significantly reduce the availability of trace elements to plants and suggests that biochar application can manage soils contaminated by trace elements.

In a study of the uptake of Pb by radishes, Digman (2010) found that biochar reduced lead uptake by radishes by 40-50%. Additionally, radishes grown in soil amended with biochar were consistently larger than radishes that were grown in un-amended soils.

Zheng and Zha (2009) studied the ability of two biochars prepared from pinewood and rice husk to remove lead from aqueous solution. The results indicated that the biochars contained a large amount of oxygen-containing groups on the surface, which were quite effective for lead removal with capacities of 4.25 and 2.40 mg/g for the pine and rice biochars, respectively. The adsorption equilibrium was achieved at 5 hrs.

Biochar has also been shown to be effective in removing metals from aqueous solutions. Cao et al. (2009) The objective of this study was to determine the effectiveness of biochar as a sorbent in removing Cd, Cu,

and Zn from aqueous solutions using biochar produced from dairy manure (DM) at two temperatures: 200°C and 350°C, referred to as DM200 and DM350, respectively.

The DM350 biochars were more effective in sorbing all three metals than DM200. Both biochars had the highest affinity for Cu, followed by Zn and Cd. The maximum sorption capacities of Cu, Zn, and Cd by DM200 were 48.4, 31.6, and 31.9 mg g⁻¹, respectively, and those of Cu, Zn, and Cd by DM350 were 54.4, 32.8, and 51.4 mg g⁻¹, respectively. Sorption of the metals by the biochar was mainly attributed to their precipitation with PO₄³⁻ or CO₃²⁻ originating in biochar, with less to the surface complexation through -OH groups or delocalized π electrons. At the initial metal concentration of 5 mM, 80–100 % of Cu, Zn, and Cd retention by DM200 resulted from the precipitation, with less than 20 % from surface adsorption through phenolic -OH complexation. Among the precipitation, 20–30 % of the precipitation occurred as metal phosphate and 70–80 % as metal carbonate. For DM350, 75–100 % of Cu, Zn, and Cd retention were due to the precipitation, with less than 25 % to surface adsorption through complexation of heavy metal by phenolic -OH site or delocalized π electrons. Among the precipitation, only less than 10 % of the precipitation was present as metal phosphate and more than 90 % as metal carbonate.

The authors concluded that the results indicated that dairy manure waste can be converted into value-added biochar as a sorbent for sorption of heavy metals, and the mineral components originated in the biochar play an important role in the biochar's high sorption capacity.

3.0 Biochar reduces Concentrations of Organic Contaminants (including PAHs, petroleum hydrocarbons, legacy pesticides)

Biochars have been shown to be very effective in adsorbing and sequestering organic contaminants in soils and sediments including, for example, a class of compounds called anthropogenic organic compounds (HOC) which includes PAHs (polyaromatic hydrocarbons) PCBs (Polychlorinated biphenyls), petroleum hydrocarbons (deLeij 2006), pesticides and herbicides, thus making it well suited to remediate soils contaminated by organic compounds (Cao et al. 2012, Kookana 2011). Sequestering organic compounds means that the compounds are no longer biologically available to plants, animals or humans; and that they are not available for transport offsite in water or air.

Biochar thus reduces exposure potential to plants, animals and humans. Reducing phytotoxicity allows soils that were once contaminated to support diverse and healthy vegetation, which is critical to restoring ecological services.

Recently, several studies have also shown that biochar affects the transport and fate of organic contaminants in soils (Yang et al. 2003, Yang et al. 2006, Smernik 2009, Wen et al. 2009; Yu et al. 2009). Yang and Sheng (2003) found that addition of wheat-straw derived biochar into soil effectively sorbed diuron. Yu et al. (2009) indicated the biochar produced from wood chips was effective in immobilizing chlorpyrifos and

carbofuran insecticides in a soil. Application of biochar into contaminated soils can also reduce the bioavailability of organic contaminants to plants, microbes, and earthworms in contaminated soils, Smernik 2009, Wen et al. 2009; Yu et al.. 2009) .

Previous studies have demonstrated that adsorption to charcoals is mainly influenced by the structural and chemical properties of the contaminant (i.e. molecular weight, hydrophobicity, planarity) (Cornelissen et al., 2004, 2005; Zhu and Pignatello, 2005; Zhu et al., 2005; Wang et al., 2006), as well as pore size distribution, surface area and functionality of the charcoal (e.g. Wang et al., 2006; Chen et al., 2007). For example, sorption of tri- and tetra-substituted-benzenes (such as trichlorobenzene, trinitrotoluene and tetramethylbenzene) to maple wood charcoal (400°C) was sterically restricted, when comparing to that of the lower size benzene and toluene (Zhu and Pignatello, 2005). Among most classes of common organic compounds, biochar has been shown to adsorb PAHs particularly strongly, with desorption having been regarded as 'very slow' (rate constants for desorption in water of 10⁻⁷-10⁻¹ /h, and even lower in sediments) (Jonker et al., 2005). This can be explained both by the planarity of the PAH molecule, allowing unrestricted access to small pores (Bucheli and Gustafsson, 2003; van Noort et al., 2004), and the strong π - π interactions between biochar's surface and the aromatic molecule (e.g. Sander and Pignatello, 2005).

Beesley et al.. (2010) studied biochar and compost to determine the most effective means of reducing PAHs in contaminated soils. Following 60 days field exposure of soils, biochar treatment was most effective

at reducing the concentrations of both total and bioavailable PAH groups; more than 50% relative to the untreated soil for the heavier 4- and 5-ringed PAHs and over 40% for the lighter 2- and 3-ringed PAHs.

Differences relative to the untreated soil were only statistically significant for the total and bioavailable fractions of the 2-ringed PAHs and the total concentration of the 5-ringed PAHs ($p < 0.05$). Total PAH concentrations for all groups were reduced in the biochar treated soil significantly more than both those in the compost and combined biochar with compost treatments, with the exception of the 5-ringed PAHs in the combined treatment ($p < 0.05$). The bioavailable PAH concentrations responded similarly but only the 2- and 3-ringed PAHs were significantly reduced after 60 days ($p < 0.05$). The compost treatment reduced both the total and bioavailable PAH concentrations by over 25% and was also generally more effective than the combined biochar with compost treatment. However, the total and bioavailable PAH concentrations were only significantly smaller relative to the untreated soil for the 2- and 3-ringed PAHs ($p < 0.05$).

De Leij et al. (2006) identified the effective degradation of PAHs and the degradation of diesel fuel. Diesel fuel spills were enhanced more than 10 fold by the use of biochar.

Wade et al. (2009) examined two soils contaminated with the legacy pesticides chlordane and DDX (DDT + DDE + DDD) that were amended with biochar at 0, 0.1, 1.0, and 10% (w/w) levels and then planted with zucchini (*Cucurbita pepo*). The amount of contaminant accumulated by the plants decreased significantly with increasing

amounts of biochar. At the 10% amendment level, total chlordane and DDX content in the plants was reduced by 68 and 79%, respectively, relative to the control plants. They further studied the effects of biochar on the plant systems known to be impacted negatively by natural allelochemicals. The addition of biochar (0.32, 1.60 and 3.20 % (w/w)) to asparagus soils infested with *Fusarium* root rot pathogens increased asparagus plant weights and reduced *Fusarium* root rot disease.

Hale et al. (2011) studied the feasibility of the use of biochar in polycyclic aromatic hydrocarbon (PAH) contaminated soil remediation and compared the biochar to activated carbon (AC). This was achieved by quantifying the sorption of d_{10} pyrene to biochar and AC, with and without soil, before and after artificial aging. Biochar may be a suitable material to add to contaminated soil in order to immobilize contaminants in the same way AC is currently used. Although biochar does not have as strong a sorption capacity as AC, they demonstrated in the present study that the biochar sorption capacity was not affected to a great extent by the presence of soil and/or harsh aging, despite some observed changes in physicochemical properties. In agricultural applications, biochar may also be added in several consecutive growing cycles and in such a scenario, aging with time would become less important. In comparison to anthracite AC, the source material and production process for biochar is likely less costly. In addition, biochar amendment to soil provides the additional benefits of carbon sequestration (Lehmann 2007) and soil fertility improvement (Glaser et al. 2002). Despite the stronger sorption capacity of

AC, its use could result in an overall negative environmental impact when considered in the context of a full life cycle assessment (Sparraik et al. 2011). Thus, from an overall environmental perspective, biochar could be preferable to AC for the remediation of contaminated soil.

Pesticides and herbicides have shown the same affinity for biochar as PAHs and thus biochar provides an excellent media for reducing their bioavailability and toxicity. For example, biochars produced from wheat and rice were reported to be up to 2500 times more effective than soil in sorbing the herbicide diuron (Yang and Sheng 2003). A number of studies have been published in recent years demonstrating similar observations on a range of insecticides and herbicides, including chlorpyrifos, carbofuran, atrazine, benzonitrile, ametryn. Such extraordinary sorption ability by biochars arises from their high steady state approximation, aromaticity, and microporosity. This is also consistent with the well-known relationships of chemistry of soil organic carbon in relation to sorption of chemicals (Kookana et al. 2011). However, it has been suggested that adsorption by biochar is a less reversible process (Gustafsson et al., 1997; Chiou and Kile, 1998; Jonker et al., 2005).

Ahmad et al. (2001) noted that among various molecular components of the soil organic carbon, lignin and charcoal contents were highly correlated with the Koc (sorption coefficient normalized to soil organic carbon) of pesticides. Therefore it is not surprising that biochars, being highly aromatic in nature, are very effective in sorption of herbicides.

Uchimiya et al. (2010a) examined the adsorption of deisopropylatrazine, a stable metabolite of the widely applied herbicide atrazine, to further understand the adsorption mechanisms of biochars. In this study, sorption isotherms for deisopropylatrazine were obtained in acidic aqueous media (pH 5.5) for broiler litter-derived biochars formed by pyrolysis at 350 and 700 °C with and without steam activation at 800 °C. An increase in the Freundlich distribution coefficient (K_F) and isotherm nonlinearity (n_F) was observed with pyrolysis temperature and steam-activation, suggesting that the surface area and aromaticity (degree of carbonization) are the factors controlling the sorption capacity of chars at low surface coverage. At high surface coverage, the isotherms became increasingly linear, suggesting sorption on noncarbonized fraction of biochars. In binary-solute experiments, the sorption of deisopropylatrazine was significantly diminished by Cu^{II} , further suggesting the predominance of the surface adsorption mechanism at low surface coverage of biochars.

Cao et al. (2011) analyzed the change in CaCl_2 extractable atrazine relative to biochar application. Dosages to also determine absorption mechanisms. Their study showed an exponential decrease of the extractable atrazine with increasing organic carbon in the biochar in both soils studied ($r^2 = 0.98$ and 0.99) indicating atrazine immobilization may result from its adsorption onto the organic carbon of biochar. A similar experiment showed an exponential sorption of diuron onto soils containing wheat-straw biochar and the organic carbon in the biochar was the primary component for diuron sorption (Yang & Sheng 2003). The impact of ashes

from burning crop residue on pesticide sorption in soils was first noticed in 1960s by Hilton and Yuen who found that many Hawaiian soils have high sorption ability for s-triazines even after removing organic matter with Hydrogen peroxide (1963). The observation was attributed to the presence of charcoals (chemically the same as biochar) in the soils receiving the regular burning of cane residue.

Studies have begun on different types of organic chemicals. One class of chemicals, endocrine disrupters, has received attention because of their uniqueness' in the environment, and the potential effect on humans. Sun et al., (2011) report that sorption of endocrine disrupting chemicals (EDCs) such as common estrogenic compounds, bisphenol A (BPA) and 17 α -ethinyl estradiol (EE2), and a polycyclic aromatic hydrocarbon, phenanthrene (Phen) with demonstrated that biochar could absorb a wide spectrum of both polar and non-polar organic contaminants.

4.0 Biochar reduces Concentrations at Multi-Contaminated Sites

Co-contamination refers to multiple pollutants at a given location; for example, heavy metals and organics in the same location. Studies have begun to examine the effects of biochar on concentrations of the pollutants in the co-contaminated matrix. Two notable studies are summarized below.

Cao et al. (2011) determined the ability of biochar to immobilize the heavy metal lead (Pb) and the organic pesticide

atrazine in contaminated soils. Biochar prepared from dairy manure was incubated with contaminated soils at rates of 0, 2.5, and 5.0% by weight for 210 days. A commercial activated carbon (AC) was included as a comparison. The AC was effective in immobilizing atrazine, but was ineffective for Pb. However, biochar was effective in immobilizing both atrazine and Pb and the effectiveness was enhanced with increasing incubation time and biochar rates. After 210 d, soils treated with the highest rate of 5.0% biochar showed more than 57% and 66% reduction in Pb and atrazine concentrations in 0.01 M CaCl₂ extraction, respectively. Lead and atrazine concentrations in the toxicity characteristic leaching procedure (TCLP) solutions were reduced by 70_89% and 53_77%, respectively. Uptake of Pb and atrazine by earthworms (*Eisenia fetida*) was reduced by up to 79% and 73%. Phosphorus originally contained in biochar reacted with soil Pb to form insoluble hydroxypyromorphite Pb₅(PO₄)₃(OH), as determined by X-ray diffraction, which was presumably responsible for soil Pb immobilization, whereas atrazine stabilization may result from its adsorption by biochar demonstrated by the significant exponential decrease of extractable atrazine with increasing organic carbon in biochar ($r^2 > 0.97$, $p < 0.05$). The results highlighted the potential of biochar as a unique amendment for immobilization of both heavy metal and organic contaminants in co-contaminated soils.

Beesley et al. (2009) studied soils that were co-contaminated with heavy metals (Cd,Zn) and PAHs Biochar was most effective, resulting in a 10-fold decrease of Cd in pore water and a resultant reduction in

phytotoxicity. Concentrations of PAHs were also reduced by biochar, with greater than 50% decreases of the heavier, more toxicologically relevant PAHs. The results highlight the potential of biochar for contaminated land remediation. What is clear is that both compost and biochar amendments can usefully reduce PAH concentrations, especially the heavier and more toxicologically relevant ones, with the affinity of biochar for these organic contaminants being particularly encouraging for the remediation of contaminated soils. Biochar has greater potential to beneficially reduce bioavailability of both organic and inorganic contaminants than green-waste compost in this multi-element contaminated soil, being especially effective at reducing phytotoxic concentrations of water-soluble Cd and Zn as well as heavier PAH groups.

5.0 Carbon Sequestration and Credits

Extensive work has been done on biochar to slow global warming by sequestering carbon from atmosphere into soil (Marris 2006; Lehmann 2007; Woolf et al. 2010). Plants absorb atmospheric CO₂ through photosynthesis and store it in their biomass. By heating under oxygen-limited conditions and at relatively low temperatures, 30 to 50% carbon in the biomass is converted to stable biochar, which is primarily composed of condensed aromatic carbon (Lehmann 2007). Incorporation of biochar into soil has the potential to lock atmospheric carbon in the solid phase for hundreds to thousands of years (Marris 2006; Lehmann 2007).

Biochar has also been shown to significantly lower emissions of nitrous oxide (a greenhouse gas 300 times more potent than carbon dioxide). For example, Singh et al. (2009) determined reductions in N₂O of 14-73% and 23-52% in two different soils with different concentrations of biochar.

Lehman *et al.* (2006) undertook a global analysis of biochar sequestration potential and concluded that biofuel production using modern biomass could produce a biochar by-product through pyrolysis that results in 30.6 kg C being sequestered for every GJ of energy produced. They subsequently summarized that by 2100, biochar sequestration could amount to 5.5 – 9.5Gt C yr⁻¹ if renewable energy demand was met through pyrolysis, which exceeds current emissions from fossil fuels (5.4Gt C yr⁻¹). More cautious estimates predict that global-scale biochar sequestration could reduce atmospheric carbon dioxide levels by 10ppm by 2050 and 37ppm by 2100 (Collison et al. 2009). Estimates, such as these, indicate that the sequestration potential for biochar is very significant world-wide.

One of the most significant factors in carbon sequestration is the length of time that the carbon is sequestered. In studies to determine lead and atrazine adsorption by biochar, Cao et al. (2011) found no significant loss ($p < 0.05$) of soil organic carbon occurred during the study's 210 day incubation period. They noted that this is consistent with biochar's high stability in soil environment and suggests that addition of biochar to soil may be an effective means of sequestering carbon in soils in addition to remediating contaminated soils. Therefore, biochar production from biomass, especially

from waste materials, may bring multiple benefits: reuse of solid waste, mitigation of global warming, and remediation of contaminated soils. Other studies have addressed the stability of carbon in biochar and have found that different types of biochars may have different decay rates. However, residence times on average appear to be greater than 500 years (Lehmann et al.. 2007; Lehmann et al.. 2008; Lehmann 2009; Lehmann et al.. 2009); although some short term studies have shown residence times in decades (Collinson et al. 2009).

Carbon Credits may also be obtained in the near future from biochars. Currently, there is no mechanism for accounting for carbon storage in soils by biochars, and thus, credits are not available through the Kyoto Protocols. The key features of the Kyoto Protocol, including the accounting framework and rules governing the inclusion of sequestration activities and methods for estimation of emissions and removals, have had and will continue to have a strong influence over national emission trading schemes emerging in many countries around the world (Gaunt and Cowie 2009).

Work is ongoing to move forward key legislative protocols that may grant Certified Emissions Reduction for biochar that could help mitigation and adaptation by developing a carbon credit system to support biochar use.

6.0 Biochar Improves Soil Quality

Soil improvements from Biochar can be summarized as follows:

1. Biochar is effective in significantly enhancing soil carbon, organic matter, available and exchangeable potassium, CEC, and pH on a relatively short timescale.
2. Biochar is a relatively low density material that helps to lower the bulk density of high clay soils, increasing drainage, aeration, and root penetration,
3. Biochar increases the ability of soils (especially sandy or poor soils) to retain water and nutrients.
4. Biochar is a liming agent that will help off- set the acidifying effects from acid mine drainage, thereby reducing the need for liming.
5. Biochar is an excellent adsorbent and when present in soils it increases the soil's capacity to adsorb plant nutrients and agricultural chemicals and thereby reduces leaching of those chemicals to surface and ground water
(1-5 from Glaser et al.. 2002; Lehmann et al.. 2003; Rondon et al.. 2007; Laird 2008; Lehmann and Joseph 2009; Sohi et al.. 2010, Steiner 2010).

Several soil benefits arise from the physical properties of biochar. The highly porous nature of biochar results from retaining the cell wall structure of the biomass feedstock. A wide range of pore sizes within the biochar results in a large surface area and a low bulk density. Biochar incorporation can alter soil physical properties such as structure, pore size distribution and density, with implications for soil aeration, water holding capacity, plant growth, and soil workability (Downie et al.. 2009).

Evidence suggests that biochar application into soil may increase the overall net soil surface area (Chan et al., 2007) and consequently, may improve soil water and nutrient retention (Downie et al., 2009) and soil aeration, particularly in fine-textured soils (Kolb 2007).

Biochar has a bulk density much lower than that of mineral soils ($\sim 0.3 \text{ Mg/m}^3$ for Biochar compared to typical soil bulk density of 1.3 Mg/m^3); therefore, application of biochar can reduce the overall total bulk density of the soil which is generally desirable for most plant growth (Brady and Weil 2004).

Water retention of soil is determined by the distribution and connectivity of pores in the soil matrix, which is largely affected by soil texture, aggregation, and soil organic matter content (Brady and Weil, 2004). Biochar has a higher surface area and greater porosity relative to other types of soil organic matter, and can therefore improve soil texture and aggregation, which improves water retention in soil.

Biochar generally has a high CEC, increasing its potential to act as a binding agent of organic matter and minerals. Macro-aggregate stability was reported to increase with 20 to 130% with application rates of coal derived humic acids between 1.5 Mg/ha and 200 t/ha (Mbagwu and Piccolo, 1997).

Please see the 2012 Whitepaper: *Biochar as a Soil Amendment for Gardens, Lawns and Agriculture* for more detailed information on biochar and soil quality.

7.0 Biochar Reduces Bioavailability of Contaminants

Bioavailability of contaminants in soil can be measured with earthworm exposure and uptake.

Cao et al. (2012) observed that all earthworms were alive after 15 d of exposure in a co-contaminated soil (Pb and Atrazine) with no apparent toxicity symptoms. Earthworms in the biochar amended soil produced higher biomass than those in the control soils and the biomass increased with increasing biochar application rate of biochar. The average fresh weight of earthworm harvested from the soils at the rate of 2.5% biochar treatment was 6.81 g, increasing to 7.24 g at 5.0% biochar, in comparison with 5.72 g in the control soil. Biochars produced from incomplete combustion of dairy manure contained a considerable amount of nutrients (e.g., P, Ca, and Mg), which may improve earthworm growth. Lower Pb accumulated in the earthworm body ($\sim 50 \text{ mg/kg}$) was expected due to relatively low Pb concentration in the soil. Addition of biochar further significantly reduced Pb concentration in the earthworm by 62-79%. However, activated carbon had little effect on Pb uptake by earthworm where Pb concentrations remained similar between the untreated and treated soils. Substantial amounts of atrazine were taken up by the earthworms, with body concentrations of 15.5-25.4 mg/kg in the soils after 15 d of exposure. Elevated atrazine loading in the earthworms from the soil was related to higher available atrazine in this soil. However, biochar significantly reduced atrazine uptake by earthworms by 47-73%.

Similar to biochar, activated carbon also significantly reduced atrazine uptake by earthworm with 66-83% reduction in atrazine.

Polycyclic aromatic hydrocarbons (PAHs) and potentially toxic elements (PTEs) were monitored over 56 days in calcareous contaminated-soil amended with either or both biochar and the earthworm, *Eisenia fetida* (Gomez-Eyles (2011)). Biochar reduced total PAHs (449 to 306 mg kg⁻¹) and bioavailable (cyclodextrin extractable) (276 to 182 mg kg⁻¹) PAHs, PAH concentrations in *E. fetida* (up to 45%) but also earthworm weight. Earthworms increased PAH bioavailability by >40%. Combined treatment results were similar to the biochar-only treatment. Earthworms increased water soluble Co (3.4 to 29.2 mg kg⁻¹), Cu (60.0 to 120.1 mg kg⁻¹) and Ni (31.7 to 83.0 mg kg⁻¹) but not As, Cd, Pb or Zn; biochar reduced water soluble Cu (60 to 37 mg kg⁻¹). Combined treatment results were similar to the biochar-only treatment but gave a greater reduction in As and Cd mobility. The authors conclude that biochar has contaminated land remediation potential, but its long-term impact on contaminants and soil biota needs to be assessed.

8.0 Summary

Disturbed lands can be improved with the addition of biochar. Biochar is an effective remediation tool for soils because it effectively immobilizes heavy metals, adsorbs organic compounds, and fosters the introduction of beneficial microbes, as well as improving the overall soil quality.

The addition of biochar has also been shown to be effective in reducing concentrations of co-contaminated pollutants. All of which foster a return to pre-disturbed conditions.

Biochar reduces the phytotoxicity of soils that have been disturbed, thus allowing establishment of vegetation on soils. Re-vegetation is an important step in land reclamation because it reduces runoff and soil erosion, further improves soil quality, and improves habitat value. Successful reclaimed land areas can return up to 93% of native land benefits to an area within one decade.

Carbon sequestration with biochar is being studied as a mechanism to reduce greenhouse gases.

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Appendix 1

Matrix Showing Various Contaminants of Concern And Ability of Biochar to Clean Lands and Water

Environmental Problem	Biochar Captures & Resiliently Holds:			Biochar Supports Biological Degradation of:			Biochar Reduces:	University Studies
	Soil Contaminants	Water Pollutants	Air Emissions (Offensive Odors)	Soil Contaminants	Water Pollutants	Air Emissions (Offensive Odors)		
NUTRIENTS								
Nitrogen	X	X		X	X			Lehmann et al., 2003; Steiner et al. 2008;Major et al., 2009; Novak et al., 2009; Ding et al., 2010; Laird et al., 2010; Singh et al 2010, Knowles et al. 2011, Gathorne-Hardy et al. 2012
Phosphorus	X	X		X	X			LaLehmann et al., 2003; Major et al., 2009, Laird et al. 2010; Masud 2013
METALS								
Arsenic (As)	X	X		X	X		X	Wingate et al. 2008; Namgay et al. 2010, Namgay et al. 2010a, Beesley et al. 2011,; Samsuri et al 2013
Cadmium (Cd)	X	X		X	X		X	Wingate et al. 2008; Regemi et al. 2009; Beesley et al. 2010; Namgay et al. 2010; Namgay et al. 2010a ; Uchimaya et al. 2010; Beesley et al. 2011, Cui et al. 2011, Park et al. 2011, Uchimaya et al. 2011; Regimi et al 2012; Cao et al 2013; Mohan et al 2014
Chromium (Cr)	X			X	X		X	Wingate et al. 2008; Van Zwieten et al 2010; Dong et al 2011; Mohan et al 2011; Ding et al 2013; Hyder 2013; Yang et al 2013; Agrafioti et al 2014
Copper (Cu)	X	X		X	X		X	Wingate et al. 2008; Regemi et al. 2009; Namgay et al. 2010a, Uchimaya et al. 2010, Chen et al 2011;Uchimaya et al. 2011, Park et al. 2011; Regemi et al 2012; Cao et al 2013; Tong & Xu 2014
Lead (Pb)	X	X		X	X		X	Wingate et al. 2008; Regemi et al. 2009; Namgay et al. 2010a; Park et al. 2011, Uchimaya et al. 2011; Mohan et al 2014
Mercury (Hg)	X		X	X	X		X	Wingate et al. 2008; Kong et al 2011; Ghosh et al 2012; De et al 2013; Dong et al 2013
Nickel (Ni)	X			X	X			Wingate et al. 2008; Uchimaya et al. 2010, Uchimaya et al. 2011
Zinc (Zn)	X	X		X	X		X	Wingate et al 2008; Namgay et al. 2010a, Beesley et al. 2011; Chen et al 2011; Cao et al 2013

Environmental Problem	Biochar Captures & Resiliently Holds:			Biochar Supports Biological Degradation of:			Biochar Reduces:	University Studies
	Soil Contaminants	Water Pollutants	Air Emissions (Offensive Odors)	Soil Contaminants	Water Pollutants	Air Emissions (Offensive Odors)	Availability of Toxins to Plants, Animals, & Humans	
ORGANICS								
Petroleum Hydrocarbons	X	X		X	X			De Leij et al. 2006, Kookana 2011; Cao et al. 2012,
Polycyclic Aromatic Hydrocarbons-PAH	X	X		X	X			De Leij et al. 2006, Beesley et al. 2010, Hale et al. 2011, Kong et al 2011; Kookana 2011; Cao et al. 2012; Ghosh et al 2012; Produna 2013;
Polychlorinated Biphenyls - PCBs	X	X		X	X		X	Kookana 2011; Cao et al. 2012; Ghosh et al 2012; Gupta 2013; Wang et al 2013
Pesticides-Herbicides, Insecticides	X	X		X	X		X	Gustafsson et al. 1997;Chiou and Kile 1998; Ahmad et al. 2001, Yang et al. 2003; Jonker et al. 2005; Yang et al. 2006; Smernik 2009, Wade et al. 2009, Wen et al. 2009, Yu et al. 2009, Yang et al 2010
Endocrine Disruptors (EDC) – BPA, Estradiol				X	X		X	Sun et al. 2011
Odors – Ammonia, Hydrogen Sulfide			X			X		Lyobe et al. 2004, Hua et al. 2009, Steiner et al. 2010, Azargohar and Dalai 2011
Mfg – Oxygen Consuming Wastes		X			X			The Smart Group 2012
Mfg – Colored Wastes		X			X			The Smart Group 2012
Aircraft Deicing Fluid-ADF (glycol)	X	X		X	X			The Smart Group 2012