Report on the Production and Characterization of Biochar Produced at Burt's Greenhouses (Odessa, ON)

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1. Forward

This report on the production and characterization of biochar produced at Burt's Greenhouses provides characterization data pertinent to the production of biochar in biomass boiler at Burt's greenhouses facility and the use of biochar as a soil amendment. The objectives of this study were i) to produce multiple biochars while monitoring production rates and temperatures, ii) to provide and ii) to thoroughly characterize physical and chemical characteristics of the biochars according to standards set by the International Biochar Initiative (IBI) in Standardized Product Definition and Product Testing Guidelines for Biochar (2013). In addition the characteristics were to be linked, where possible, to the performance of the biochar as an agricultural amendment and its ability to sorb contaminants. This document predominantly reports on the characterization of the biochar. The data from monitoring the production will be compiled in a subsequent report.

Biochar is the carbon-rich by-product produced from the pyrolysis of organic matter. Interest in adding biochar to soils stems from its ability to improve soil quality and thus plant growth, sustainably sequester carbon, and sorb harmful contaminants. Simultaneously, biochar offers alternatives for waste management and energy production.

Biochars are being produced by numerous companies and organizations worldwide. Although biochar is generally produced by the pyrolysis of organic matter, many types of organic matter can be used including sawdust, woodchips, corn stalks, chicken manure, construction wastes, etc. under different pyrolysis conditions. These differences are expected to alter the biochars' physical and chemical properties and thus their ability to improve substrates, long term stability and sorption capabilities. Care must be taken to ensure that the biomass itself does not contain any contaminants (e.g. toxic metals, PAHs, PCBs). Thus, before this technology

is made commercially available and applied on a large scale, careful characterization of the feedstock and the biochar for parameters such as contaminants, organic matter, specific surface area, cation exchange, etc. (see IBI for full list) must be conducted.

The majority of the chemical analyses were conducted at the Analytical Services Unit (ASU) which is in the School of Environmental Studies at Queen's University (Kingston, ON). The ASU is accredited by the Canadian Association for Laboratory Accreditation (CALA) for specific tests listed in the scope of accreditation. Other analysis including greenhouse trials were conducted at The Royal Military College of Canada (Kingston, ON) by Mackenzie Denyes under the supervision of Dr. Barbara Zeeb in the Department of Chemistry and Chemical Engineering. The production conditions were characterized by *in situ* measurements at the Burt's Greenhouses heating facility by Dr. Darko Matovic, professor at the Department of Material and Mechanical Engineering at Queen's University (Kingston, ON).

2. Biochar Production

In this section a basic description of the production of biochar at Burt's Greenhouses is provided. The details of the Blue Flame boiler and the sampling probe are followed by the outline of the normal (heating) and biochar (pyrolysis) production mode.

2.1. Boiler and measurement equipment details

Gas sampling and internal temperature measurements were obtained by a combination probe that served the role of a suction pyrometer and a gas sampling device. The sketch of the probe is shown below (Figure 1). The sampling probe is made of standard steel and copper tubing, with the outer diameter of 42 mm (1.25" schedule 40 pipe), with the main body length of 3022 mm, and a triple layer ceramic tip with the outer diameter of 15 mm and the length of 180 mm. The tip has a side-facing hole oriented so that the suction of chamber gases was done from the bottom of the sampling probe tip.

Figure 1. Suction pyrometer and gas sampling probe sketch. The depth marker corresponds to the innermost position of the probe. It is aligned with the entry port for the "0" position.
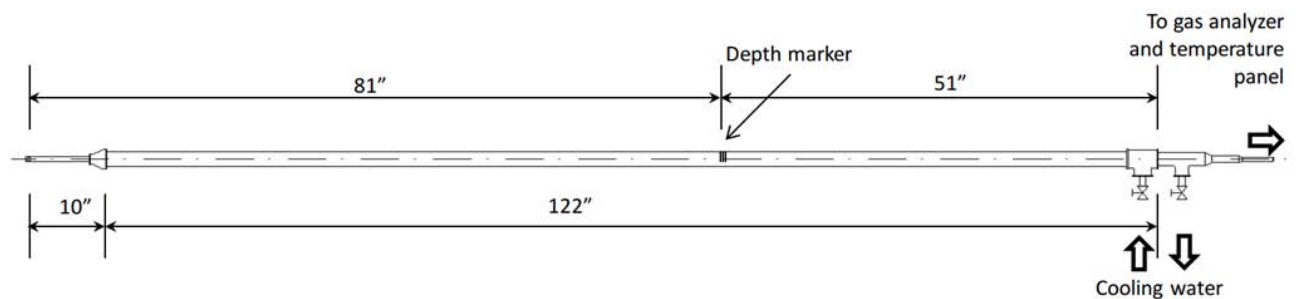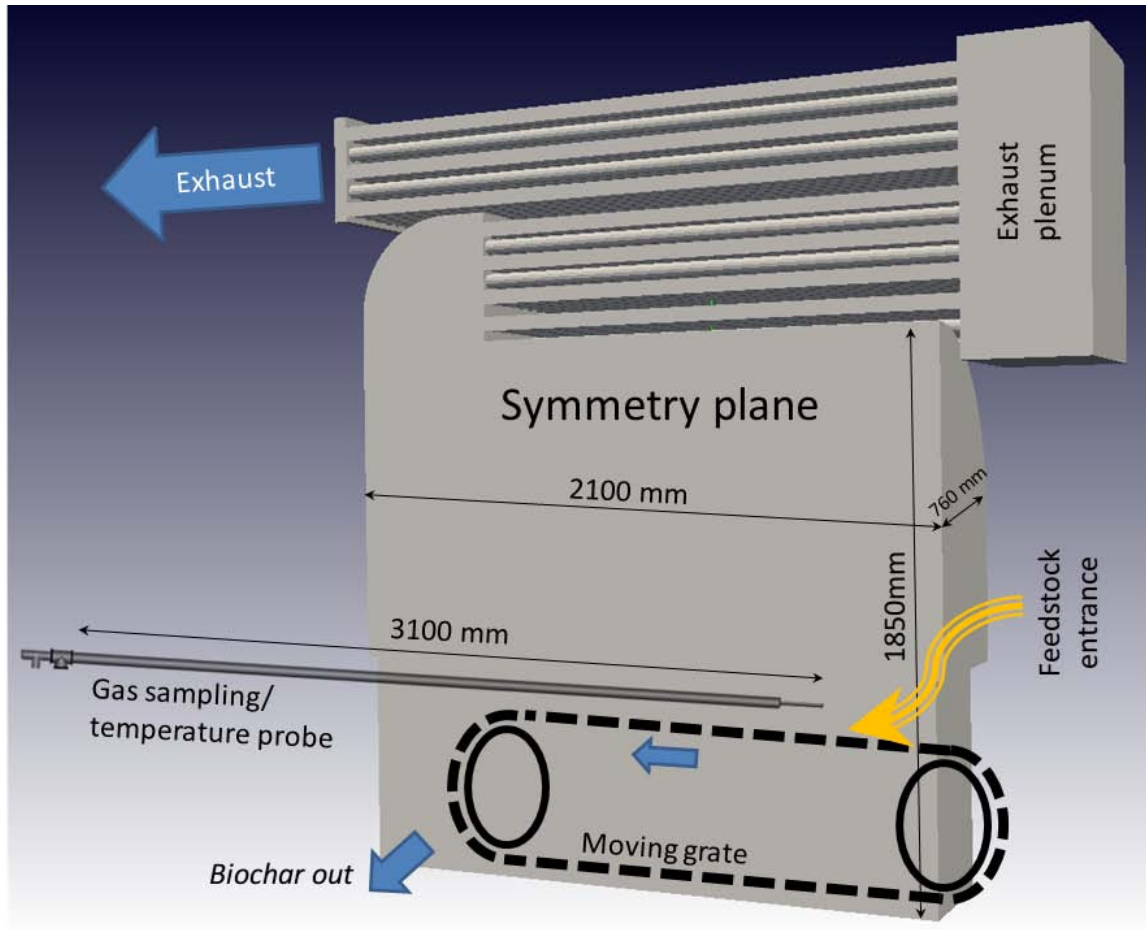
Figure 2. A Blueflame boiler shown as one half of the interior, viewed from the symmetry plane, with the probe and the moving grate sketch. The dimensions shown are approximate. The feedstock side of the moving grate extends into a box behind the boiler wall.

The overall layout of the BlueFlame boiler, adapted for biochar production, with the probe inserted, is shown in Figure 2. The figure shows the cutout of the boiler model, along the symmetry plane, with the 3D probe model inserted.

Gas and temperature were sampled ~20 cm above the biomass bed at five points extending 48 in (~1.2 m) from the moving grate end, as shown in Figure 3. Temperature measurements were done by K type thermocouple (chromel-alumel), connected to off-the-shelf multimeter with thermocouple input. The suction pyrometer thermocouple was shielded type with the stainless steel cladding 1.6 mm dia. The grate temperature was periodically measured by

the optic pyrometer, CEM model DT-9862 with temperature range of –50–2200°C and the spot to distance ratio of 1:50. Gas analysis was done by feeding the sampled gas to an IR gas analyzer Gasboard 3100P with measurement ranges (vol) of 0–40% for CO_2, 0–50% for CH_4, 0–10% for C_nH_m, 0–40% for CO, 0–50% for H_2 and 0–25% for O_2. The instrument precision, according to the manufacturer, is 2% for all gases except for hydrogen and oxygen, for which it I 3%.
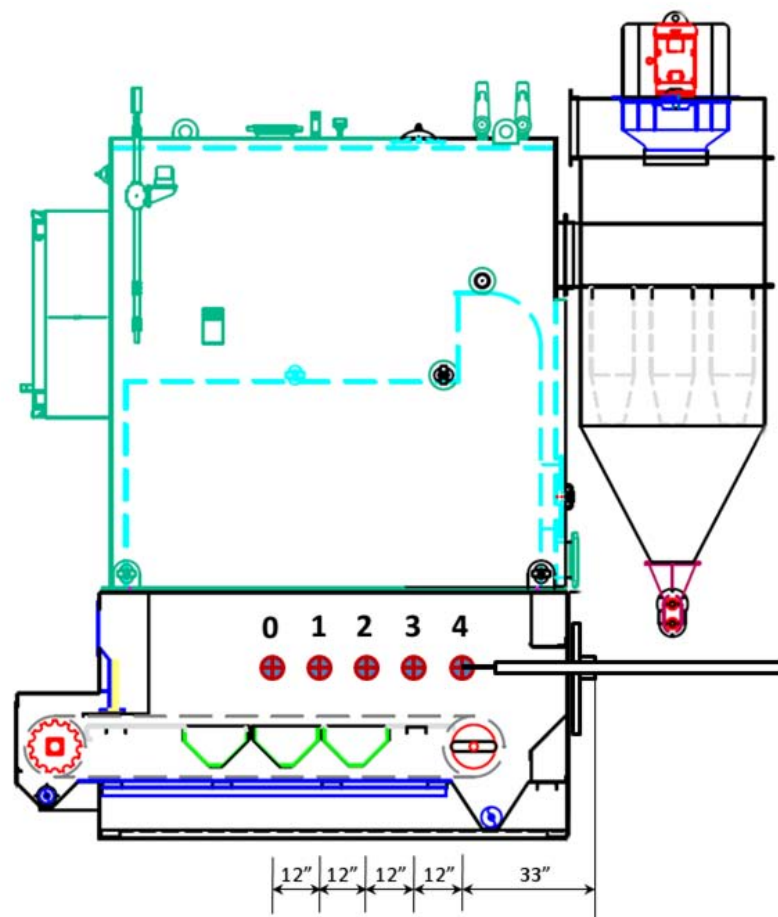

Figure 3. The sketch of BlueFlame boiler with the five measurement point locations indicated by circles with cross. The probe tip is shown at position 4, about 20 cm (8") above the moving grate end.

2.2. *Biochar production process*

The BlueFlame boiler is equipped with two sets of air inlets: the primary air inlets below the grate and the secondary inlets approximately in the middle of the main combustion chamber. In normal (combustion) operation regime, the primary air reacts with the fuel (coal or biomass) at the grate, partially combusting it and driving more volatile components out. This half-burnt gas mixture (rich in carbon monoxide) mixes with the secondary air and proceeds to a full combustion reaction while transferring heat to the water tubes located in two banks above the combustion chamber. The heat transfer is done through a cascade of two cross-flow heat exchangers, illustrated in the upper part of Figure 2. In the biochar production mode, the bottom air inlets are closed and the only air supply is provided at the secondary air level. Thus, the fuel rich gas, made of volatile biomass fraction is mixed with air above the moving fuel bed and combusts there. The process can be seen essentially as the pyrolysis process where the heat is provided by radiation from the hot top half of the combustion chamber, rather than by external heating, typical in a more classical pyrolysis setup. These two regimes are illustrated below (Figure 4) for the typical biochar-making mode (A) and for the standard combustion mode (B). The temperature and gas composition graphs below the sketches are taken from measurements on Jan. 5th and March 26th 2013. The temperature in the biochar-making mode reaches a maximum near the end of the moving grate, where no more heat is being consumed for evaporation of the volatile fraction. In contrast, in the normal combustion mode, the main combustion reaction occurs in the first half of the grate, where the temperature reaches its maximum. After that, mainly ash is transported, and consequently the temperature drops significantly.

Figure 4 also shows differences in gas concentration in the two production modes. In the biochar mode (A), there is a high CO and CO_2 concentration over most parts of the grate, indicating anaerobic evaporation of the volatiles. The rise of oxygen concentration near the grate end is in the zone where almost no volatiles are present, and the small amount of oxygen from the limited air supply is not consumed. In the combustion mode (B), most of the reaction is completed in the first half of the grate, characterized by the drop in CO and CO_2 concentrations and corresponding rise in oxygen concentration.
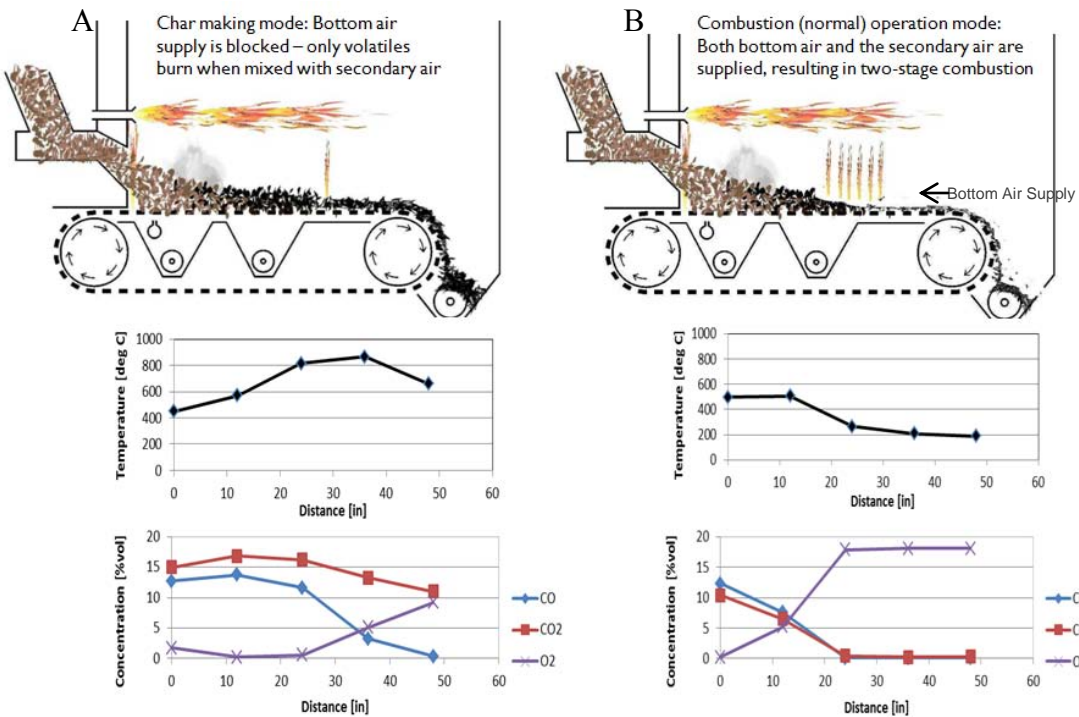

Figure 4. Pyrolysis conditions: A) Biochar-making mode: Bottom air supply is blocked – only volatiles burn when mixed with secondary air, and B) Combustion (normal) operation mode: Both bottom and secondary air are supplied, resulting in a two-stage combustion process.

Three feedstocks were used in the production of the biochar, producing six different biochars (Table 1) All three feedstocks used were analyzed as per the IBI guidelines. All three biomass feedstocks were from waste wood, however Old Burt's was made from used shipping pallets and construction wastes, and subsequent feedstocks were more carefully selected to ensure no contaminants were present.

Table 1: Burt's biochars characterized in this report.

Sample Name	Date Produced	Feedstock	Pyrolysis Temperature (^{o}C)
Old	2010	1	>700
New	2012	2	700
Low Temp	Jan 5th 2013	2	500
High Temp	Feb 7th 2013	2	>700
Third Feedstock	Feb 28th 2013	3	700
High Temp-2	March 12th 2013	3	>700

Details of gas sampling and temperature measurements will be presented in a separate report.

3. Characterization Methods

The six biochars produced were analyzed for all chemical and physical parameters described below with the exception of polycyclic aromatic hydrocarbons (PAHs) and proximate/ultimate analysis. For proximate/ultimate analysis, four samples were analyzed: Low, High, Standard Fuel and High 2. PAH analysis was carried out on Low, High, and Standard Fuel. These were chosen as representative of the biochars produced since 2012.

3.1 Chemical and Physical Properties

Cation exchange capacity (CEC) for all biochars was determined using the sodium acetate method for CEC described by Laird and Fleming (2008). The Brunauer–Emmett–Teller (BET) surface area of the biochars were measured by N_2 gas sorption analysis at 77 K in a relative pressure range from 0.01 to 0.10 using an ASAP 2000 surface area analyzer (Micromeritics, USA) after degassing at 120°C for a minimum of 2 h. The percent organic matter and moisture of the carbon amendments were determined using the loss on ignition procedure outlined by Nelson and Sommers (1996), and pH was determined as outlined in Ahmedna et al. (1997). Particle size distribution of all materials was determined via progressive dry sieving (in triplicate) adapted from ASTM D5158-98 (American Society for Testing and Materials (ASTM), 2005) using seven U.S. Standard sieves (4.7, 2.0, 1.0, 0.50, 0.25, 0.15, and 0.0075 mm).

Proximate and Ultimate analyses were conducted at Keystone Materials Testing Inc. based on methods: ASTM D3172-07a and D3176-09, Standard Practice for Proximate and Ultimate Analysis of Coal and Coke, respectively. PAHs were analyzed at Paracel Laboratories by solvent extraction and GC-MS based on EPA 8270.

Polychlorinated biphenyl (PCB) concentrations in biochar samples were analyzed via Soxhlet extraction. Samples were dried overnight in a vented oven at 25°C for approximately 12–18 h, and then ground with sodium sulphate and Ottawa sand. Decachlorobiphenyl (DCBP) was used as an internal surrogate standard. All samples were extracted in a Soxhlet apparatus for 4 h at 4–6 cycles per hour in 250 mL of dichloromethane. Biochar extracts were analyzed for total Aroclors, using an Agilent 6890 Plus gas chromatograph equipped with a micro-[63]Ni electron capture detector (GC/μECD), a SPB™-1 fused silica capillary column (30 m, 0.25 mm ID × 0.25 μm film thickness) and HPChem station software. The carrier gas was helium, at a

flow rate of 1.6 mL/min. Nitrogen was used as the makeup gas for the electron capture detector (ECD). Detection limits were 0.1 µg/g. All values were reported as µg/g dry weight.

Samples for metals (30 elements) were air-dried and ground to a fine powder with a mortar and pestle. Approximately 0.5 g of powdered sample was heated with 2 mL nitric acid and 6 mL hydrochloric acid overnight so that the volume was reduced to 1-2 mL. This solution was then made up to 25 mL with distilled, deionized water, filtered through a Whatman No. 40 filter paper and analyzed by a Varian Vista AX simultaneous inductively coupled plasma atomic emission spectrometer (ICP-AES). Although not all metals may be brought into solution by this procedure (some may be locked into silicate minerals), metals that are released are considered to be of greater environmental significance than are true total metals.

Analysis for mercury in biochar used cold vapour atomic absorption spectrophotometry. The instrumentation (DMA-80) allows for direct measurement was been designed to meet the criteria outlined in US EPA Method 7473.   Very small quantities of liquid or solid sample are required with little or no preparation. Samples were weighed into boats (quartz or nickel). The boats enter a chamber in the instrument where the sample is first dried and then thermally decomposed in a continuous flow of oxygen. The combustion products are carried off in the oxygen flow and are then further decomposed in a hot catalyst bed. Mercury vapors are trapped on a gold amalgamator tube and are subsequently desorbed for spectrophotometric quantitation at 254 nm.

Nutrient analysis of the biochar samples included KCl extractable nitrate, nitrite, and ammonia and formic acid extraction of phosphorus. For the nitrogen compounds, stock standards were prepared using potassium nitrate, sodium nitrite, and ammonium chloride. Dilute working standards were prepared on the day of analysis and quality control was maintained through the

analysis of a sample with a known concentration. Soil samples were extracted using a 2N KCl solution. When only analyzing for NO_2 and NO_3, 5 g of dried soil was used. If the analysis included NH_3, all three parameters were sampled from wet soils and a wet/dry ratio was calculated in order to estimate a 5 g dry sample. Each sample was weighed into a plastic vial and 25 ml of KCl was added. The vials were put on a rotating shaker for 30 min at 200 rpm. Samples were then filtered through P5 filter paper and analyzed on a SEAL Autoanalyzer. To extract the orthophosphate in the soil, a formic acid solution was used and the sample was shaken and filtered as above. The phosphorus content was measured spectrophotometrically at 882 nm on a SEAL autoanalyzer.

3.2 Biological Tests

3.2.1 Earthworm Avoidance

The soil invertebrate *Eisenia fetida* is used frequently as a terrestrial organism model in contamination experiments because this species is capable of surviving at high concentrations of organic contaminants, is very well researched, and is ecologically relevant in many areas of the globe (Belfroid et al., 1995; Denyes et al., 2012; Environment Canada (EC), 2007; Gomez-Eyles et al., 2011; Li et al., 2011; Paul and Ghosh, 2011; Zhang et al., 2000). Furthermore, soil invertebrates play an important role in the soil matrix, as they degrade organic matter, cycle nutrients, and transfer water. *E. fetida* were purchased from ` The Worm Factory` (Westport, ON), and stored in a healthy soil matrix comprised of peat moss and potting soil. The soil moisture was maintained ~30%. Worm selection for avoidance assays was based on the method described by Li et al. (2011), and worms ranging from 0.3-0.6 g were used.

Six avoidance wheels were constructed using a modified design from Environment Canada's Acute Avoidance Test (Environment Canada, 2004). Old Burt's biochar and New Burt's biochar were selected for avoidance assays. Both biochar types were mixed separately using a spade and bucket with potting soil at a rate of 2.8% (by weight). Each of the six compartments was filled with 120 g of soil or soil/biochar mixture, with every other compartment serving as an unamended control (Figure 5).

Figure 5. Earthworm avoidance wheel.

During tests, wheels were covered with aluminum foil to prevent worm escape. Amendments for each soil were run in triplicate and each run used ten (*n*=10) worms, exposed for a period of 48 hours. Avoidance wheels were kept under controlled greenhouse conditions (20-25°C), and soil moisture was monitored during 48-hour long exposures. After trials were completed, the worms were placed in a separate vessel, and not used for further testing, in an effort to prevent cross contamination of biochar types.

3.3.2 Germination Tests

Seed germination testing was adapted from the method outlined by Solaiman et al. (2012) (Solaiman et al., 2012). Briefly, five *Cucurbita pepo* spp. *pepo* (pumpkin) seeds and 50 *Medicago sativa* (alfalfa) seeds were sown in Petri dishes (8.5 cm in diameter). Each biochar was tested in triplicate for both pumpkin and alfalfa seed types. Filter paper and potting soil were used as controls, and these were also completed in triplicate. Each Petri dish contained either 3 g of the biochar, 10 g of potting soil, or 1 piece of filter paper. The amounts were based on volume in the Petri dish so that each dish was ~50% full (by volume). All Petri dishes received 15 mL of water and were covered with lids. Temperature was maintained at 27ºC (±6ºC) and seeds were germinated under a 14:10 h (day:night) fluorescent photoperiod. Observations were recorded at seven days. Root length of germinated seeds was measured in fresh roots using a ruler, and summed for each Petri dish (cm/Petri dish).

4. Results

4.1 Summary

A summary of all results including a comparison to the criteria set by the IBI (International Biochar Inititive (IBI), April 2013) can be found in Tables 2 (New, High, Low, Standard Fuel and High-2) and 3 (Old Burt's biochar). Full physical, chemical and biological characterization results are located in the appendix. **All biochars and feedstocks used in 2012 and 2013 (Table 2) were well within the criterion set by the IBI and there were little differences among biochars.** Old Burt's biochar (Table 3) which was the first biochar submitted for testing was made from used shipping pallets and construction wastes and was determined to have elevated levels of the metals arsenic, chromium, copper, and lead. Old Burt's biochar also had the lowest levels of organic carbon (63.2%) as determined by loss on ignition. This biochar had the highest levels of extractable phosphorus (850 mg/kg) and CEC (34.8 cmol/kg), as well as

the highest percentage of fine particles (<0.5 mm, 48%). Old Burt's biochar was also the only biochar to fail the germination test and it was determined that *Eisenia fetida* significantly avoided the 2.8% amendment, whereas they preferred the 2.8% amendment of the New Burt's biochar.

4.2 Test Category A: Basic Biochar Utility Properties

Biochar production via pyrolysis is essentially the carbonization of biomass. The organic carbon fraction of biochar feedstocks is comprised of biologically degradable carbon-containing compounds such as sugars, starches, proteins, fats, cellulose and lignocellulose, which are thermochemically degradable. This fraction does not include inorganic carbonates such as calcium and magnesium. The carbonization process allows for the transformation of these structured organic molecules of wood and cellulose materials into carbon, or carbon-containing residues, which are often aromatic in nature (Bakker, 2012; Demirbas, 2009; McBeath and Smernik, 2009; Preston and Schmidt, 2006; Schmidt and Noack, 2000). Carbonization is obtained through the elimination of water and volatile substances from the biomass feedstock, due to the action of heat during the pyrolysis process (Yaman, 2004). All of the biochars produced at Burt's greenhouses contained a relatively low moisture percentage (< 5%) with the exception of Old Burt's biochar. Also all biochars are categorized as Class A (> 60%) in terms of their composition of organic carbon as a result of complete carbonization of the feedstock material via pyrolysis. Thus due to the high percentage of organic carbon, all biochars produced have a low percentage of ash (< 2.5%), which is the inorganic or mineral component of the biochar (International Biochar Inititive (IBI), April 2013). Although these low ash biochars do not provide substantial amounts of nutrients directly to the soil as do their high-ash biochar (often made from manures and bones) counterparts; the carbon content of these biochars is much

higher and therefore they have higher long-term nutrient retention functions (Brewer et al., 2009; Cantrell et al., 2012; Enders et al., 2012).

The hydrogen to carbon ratio (H:C) is a term often used to measure the degree of aromaticity and maturation of the biochar, which has been linked to their long term stability in the environment (Schmidt and Noack, 2000). For biomass feedstock containing cellulose and lignin, the H:C ratios are approximately 1.5. However, pyrolysis of these materials at temperatures greater than $400^{\circ}C$ is expected to produce biochars with H:C rations less than 0.5. It has been reported that biochars with an H:C ratio < 0.1 indicated a graphite-like structure (Krull et al., 2009). All biochars in this report have H:C rations less than 0.02, indicating that these biochars are highly aromatic in nature and will have long term stability in the environment.

Soil pH is a measure of soil acidity, and unfortunately many agricultural soils in Canada and worldwide are acidic (pH < 7), meaning that they are not ideal for crop growth. Biochars with an alkaline pH (> 7), such as those being produced at Burt's Greenhouses, can be added to acidic soils to increase the soil pH to levels that are more appropriate for plant growth. Another important soil characteristic for plant growth is particle size distribution (PSD). Biochars that have a higher percentage of coarse particles may favorably increase soil aeration and prevent biochar movement into the subsoil over time, thereby increasing the length of time biochar offers benefits to plant growth (Atkinson et al., 2010). However, smaller particle sizes are favored for biochars that are being produced for remediation purposes with the intent to sorb contaminants and minimize their bioavailability (Denyes et al., 2013; Sun et al., 2009). Smaller particles sizes generally increase the external surface area, and thus the ability of contaminants to access pore space for binding (Sun and Ghosh, 2007). Additionally, smaller particle sizes are favored for sorption as this increases the number of particles per unit volume of soil (Hale and Werner,

2010). The biochars named New-, High- and Standard Fuel Burt's biochar have a high proportion of coarse particles (~98%), and a low proportion of fine particles (~2%). The biochar produced at a slightly lower temperature had 89% coarse and 11% fine particles sizes. All of these biochars may offer substantial improvements to soil texture and aeration especially in degraded or clay type soils. The Old Burt's biochar had a PSD that differed substantially from the others, having 52% coarse and 48% fine particles. This biochar may be preferable for use at contaminated sites, where contaminant sorption is the primary focus.

4.3 Test Category B: Toxicant Reporting

Biological testing of biochar is important to assess the toxicity (if any) of these materials to soil invertebrates and plants. To date, there is little existing literature on the potential impact of biochar amendment on terrestrial organisms and their associated response, and often the literature that does exist presents conflicting results. Earthworms perform many essential functions in soils, including decomposition, nutrient mineralization, and soil structure improvement, and their ability to perform these functions can be inhibited upon exposure to contaminants (and in certain cases biochar) (Li et al., 2011). All biochars in this study with the exception of Old Burt's biochar showed no detrimental effects on the earthworm *Eisenia fetida* as assessed by earthworm avoidance. Germination assays are a technique used to evaluate the toxicity of a particular material to plants. As with the earthworm avoidance studies, the only biochar that showed toxicity to plants was the Old Burt's biochar; - all other biochars evaluated showed no detrimental effects to seed germination.

Although some types of biochar have the potential to sorb organic contaminants and reduce their toxicity in the environment, careful characterization of the biochar is required to

ensure that it does not contain harmful contaminants such as PAHs, PCBs, and metals as a result of contaminated feedstocks or pyrolysis conditions. None of the biochars produced at Burt's greenhouses had PAH concentrations exceeding IBI guidelines which is consistent with a study by Hale et al. (2012, unpublished data) who examined more than 40 biochars produced from a wide range of pyrolysis conditions. They determined that all the biochars, except the one produced from gasification, were well within regulatory guidelines (Hilber et al., 2012). Biochars could become contaminated with PCBs if the biomass material used for pyrolysis was contaminated with PCBs from paint, transformer fluid, or plasticizers. Although Old Burt's biochar shows a slightly elevated concentration of PCBs, it is not believed that this came from the source material or production process at Burt's Greenhouses, and all other biochars were well below the IBI guideline. The sample of Old Burt's biochar came from the greenhouse at RMC where there are ongoing experiments with PCB-contaminated soil and occasionally dust is produced which may have cross-contaminated the sample. Old Burt's biochar was determined to have elevated levels of the metals arsenic, chromium, copper, and lead, however none of the biochars produced from the other two biomass materials contained metals above IBI guidelines. Old Burt's biochar was produced from used shipping pallets and construction wastes which is likely the source of the metal contamination. Although Old Burt's biochar would not be suitable for use in agricultural soils or home gardens, all other biochars could be used for these purposes.

4.4 Test Category C- Biochar Advanced Analysis and Soil Enhancement Properties

Mineral nitrogen (ammonium and nitrate) along with organic nitrogen, nitrite, nitrous oxide, nitric oxide and inorganic nitrogen gas are the chemical forms of nitrogen present in the environmental nitrogen cycle, which converts nitrogen from one form to another via microbial activity. Nitrous oxide (N_2O), although naturally present in the Earth's atmosphere, has become

an environmental pollutant due to increasing concentrations as a result of human activities in agriculture, fossil fuel combustion, wastewater management, and industrial processes (U.S. Environmental Protection Agency (EPA), 2013). Also because N_2O molecules stay in the atmosphere for a very long period of time before being degraded, the negative environmental impact of nitrous oxide is approximately 300 times that of carbon dioxide. Nitrous oxide is produced in a process called nitrification where ammonium is converted biologically to nitrite and then via an oxidation reaction to nitrates. The agriculture industry relies heavily on nitrogen containing synthetic fertilizers and is the largest source of N_2O emissions. Nitrous oxide is also emitted during the breakdown of nitrogen in livestock manure and urine. Nitrates (NO_3) are also released from these agricultural activities and are known to leach into ground and surface waters contaminating drinking water sources and posing a risk to human health (U.S. Environmental Protection Agency (EPA), 2012). Although sorption of ammonium and nitrate to biochar has been cited as a possible mechanism for the suppression of soil N_2O production and nitrate leaching, it is important to consider the mineral nitrogen (ammonium and nitrate) composition of the biochars themselves. Biochars containing a high concentration of ammonium and nitrate if applied on a large scale in remediation or agricultural activities could increase the atmospheric N_2O concentration and further contaminate drinking water sources with nitrates. None of the biochars studied contained elevated amounts of ammonium or nitrate.

Phosphorus is an essential component for many physiological processes related to proper energy utilization in both plants and animals. It is also a component of animal wastes and synthetic chemicals used in agriculture. Phosphorus is of concern in surface waters because it can lead to eutrophication. Therefore, biochars too high in phosphorus could present a concern in terms of surface water contamination. However, biochars with a reasonable level of available

phosphorus will act as an important plant fertilizer. In Ontario, soils containing 15-30 mg/kg phosphorus are considered low, 31-60 mg/kg moderate, and 61-100 mg/kg high (Ontario Ministry of Agricultural Food and Rural Affairs (OMAFRA), 2005). Old Burt's biochar was highest in available phosphorus at 850 mg/kg and may not be suitable for adding to soils already classified as high in phosphorus. However, all other biochars tested had a much lower amount of available phosphorus and would not be expected to cause eutrophication problems when added at rates up to 10% (w/w).

Volatile matter refers to the components of biochar, except for moisture, which are liberated at high temperature in the absence of air (i.e. during pyrolysis). This is usually a mixture of short and long chain hydrocarbons, aromatic hydrocarbons and some sulfur. Volatile matter was determined via proximate analysis which also determines the moisture and ash content of biochars (discussed in section 4.2). The volatile content affects the stability of the material (Zimmerman, 2010), N availability and plant growth (Deenik et al., 2010). In theory, biochars high in volatile matter are less stable and have a higher proportion of labile carbon that provides energy for microbial growth and limits the availability of nitrogen necessary for plant growth. A study by Deenik et al., (2010) considered 35% volatile matter to be high (inducing nitrogen deficiency), and 10% volatile matter to be low. All biochar in this report contained less than 20% volatile matter, and hence would not be expected to limit plant growth. Proximate analysis determination of volatile matter is most useful for biochars with low ash concentrations such as those biochars produced at Burt's Greenhouses.

Specific surface area (SSA) is a measure of the porosity of a biochar. It includes not only the external biochar surface area, but also the surface area within the pore spaces and is an important characteristic used to predict the ability of a biochar to sorb organic contaminants.

Many studies have reported that organic contaminants such as polyaromatic hydrocarbons (PAHs) (Oleszczuk et al., 2012) and polychlorinated biphenyls (PCBs) (Denyes et al., 2012; Denyes et al., 2013) are sorbed particularly strongly to biochar. This has been attributed to π-π interactions (attractive, non-covalent binding) between the aromatic ring(s) of the contaminant and those of the biochar (Sander and Pignatello, 2005). Activated carbon (AC) is a charcoal-like material that is treated with steam, carbon dioxide or other chemical reagents during its production to maximize its porosity. It therefore has a SSA much higher than most biochars, but is also a more expensive material (Marsh and Rodríguez Reinoso, 2006). Currently AC is the standard material used for contaminant sorption and remediation technologies (Ghosh et al., 2011), however, there are an increasing number of studies available which report the potential of biochar to serve as an alternative, more cost effective and greener technology than AC (Chai et al., 2012; Denyes et al., 2012; Denyes et al., 2013). Although all the of biochars presented in this report have SSAs in the 300 m^2/g range (i.e. much less than that of AC; ~800 m^2/g), as outlined in sections 5.1 and 5.2, Old Burt's and New Burt's biochar have both shown significant potential to serve as a soil amendment for the remediation of PCBs..

Cation exchange capacity (CEC) is a measure of the number of cations (positively charged ions) that a soil particle is capable of holding at a given pH. The ability of the soil to hold cations is due to electrostatic interactions with negatively charged sites on the surface of a particle, such as hydroxyl (OH^-) and carboxyl groups (COO^-) (Chan et al., 2007; Liang et al., 2006). It gives an indication of the potential of the soil to hold plant nutrients, by estimating the capacity of the soil to retain cations from fertilizers. Also, many environmental contaminants such as lead, cadmium and zinc have positive charges; therefore soils with a high CEC may function to prevent the leaching of these contaminants into drinking water sources. Biochars

have been reported to increase the CEC of soils, due to the slow oxidation of the biochar surface which increases the number of negatively charged sites, and therefore may reduce fertilizer requirements and immobilize positively charged contaminants in soils (Liang et al., 2006). Typically, sandy soils have a CEC between 1-5 cmol/kg, loam soils 5-15 cmol/kg, clay type soils >30 cmol/kg and organic matter 200-400 cmol/kg. The methods for determining the CEC of biochar are still in their infancy and therefore should be considered in relative terms. The CEC of the biochars produced at Burt's Greenhouses are higher than the CEC of PCB-contaminated soils (Denyes et al., 2012), but lower than compost amended soils.

Table 2. Summary Criteria and Characteristics for New, High, Low, Standard Fuel and High-2 Burt's Biochars and Feedstocks

Requirement	IBI Criteria	Biochar Range	Feedstock Range	Unit
Test Category A- Basic Biochar Utility Properties - Required for All Biochars				
Moisture	Declaration	<0.1-4.3		%
Organic Carbon	Class 1 $\geq$ 60% Class 2 $\geq$ 30% Class 3 $\geq$ 10 < 30%	96.2-97.8 (LOI) 92.44-97.93(Pro/Ult)		%
$H:C_{org}$	0.7 max	0.01-0.02		Ratio
Total Ash	Declaration	1.38-2.26		%
Total N	Declaration	0.28-1.06		%
pH	Declaration	8.4-9.6		pH
Particle Size Distribution	Declaration	86-98 1.3-14		% Coarse % Fine
Test Category B: Toxicant Reporting- Required for All Feedstocks				
Germination	Pass/Fail	Pass		
Earthworm Avoidance	Declaration	No Avoidance		
Polyaromatic Hydrocarbons (PAHs)	6-20	<2.0		mg/kg
Polychlorinated Biphenyls (PCBs)	0.2-0.5	<0.1		mg/kg
Arsenic	12-100	<1.0	<1.0	mg/kg

Cadmium	1.4-39	<1.0	<1.0	mg/kg
Chromium	64-1200	<2.0	<2.0-2.6	mg/kg
Cobalt	40-150	<1.0	<1.0	mg/kg
Copper	63-1500	3.6-6.5	<2.0-5.9	mg/kg
Lead	70-500	<2.0-2.7	<2.0-8.1	mg/kg
Mercury	1000-17000	<5.0-294		ng/g
Molybdenum	5-20	<2.0	<2.0	mg/kg
Selenium	1-36	<10	<10	mg/kg
Zinc	200-7000	5.6-56.2	7.8-30.5	mg/kg
Chlorine	Declaration			mg/kg
Sodium	Declaration	137-878	<75-770	mg/kg

Test Category C: Biochar Advanced Analysis and Soil Enhancement Properties- Optional for All Biochars

Mineral N (Ammonium and Nitrate)	Declaration	<0.2-6.1		mg/kg
Total Phosphorus	Declaration	69.5-276	52.5-74	mg/kg
Available Phosphorus	Declaration	9-80		mg/kg
Volatile Matter	Declaration	12.47-19.09		%
Specific Surface Area	Declaration	244-428		m^2/g
Cation Exchange Capacity	Declaration	11.1-17.1		cmol/kg

Table 3. Summary Criteria and Characteristics for Old Burt's Biochar and Feedstock

Requirement	IBI Criteria	Biochar Range	Feedstock Range	Unit
Test Category A- Basic Biochar Utility Properties - Required for All Biochars				
Moisture	Declaration	20		%
Organic Carbon	Class 1 ≥ 60%	63.2 (LOI)		%
	Class 2 ≥ 30%			
	Class 3 ≥ 10 < 30%			
H:C$_{org}$	0.7 max			Ratio
Total Ash	Declaration			%
Total N	Declaration			%
pH	Declaration	9.3		pH
Particle Size Distribution	Declaration	52		% Coarse
		48		% Fine
Test Category B: Toxicant Reporting- Required for All Feedstocks				
Germination	Pass/Fail	Fail		
Earthworm Avoidance	Declaration	Avoided		
Polyaromatic Hydrocarbons (PAHs)	6-20			mg/kg
Polychlorinated Biphenyls (PCBs)	0.2-0.5	1.2		mg/kg
Arsenic	12-100	167	<1.0	mg/kg
Cadmium	1.4-39	<1.0	<1.0	mg/kg
Chromium	64-1200	206	<20	mg/kg
Cobalt	40-150	5.3	<5.0	mg/kg
Copper	63-1500	558	<5.0	mg/kg
Lead	70-500	314	<10	mg/kg
Mercury	1000-17000	<5.0		ng/g
Molybdenum	5-20	<2.0	<2.0	mg/kg
Selenium	1-36	<10	<10	mg/kg
Zinc	200-7000	498	<15	mg/kg
Chlorine	Declaration			mg/kg
Sodium	Declaration	6460	<75	mg/kg

Test Category C: Biochar Advanced Analysis and Soil Enhancement Properties- Optional for All Biochars

Mineral N (Ammonium and Nitrate)	Declaration	2.6	mg/kg
Total Phosphorus	Declaration		mg/kg
Available Phosphorus	Declaration	850	mg/kg
Volatile Matter	Declaration		%
Specific Surface Area	Declaration	373.6	m^2/g
Cation Exchange Capacity	Declaration	34.8	cmol/kg

5. Field and Greenhouse Trials

The Royal Military College of Canada and Queen's University first began working with Burt's biochar in 2010. The primary objectives of these trials were to immobilize contaminants in soil while simultaneously improving the soil quality. This work is described in detail in two papers published in 2012 and 2013 (Appendix B).

5.1 Preliminary Greenhouse Experiment

Briefly, in a preliminary greenhouse experiment, highly PCB-contaminated industrial soil (136 µg/g) was amended with 0.2, 0.7, 2.8 and 11.1% Old Burt's biochar. The addition of 2.8% (by weight) biochar to the contaminated soil reduced PCB root concentrations in pumpkin plants (*Cucurbita pepo* ssp. *pepo*) by 77%. At 11.1% biochar, even greater reductions of 89% were recorded, while a shoot reduction of 22% was observed. PCB concentrations in *Eisenia fetida* tissue were reduced by 52% and 88% at 2.8% and 11.1% biochar, respectively. Biochar addition at 11.1% also significantly increased shoot weights of the pumpkin plants by 90% and improved worm survivorship 17.5 fold compared to the plants and worms exposed solely to PCB-contaminated soil (Denyes et al., 2012).

5.2 In situ experiment at a PCB-Contaminated Brownfield Site

In 2011, a field experiment was implemented at a PCB-contaminated Brownfield site in Etobicoke, ON. The performance of Old Burt's biochar in reducing PCB uptake into plants was compared to that of another biochar and granular activated carbon (GAC). The addition of GAC at ~3% to sediments and soils is already an acceptable form of remediation in both Europe and the United States (Ghosh et al., 2011). The results showed that the Burt's biochar performed statistically equal to GAC, and PCB concentrations in *Cucurbita pepo* root tissue were reduced by 74%, 72% and 64%, with the addition of 2.8% GAC, Burt's biochar and BlueLeaf biochar, respectively (Denyes et al., 2013). In a complimentary greenhouse experiment, pumpkins grown in PCB-contaminated soil amended with 2.8% Burt's or BlueLeaf biochar grew larger (97% and 100%, respectively) than the control pumpkins and these treatments produced *C. pepo* plants that were 72% and 75% larger than the *C. pepo* plants grown in the 2.8% GAC amendment.

Given that in both these studies (Denyes et al. 2012 and 2013), the biochars offered agronomic and environmental benefits, significantly reduced contaminant uptake, and performed statistically as well as GAC, it was concluded that biochar may offer a lower cost, greener alternative to GAC amendment for soil remediation.

5.3 Ongoing Experiments

For the past two growing seasons (2012-2013) research has been conducted at Point Pelee National Park which is heterogeneously contaminated with DDT (dichlorodiphenyltricloroethane). The performance of New Burt's biochar is being compared to another biochar and GAC. This project includes germination and earthworm avoidance studies, as well as toxicity testing and characterization of the microbial communities. Other experiments

utilizing biochar produced from Burt's Greenhouses are also underway at sites contaminated with high cadmium and salt concentrations.

Acknowledgments

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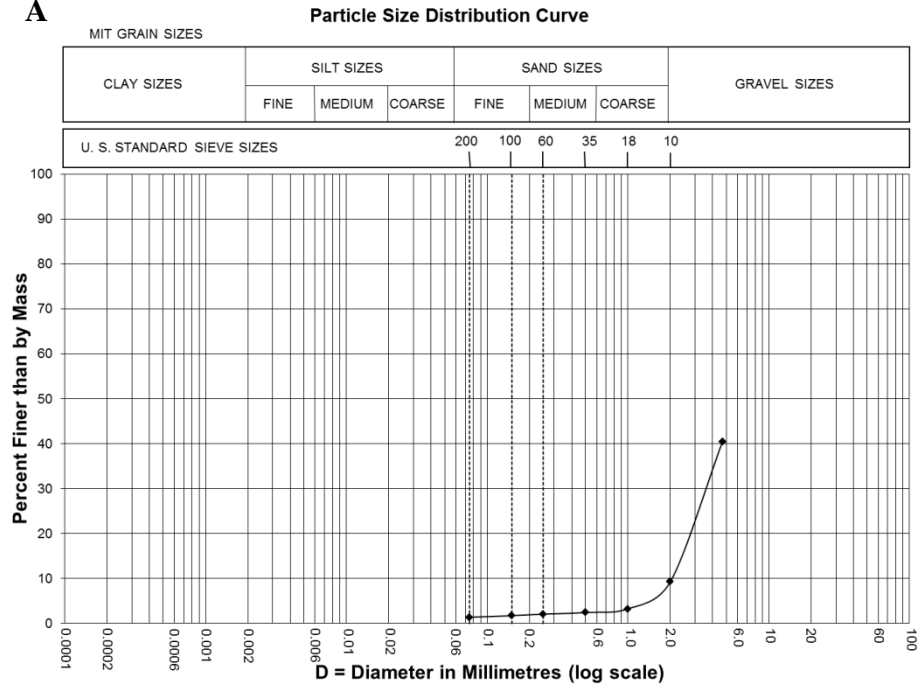
Appendices:

Denyes MJ, Langlois VS, Rutter A, Zeeb BA. The use of biochar to reduce soil PCB bioavailability to *Cucurbita pepo* and *Eisenia fetida*. Sci Total Environ 2012;437:76-82.

Denyes MJ, Rutter A, Zeeb BA. *In situ* application of activated carbon and biochar to PCB-contaminated soil and the effects of mixing regime. Environmental Pollution 2013;182:201-8.

Table A-1. Summary of Physical Characterization

Sample	Feedstock	Pyrolysis Temperature	Organic Matter (LOI)	pH	CEC	PSD Coarse	PSD Fine	SSA
		°C	%		cmol/kg	%	%	m^2/g
Old	1	>700	63.2	9.3	34.8	51.7	48.3	373.6
New	2	700	97.8	9	16	98.7	1.3	324.6
Low Temp	2	500	96.7	8.7	15.9	86.2	13.8	336.9
High Temp	2	>700	97.9	8.4	11.1	98.1	1.9	419.5
Third Feedstock High Temp	3	700	96.2	9.6	13.2	97.6	2.4	244.4
High Temp-2	3	>700	97.1	9.1	17.1	97.9	1.9	428

A

Particle Size Distribution Curve

MIT GRAIN SIZES

CLAY SIZES	SILT SIZES			SAND SIZES			GRAVEL SIZES
	FINE	MEDIUM	COARSE	FINE	MEDIUM	COARSE	

U. S. STANDARD SIEVE SIZES	200	100	60	35	18	10

Percent Finer than by Mass

D = Diameter in Millimetres (log scale)

B

Particle Size Distribution Curve

MIT GRAIN SIZES

CLAY SIZES	SILT SIZES			SAND SIZES			GRAVEL SIZES
	FINE	MEDIUM	COARSE	FINE	MEDIUM	COARSE	

U. S. STANDARD SIEVE SIZES	200	100	60	35	18	10

Percent Finer than by Mass

D = Diameter in Millimetres (log scale)

32

C

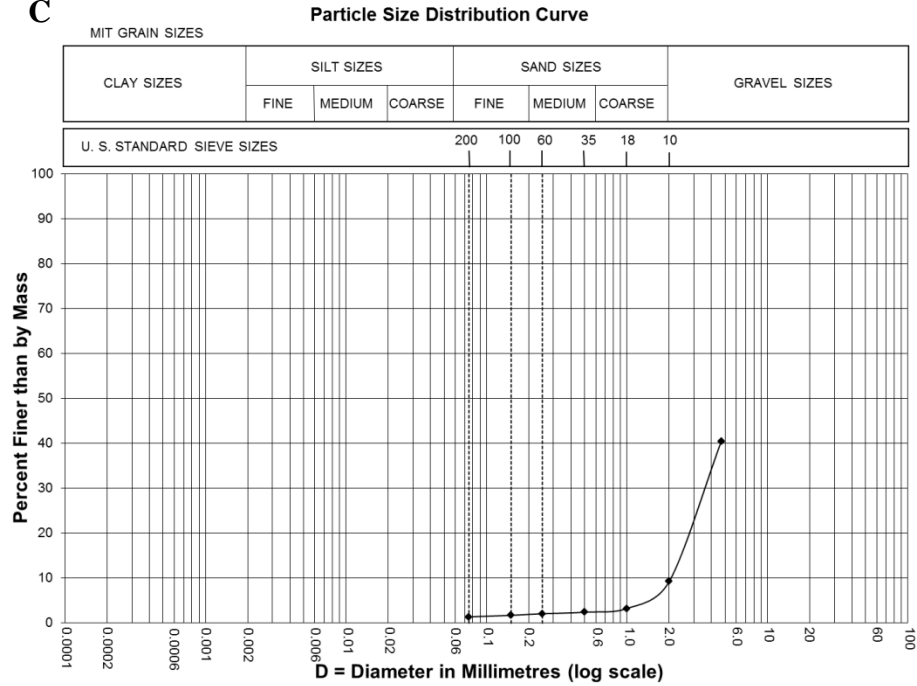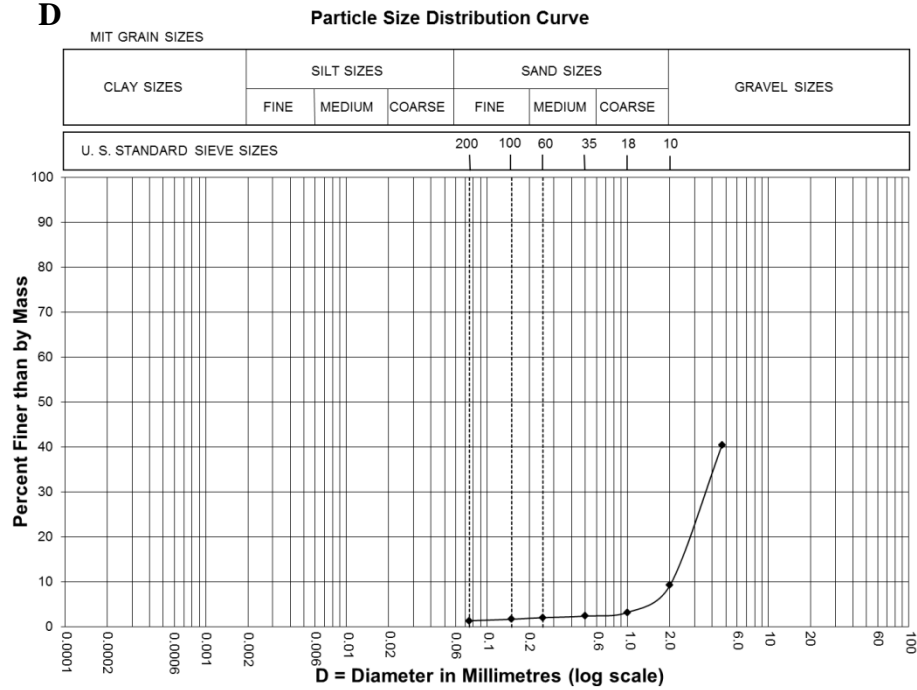Particle Size Distribution Curve

D
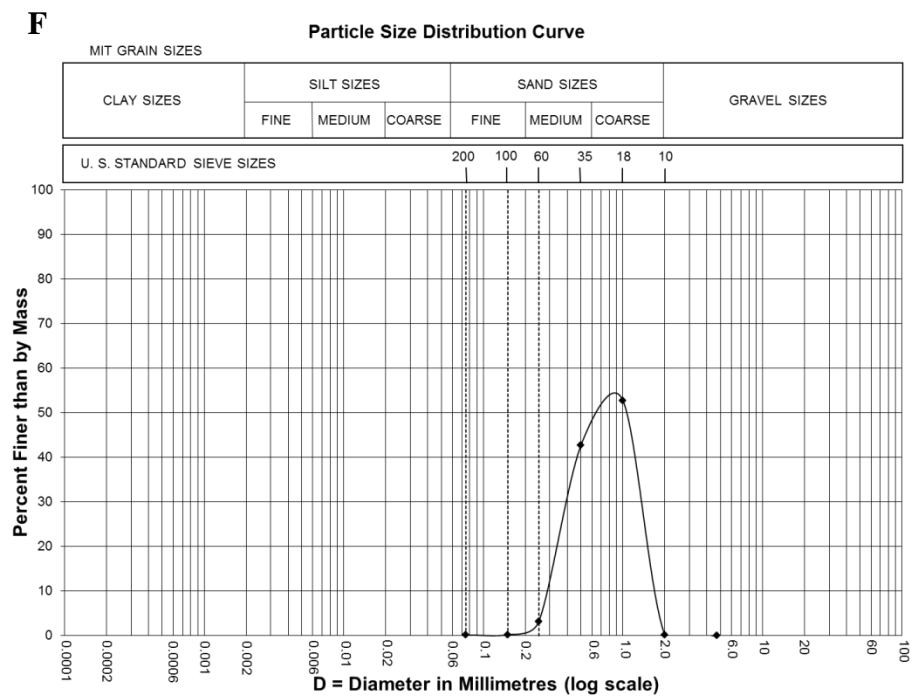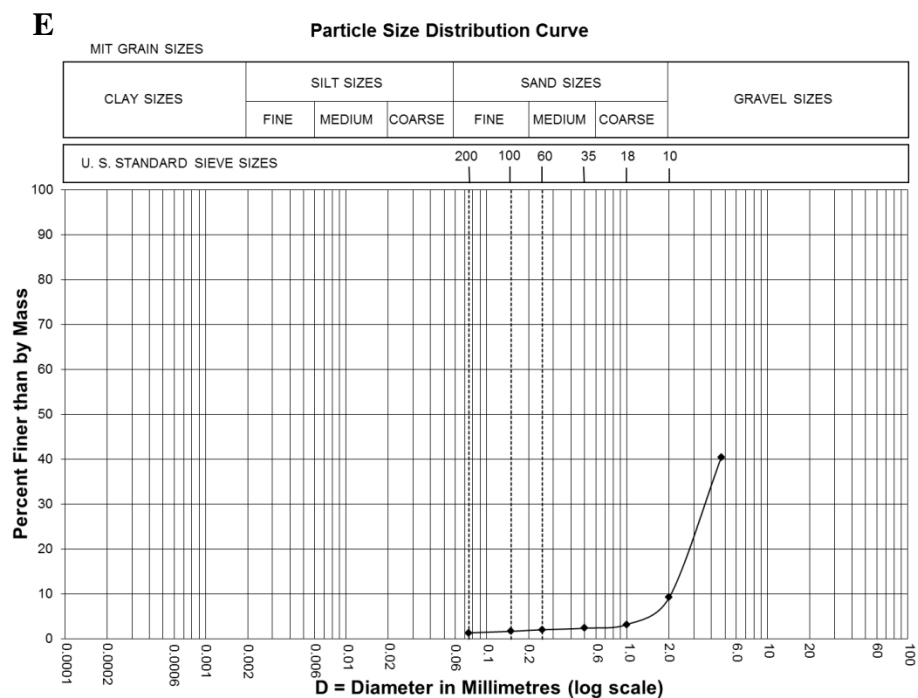

Particle Size Distribution Curve

Figure A-1. Particle Size Distribution Curves of A) Old, B) New, C) High, D) Low, E) Standard Fuel, F) High-2 Burt's Biochars. The average of triplicates are presented.

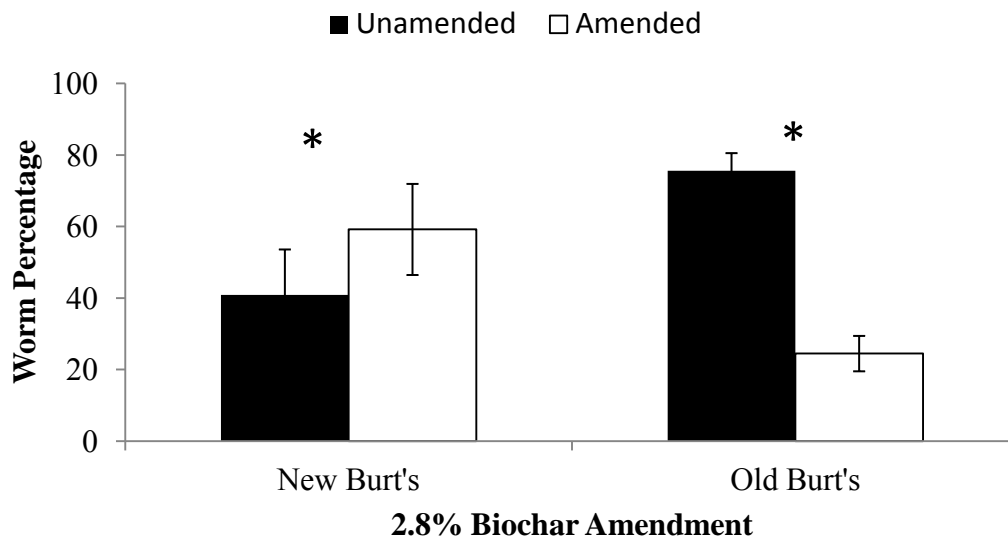**Figure A-2 .** Earthworm avoidance assay of Old and New Burt's biochars. * indicates a significant difference between unamended potting soil and potting soil amended with 2.8% of either biochar ($p < 0.05$).
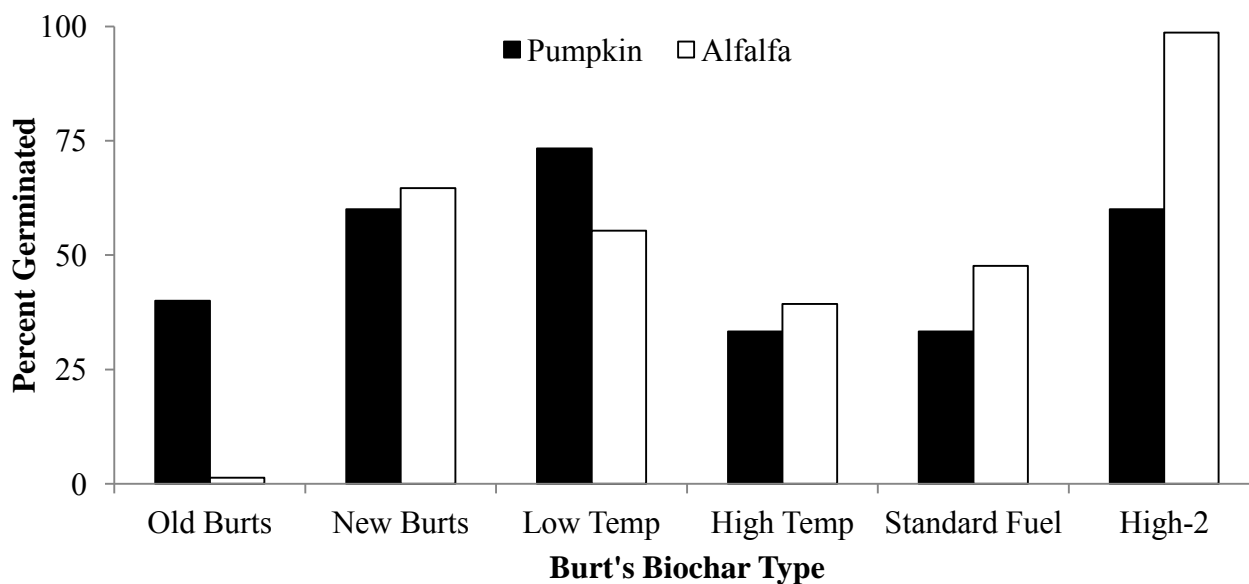

Figure A-3 . Percent germination of two different plant species; pumpkin (*Cucurbita pepo* spp. *pepo*) and alfala (*Medicago sativa*) grown in triplicate in various Burt's biochars for seven days.

Client:	FEDDEV	**Report ID:**	Burts Greenhouses-1 various
	Burts Greenhouses	**Date Reported:**	October-13

Report of Analysis
Results relate only to the items tested

Sample	pH	Organic Matter %	Cation Exchange (cec) cmol/kg	Moisture %
ASU 14347 Burts Old	9.3	63.2	34.8	20
ASU 14347 Burts New	9.0	97.8	16.0*	4.3
ASU 14538 Burts high temp	8.7	96.7	15.9	<0.1
ASU 14538 Burts low temp	8.4	97.9*	11.1	1.0
ASU 14565 Standard Fuel Char	9.6	96.2	13.2*	0.3
ASU 14573 High 2	9.1	97.1	17.1	0.2
ASU 14565 Ash	-	-	22.0	-
ASU 14455 Feedstock summer 2012 wood	-	99.8	-	-
ASU 14455 Feedstock October 2012 wood	-	99.9*	-	-
ASU 14564 Coarse wood	-	99.6	-	-
ASU 14564 Fine wood	-	99.4*	-	-

Laboaratory QA/QC

Sample	pH	Organic Matter %	Cation Exchange (cec) cmol/kg	Moisture %
ASU 14347 Burts New	-	-	19.9	
ASU 14347 Burts New	-	-	12.0	
ASU 14538 Burts low temp	-	97.9	-	
ASU 14538 Burts low temp	-	97.8	-	
ASU 14565 Standard Fuel Char	-	-	5.6	
ASU 14565 Standard Fuel Char	-	-	20.8	
ASU 14455 Feedstock October 2012 wood	-	99.9	-	
ASU 14455 Feedstock October 2012 wood	-	99.9	-	
ASU 14564 Fine wood	-	99.2	-	
ASU 14564 Fine wood	-	99.6	-	

* Average result of duplicates

Prepared by: _Paula Whitley._   Authorization _A. Nutter_

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Client:	FEDDEV	**Report ID:**	Burts Greenhouses-2 PCB and Mercury
	Burts Greenhouses	**Date Reported:**	October-13

Report of Analysis
Results relate only to the items tested

Sample	PCB ug/g	Mercury ng/g
ASU 14347 Burts Old	1.2*	<5.0
ASU 14347 Burts New	<0.1	<5.0
ASU 14538 Burts high temp	<0.1	24.2*
ASU 14538 Burts low temp	<0.1	112*
ASU 14565 Standard Fuel Char	<0.1*	17.1*
ASU 14573 High 2	<0.1*	294*

Laboaratory QA/QC

Blank	<0.1 ; <0.1 ; <0.1 ; <0.1	<5.0 ; <5.0 ; <5.0
Control	4.7 ; 4.7 ; 4.0 ; 4.6	91.2 ; 87.9 ; 92.1
Control Target	5.0	91
ASU 14347 Burts Old	0.2	-
ASU 14347 Burts Old	2.1	-
ASU 14538 Burts high temp	-	34.3
ASU 14538 Burts high temp	-	9.1
ASU 14538 Burts high temp	-	25.7
ASU 14538 Burts high temp	-	27.8
ASU 14538 Burts low temp	-	9.2
ASU 14538 Burts low temp	-	22.8
ASU 14538 Burts low temp	-	304
ASU 14565 Standard Fuel Char	<0.1	18.0
ASU 14565 Standard Fuel Char	<0.1	16.1
ASU 14573 High 2	<0.1	76.6
ASU 14573 High 2	<0.1	16.4
ASU 14573 High 2	-	18.2
ASU 14573 High 2	-	754
ASU 14573 High 2	-	607

* Average result of replicates

Prepared by: *Paula Whidley*

Authorized by: *A. Nutter*

Client: FEDDEV   **Report ID:**   Burts Greenhouses-3 ICP 30 Elements Biochar
Burts Greenhouses **Date Reported:**

Report of Analysis
Results relate only to the items tested

Sample	ASU 14347 Old Burt	ASU 14347 New Burt	ASU 14538 Low Temp.	ASU 14538 High Temp.*	ASU 14565 Standard Fuel char	ASU 14573 High 2*
Ag	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Al**	5450	<100	50.5	35.1	526	49.1
As	167	<1.0	<1.0	<1.0	<1.0	<1.0
B**	489	34.6	23.1	<20	22.4	<20
Ba	216	61.8	52.9	54.9	63.1	60.3
Be	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
Ca	45000	5550	4840	4870	15600	5220
Cd	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Co	5.3	<1.0	<1.0	<1.0	2.2	<1.0
Cr	206	<2.0	<2.0	<2.0	<2.0	<2.0
Cu	558	4.4	5.0	3.6	6.5	4.7
Fe	7370	61.6	106	235	902	92.1
K	6860	2150	1850	1840	2850	2230
Mg	5850	848	853	871	1560	864
Mn	799	752	760	658	307	718
Mo	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Na	6460	164	298	137	878	256
Ni	10.5	<2.0	<2.0	<2.0	<2.0	<2.0
P	731	69.5	89.0	54.0	276	72.2
Pb	314	<2.0	2.7	<2.0	2.4	<2.0
S	5380	79.9	88.4	70.1	262	72.3
Sb	16.1	<2.0	<2.0	<2.0	<2.0	<2.0
Se	<10	<10	<10	<10	<10	<10
Sn**	<10	<10	2.9	6.9	33.9	3.0
Sr	175	23.3	20.6	25.9	42.1	24.1
Ti	847	<10	<10	<10	945	<10
Tl	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
U	<10	<10	<10	<10	<10	<10
V	12.4	<10	<10	<10	<10	<10
Zn	498	5.6	18.5	9.6	56.2	17.9

** Detection limits raised due to interferences
* Average result of duplicate analysis

Prepared by: *Paula Whitley.*   Authorized by: *A. Netter*

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Sample	Blank	Blank	Control 1	Control 1 Target Range	Control 2	Control 2	Control 2 Target Range
Ag	<2.0	<2.0	<2.0	-	<2.0	<2.0	-
Al**	<100	<100	945	136-1150	163	198	75.4-214
As	<1.0	<1.0	1.4	0.45-2.2	<1.0	<1.0	-
B**	<25	<25	70.2	14.9-72.0	37.7	39.2	18.6-69.4
Ba	<5.0	<5.0	13.7	-	<5.0	6.2	-
Be	<4.0	<4.0	<4.0	-	<4.0	<4.0	-
Ca	<50	<50	15900	8800-22200	13000	10800	10810-16890
Cd	<1.0	<1.0	<1.0	0.46-0.91	2.0	2.2	2.0-2.9
Co	<1.0	<1.0	<1.0	0.22-0.69	<1.0	<1.0	0.12-0.69
Cr	<2.0	<2.0	<2.0	0.73-1.9	<2.0	<2.0	-
Cu	<2.0	<2.0	7.9	3.6-11.3	11.6	13.5	9.9-15.8
Fe	<20	<20	1060	641-1170	227	259	170-276
K	<20	<20	8860	6760-10600	22700	18800	17660-30620
Mg	<20	<20	4590	3500-5060	7280	7940	6760-9040
Mn	<1.0	<1.0	65.1	47.0-73.9	67.9	74.9	60.8-80.3
Mo	<2.0	<2.0	<2.0	-	<2.0	<2.0	0.0-0.7
Na	<75	<75	18100	12800-23000	15000	16500	12250-18900
Ni	<2.0	<2.0	<2.0	1.9-2.2	<2.0	2.0	0.30-0.38
P	<20	<20	998	744-1100	4290	3700	3600-5590
Pb	<2.0	<2.0	44.9	27.0-63.0	<2.0	<2.0	<2.0
S	<25	<25	6480	4920-7170	2670	2130	1670-5230
Sb	<2.0	<2.0	<2.0	-	<2.0	<2.0	-
Se	<10	<10	<10	-	<10	<10	-
Sn**	<10	<10	<10	-	6.9	3.1	-
Sr	<5.0	<5.0	236	150-281	48.5	52.5	43.9-55.9
Ti	<10	<10	34.6	-	10.3	10.7	-
Tl	<1.0	<1.0	<1.0	-	<1.0	<1.0	-
U	<10	<10	<10	-	<10	<10	-
V	<10	<10	<10	-	<10	<10	-
Zn	<5.0	<5.0	53.1	41.9-65.8	71.2	75.5	56.2-90.2

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Sample	ASU 14538 High Temp.	ASU 14538 High Temp.	ASU 14573 High 2	ASU 14573 High 2
Ag	<2.0	<2.0	<2.0	<2.0
Al**	32.1	38.1	50.8	47.3
As	<1.0	<1.0	<1.0	<1.0
B**	<20	<20	<20	<20
Ba	56.9	52.9	59.7	60.9
Be	<4.0	<4.0	<4.0	<4.0
Ca	5040	4690	5150	5290
Cd	<1.0	<1.0	<1.0	<1.0
Co	<1.0	<1.0	<1.0	<1.0
Cr	<2.0	<2.0	<2.0	<2.0
Cu	3.6	3.6	4.5	4.8
Fe	428	41.8	69.2	115
K	1890	1780	2120	2330
Mg	831	911	854	874
Mn	733	582	695	740
Mo	<2.0	<2.0	<2.0	<2.0
Na	150	123	246	266
Ni	<2.0	<2.0	<2.0	<2.0
P	52.5	55.4	74.0	70.3
Pb	<2.0	<2.0	<2.0	<2.0
S	70.8	69.4	70.3	74.3
Sb	<2.0	<2.0	<2.0	<2.0
Se	<10	<10	<10	<10
Sn**	6.8	6.9	2.7	3.3
Sr	19.9	31.8	23.8	24.4
Ti	<10	<10	<10	<10
Tl	<1.0	<1.0	<1.0	<1.0
U	<10	<10	<10	<10
V	<10	<10	<10	<10
Zn	8.7	10.4	17.6	18.1

PREPARING LEADERS AND CITIZENS FOR A GLOBAL SOCIETY

| **Client:** | FEDDEV | **Report ID:** | Burts Greenhouses-4 ICP 30 Elements Ash |
| | Burts Greenhouses | **Date Reported:** | October-13 |

Report of Analysis
Results relate only to the items tested

Sample	ASU 14565
	Ash
Ag	2.5
Al**	26600
As	75.7
B**	856
Ba	693
Be	<4.0
Ca	266000
Cd	1.2
Co	13.0
Cr	193
Cu	673
Fe	21600
K	53200
Mg	42700
Mn	10300
Mo	22.3
Na	24800
Ni	36.6
P	8120
Pb	39.8
S	3880
Sb	13.3
Se	<10
Sn**	16.2
Sr	1030
Ti	379
Tl	4.1
U	<10
V	72.5
Zn	236

** Detection limits raised due to interferences

Prepared by: _Paula Whidley_   Authorized by: _A. Nutter_

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Sample	Blank	Control 2	Control 2 Target Range
Ag	<2.0	<2.0	-
Al**	<100	198	75.4-214
As	<1.0	<1.0	-
B**	<25	39.2	18.6-69.4
Ba	<5.0	6.2	-
Be	<4.0	<4.0	-
Ca	<50	10800	10810-16890
Cd	<1.0	2.2	2.0-2.9
Co	<1.0	<1.0	0.12-0.69
Cr	<2.0	<2.0	-
Cu	<2.0	13.5	9.9-15.8
Fe	<20	259	170-276
K	<20	18800	17660-30620
Mg	<20	7940	6760-9040
Mn	<1.0	74.9	60.8-80.3
Mo	<2.0	<2.0	0.0-0.7
Na	<75	16500	12250-18900
Ni	<2.0	2.0	0.30-0.38
P	<20	3700	3600-5590
Pb	<2.0	<2.0	<2.0
S	<25	2130	1670-5230
Sb	<2.0	<2.0	-
Se	<10	<10	-
Sn**	<10	3.1	-
Sr	<5.0	52.5	43.9-55.9
Ti	<10	10.7	-
Tl	<1.0	<1.0	-
U	<10	<10	-
V	<10	<10	-
Zn	<5.0	75.5	56.2-90.2

PREPARING LEADERS AND CITIZENS FOR A GLOBAL SOCIETY

| Client: | FEDDEV | **Report ID:** | Burts Greenhouses-5 ICP 30 Elements Feedstock |
| | Burts Greenhouses | **Date Reported:** | October-13 |

Report of Analysis
Results relate only to the items tested

Sample	ASU 14455 Feedstock Oct 2012	ASU 14455 Feedstock Summer 2012*	ASU 14564 Coarse Wood*	ASU 14564 Fine Wood
Ag	<2.0	<2.0	<2.0	<2.0
Al**	27.9	<20	60.2	100
As	<1.0	<1.0	<1.0	<1.0
B**	<20	<20	<20	<20
Ba	24.5	9.7	17.2	22.6
Be	<4.0	<4.0	<4.0	<4.0
Ca	1290	914	3240	1760
Cd	<1.0	<1.0	<1.0	<1.0
Co	<1.0	<1.0	<1.0	<1.0
Cr	<2.0	<2.0	<2.0	2.6
Cu	<2.0	<2.0	<2.0	5.9
Fe	45.1	<20	106	350
K	674	417	667	678
Mg	204	110	376	344
Mn	45.1	86.8	92.1	71.3
Mo	<2.0	<2.0	<2.0	<2.0
Na	770	<75	183	341
Ni	4.4	<2.0	2.2	3.4
P	48.3	27.6	105	79.8
Pb	<2.0	<2.0	<2.0	8.1
S	106	30.9	94.6	111
Sb	<2.0	<2.0	<2.0	<2.0
Se	<10	<10	<10	<10
Sn**	5.3	<10	4.2	2.4
Sr	9.9	<5.0	12.1	8.3
Ti	<10	<10	<10	<10
Tl	<1.0	<1.0	<1.0	<1.0
U	<10	<10	<10	<10
V	<10	<10	<10	<10
Zn	17.8	7.8	16.7	30.5

** Detection limits raised due to interferences

* Average result of duplicates

Prepared by: _Paula Whitley_   Authorized by: _a. Nutter_

Sample	Blank	Blank	Control 1	Control 1	Control 1 Target Range
Ag	<2.0	<2.0	<2.0	<2.0	-
Al**	<100	<20	198	163	75.4-214
As	<1.0	<1.0	<1.0	<1.0	-
B**	<25	<20	39.2	37.7	18.6-69.4
Ba	<5.0	<5.0	6.2	<5.0	-
Be	<4.0	<4.0	<4.0	<4.0	-
Ca	<50	<50	10800	13000	10800-16890
Cd	<1.0	<1.0	2.2	2.0	2.0-2.9
Co	<1.0	<1.0	<1.0	<1.0	0.12-0.69
Cr	<2.0	<2.0	<2.0	<2.0	-
Cu	<2.0	<2.0	13.5	11.6	9.9-15.8
Fe	<20	<20	259	227	170-276
K	<20	<20	18800	22700	17660-30600
Mg	<20	<20	7940	7280	6760-9040
Mn	<1.0	<1.0	74.9	67.9	60.8-80.3
Mo	<2.0	<2.0	<2.0	<2.0	0-0.7
Na	<75	<75	16500	15000	12250-18900
Ni	<2.0	<2.0	2.0	<2.0	0.3-3.8
P	<20	<20	3700	4290	3600-5590
Pb	<2.0	<2.0	<2.0	<2.0	<2.0
S	<25	<25	2130	2670	1670-5233
Sb	<2.0	<2.0	<2.0	<2.0	-
Se	<10	<10	<10	<10	-
Sn**	<10	<10	3.1	6.9	-
Sr	<5.0	<5.0	52.5	48.5	43.9-55.9
Ti	<10	<10	10.7	10.3	-
Tl	<1.0	<1.0	<1.0	<1.0	-
U	<10	<10	<10	<10	-
V	<10	<10	<10	<10	-
Zn	<5.0	<5.0	75.5	71.2	56.2-90.2

Sample	ASU 14455 Feedstock Summer 2012	ASU 14455 Feedstock Summer 2012	ASU 14564 Coarse Wood	ASU 14564 Coarse Wood
Ag	<2.0	<2.0	<2.0	<2.0
Al	<20	<20	58.7	61.6
As	<1.0	<1.0	<1.0	<1.0
B	<20	<20	<20	<20
Ba	11.5	7.8	16.0	18.3
Be	<4.0	<4.0	<4.0	<4.0
Ca	1010	817	3080	3390
Cd	<1.0	<1.0	<1.0	<1.0
Co	<1.0	<1.0	<1.0	<1.0
Cr	<2.0	<2.0	<2.0	<2.0
Cu	<2.0	<2.0	<2.0	<2.0
Fe	<20	<20	115	97.9
K	476	358	656	677
Mg	112	107	338	414
Mn	87.8	85.8	88.6	95.5
Mo	<2.0	<2.0	<2.0	<2.0
Na	<75	<75	167	198
Ni	<2.0	<2.0	2.0	2.4
P	31.3	23.8	106	104
Pb	<2.0	<2.0	2.1	<2.0
S	35.7	26.1	94.3	94.8
Sb	<2.0	<2.0	<2.0	<2.0
Se	<10	<10	<10	<10
Sn**	6.5	8.2	4.1	4.2
Sr	<5.0	<5.0	11.4	12.7
Ti	<10	<10	<10	<10
Tl	<1.0	<1.0	<1.0	<1.0
U	<10	<10	<10	<10
V	<10	<10	<10	<10
Zn	8.1	7.4	15.8	17.6

PREPARING LEADERS AND CITIZENS FOR A GLOBAL SOCIETY

Client:	FEDDEV	**Report ID:**	Burts Greenhouses-6 Available Nitrogen and Available Phosphorus	
	Burts Greenhouses	**Date Reported:**	October-13	

Report of Analysis
Results relate only to the items tested

Sample	Ammonia (N)	Nitrate (N)	Nitrite(N)	Formic Acid Extraction Phosphorus	Olsen Extraction Phosphorus
	ug/g	ug/g	ug/g	ug/g	ug/g
ASU 14347 Burts Old	<2.0	2.3	<2.0	850	190
ASU 14347 Burts New	<2.0	3.0	<2.0	31	<5*
ASU 14538 Burts high temp	<2.0	6.1	<2.0	9.0	-
ASU 14538 Burts low temp	<2.0	<2.0	<2.0	28	-
ASU 14565 Standard Fuel Char	<2.0*	<2.0	<2.0	80	-
ASU 14573 High 2	<2.0	<2.0	<2.0	28*	-
Laboaratory QA/QC					
Blank	<2.0	<2.0	<2.0	<5	<5
Control	9.5	4.5	3.4	65	70
Control Target	10.0	5.0	5.0	95	93
ASU 14347 Burts New	-	-	-	31	<5
ASU 14347 Burts New	-	-	-	31	<5
ASU 14565 Standard Fuel Char	<2.0	<2.0	<2.0	-	-
ASU 14565 Standard Fuel Char	<2.0	<2.0	<2.0	-	-
ASU 14573 High 2	-	-	-	33	-
ASU 14573 High 2	-	-	-	23	-

* Average result of replicates

Prepared by: *Paula Whitley*   Authorized by: *A. Nutter*

| **Client:** | FEDDEV | **Report ID:** | Burts Greenhouses-7 PAH |
| | Burts Greenhouses | **Date Reported:** | October-13 |

Report of Analysis
Results relate only to the items tested

PAH ug/g dry weight	**ASU 14538** **Low Temp.**	**ASU 14538** **High temp.**	**ASU 14505** **Standard Fuel**	**Blank**	**Control**	**Control** **Target**
Acenaphthene	<0.06	<0.06	<0.06	<0.06	0.098	0.167
Acenaphthylene	<0.06	<0.06	<0.06	<0.06	0.091	0.167
Anthracene	<0.06	<0.06	<0.06	<0.06	0.140	0.167
Benzo[a]anthracene	<0.06	<0.06	<0.06	<0.06	0.185	0.167
Benzo[a]pyrene	<0.06	<0.06	<0.06	<0.06	0.140	0.167
Benzo[b]fluoranthene	<0.06	<0.06	<0.06	<0.06	0.214	0.167
Benzo[g,h,i]perylene	<0.06	<0.06	<0.06	<0.06	0.131	0.167
Benzo[k]fluoranthene	<0.06	<0.06	<0.06	<0.06	0.181	0.167
1,1-Biphenyl	<0.06	<0.06	<0.06	<0.06	-	-
Chrysene	<0.06	<0.06	<0.06	<0.06	0.195	0.167
Dibenzo[a,h]anthracene	<0.06	<0.06	<0.06	<0.06	0.134	0.167
Fluoranthene	<0.06	<0.06	<0.06	<0.06	0.145	0.167
Fluorene	<0.06	<0.06	<0.06	<0.06	0.111	0.167
Indeno[1,2,3-cd]pyrene	<0.06	<0.06	<0.06	<0.06	0.130	0.167
1-Methylnaphthalene	<0.06	<0.06	0.07	<0.06	0.085	0.167
2-Methylnaphthalene	<0.06	<0.06	<0.06	<0.06	0.091	0.167
Methylnaphthalene (1&2)	<0.12	<0.12	0.13	<0.12	-	-
Naphthalene	<0.03	<0.03	0.03	<0.03	0.090	0.167
Phenanthrene	<0.06	<0.06	<0.06	<0.06	0.148	0.167
Pyrene	<0.06	<0.06	<0.06	<0.06	0.151	0.167

** Analysis subcontracted

Prepared by: *Paula Whitley*

Authorized by: *A. Nutter*

Client:	FEDDEV		Report ID:	Burts Greenhouses-8 Ultimate-Proximate
	Burts Greenhouses		Date Reported:	October-13

Report of Analysis
Results relate only to the items tested

Analyte**	Unit	ASU 14538 High Results as received	ASU 14538 High Results Dry Weight Corrected	ASU 14538 Low Results as received	ASU 14538 Low Results Dry Weight Corrected
Moisture	wt %	4.98	-	6.98	-
Ash	wt %	1.54	1.62	1.36	1.46
Carbon	wt %	92.35	97.19	90.26	97.03
Hydrogen	wt %	1.99	1.51	2.08	1.40
Nitrogen	wt %	0.35	0.37	0.28	0.30
Oxygen by Difference	wt %	3.76	<0.10	6.00	<0.10
Fixed Carbon	wt %	79.92	84.11	77.77	83.60
Sulphur	wt %	0.02	0.02	0.02	0.02
Volatile Matter	wt %	13.56	14.27	13.89	14.94
Low Heat Value	BTU/lb	13180	13870	12990	13970
High Heat Value	BTU/lb	13370	14070	13190	14180

Analyte**	Unit	ASU 14565 Standard Fuel Results as received	ASU 14565 Standard Fuel Results Dry Weight Corrected	ASU 14573 High 2 Results as received	ASU 14573 High 2 Results Dry Weight Corrected
Moisture	wt %	5.36	-	4.42	-
Ash	wt %	2.14	2.26	1.32	1.38
Carbon	wt %	87.49	92.44	93.60	97.93
Hydrogen	wt %	2.45	1.96	1.70	1.26
Nitrogen	wt %	1.00	1.06	0.34	0.35
Oxygen by Difference	wt %	6.89	2.25	3.03	<0.10
Fixed Carbon	wt %	74.44	78.65	82.34	86.15
Sulphur	wt %	0.02	0.02	0.02	0.02
Volatile Matter	wt %	18.06	19.09	11.92	12.47
Low Heat Value	BTU/lb	12600	13310	13500	14130
High Heat Value	BTU/lb	12830	13550	13660	14290

** Analysis subcontracted

Prepared by: _Paula Whitley._

Authorized by: _A. Nutter_

The use of biochar to reduce soil PCB bioavailability to *Cucurbita pepo* and *Eisenia fetida*

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HIGHLIGHTS

► Two concentrations of weathered PCB-contaminated soil were amended with (0, 0.2, 0.7, 2.8, and 11.1% w/w) of biochar.
► Biochar additions decreased the uptake of PCBs into plant tissue by 89% after 50 days.
► Biochar amendment significantly decreased the bioavailability of PCBs to earthworms by 88% after 50 days of exposure.
► Biochar has potential to serve as a mitigation technology at Brownfield sites.

GRAPHICAL ABSTRACT
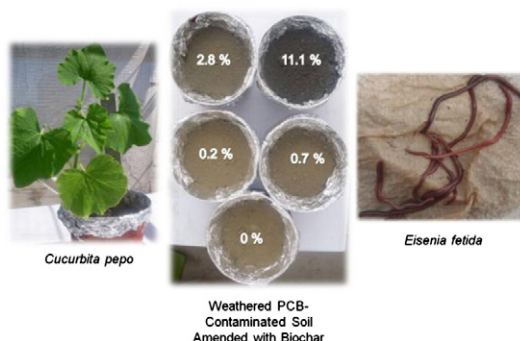
Cucurbita pepo

2.8 % 11.1 %
0.2 % 0.7 %
0 %

Weathered PCB-Contaminated Soil Amended with Biochar

Eisenia fetida

ABSTRACT

Biochar is a carbon rich by-product produced from the thermal decomposition of organic matter under low oxygen concentrations. Currently many researchers are studying the ability of biochar to improve soil quality and function in agricultural soils while sustainably sequestering carbon. This paper focuses on a novel but complimentary application of biochar – the reduced bioavailability and phytoavailability of organic contaminants in soil, specifically polychlorinated biphenyls (PCBs). In this greenhouse experiment, the addition of 2.8% (by weight) biochar to soil contaminated with 136 and 3.1 µg/g PCBs, reduced PCB root concentration in the known phytoextractor *Cucurbita pepo* ssp. *pepo* by 77% and 58%, respectively. At 11.1% biochar, even greater reductions of 89% and 83% were recorded, while shoot reductions of 22% and 54% were observed. PCB concentrations in *Eisenia fetida* tissue were reduced by 52% and 88% at 2.8% and 11.1% biochar, respectively. In addition, biochar amended to industrial PCB-contaminated soil increased both aboveground plant biomass, and worm survival rates. Thus, biochar has significant potential to serve as a mechanism to decrease the bioavailability of organic contaminants (e.g. PCBs) in soil, reducing the risk these chemicals pose to environmental and human health, and at the same time improve soil quality and decrease CO_2 emissions.

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1. Introduction

In recent years, the popularity of biochar as a soil amendment has substantially increased, mostly in response to increased global carbon emissions and deterioration of agricultural soil quality. Biochar is a carbon rich by-product produced from the pyrolysis of organic matter under zero oxygen concentrations at relatively low temperatures (<700 °C) (Verheijen et al., 2010). Due to its high porosity (Downie

et al., 2009), specific surface area (Liang et al., 2006; Yin Chan and Xu., 2009) and carbon content (Winsley., 2007), biochar decreases nutrient and water leaching loss (Atkinson et al., 2010), increases soil cation exchange (Chan et al., 2007; Cheng et al., 2008; Novak et al., 2009a), sustainably sequesters carbon and improves the overall sorption capacity of soil (Cheng et al., 2008).

Persistent organic pollutants (POPs) are organic compounds with low water solubility and, resistant to environmental degradation by biological, photoylic and chemical processes (White and Zeeb., 2007). Research has suggested that carbon rich, charcoal-like materials such as biochar and activated carbon (AC) have the ability to sorb POPs and thus limit their bioavailability in sediments and soil. However, little data exists on the potential of using biochar, which as a consequence of its production, is a greener and more cost effective material than activated carbon. The production process of biochar is different from that of AC, in that AC is further 'activated' through physical or chemical treatments to maximize the porosity (Marsh and Rodríguez Reinoso., 2006). Commercial production of activated carbon requires expensive equipment, and as a result AC has much higher associated costs than biochar. Biochar production is also more sustainable than the production of AC as it does not require chemical reagents and biochar can be made from waste materials including those from municipalities, the forestry and agriculture industries (crop and animal) (Bridgwater., 2003).

Sorption studies utilizing activated carbon predate those of biochar, and currently there is substantially more information available on ability of AC (Amstaetter et al., 2012; Beckingham and Ghosh., 2011; Cho et al., 2007, 2009; Ghosh et al., 2011; Hale et al., 2012; Langlois et al., 2011; Lunney et al., 2010; Millward et al., 2005; Oen et al., 2011, 2012; Sun and Ghosh., 2008) to sorb contaminants. A few studies have suggested that biochar amended to soil may function in the remediation of organic pollutants such as polyaromatic hydrocarbons (PAHs) (Chen and Yuan., 2011; Hale et al., 2011) and pesticides (Cao et al., 2009, 2011; Saito et al., 2011; Xu et al., 2012; Yu et al., 2011, 2010; Zheng et al., 2010), and to sediments for polychlorinated biphenyls (PCBs) (Cornelissen et al., 2005a, 2005b). A recent study, found that biochar produced from pine needles under a high pyrolytic temperature (700 °C) increased the sorption of PAHs in agricultural soils (Chen and Yuan., 2011). Another 2011 study reported a 91% suppression of dieldrin uptake into cucumber plants with biochar produced from wood chips (Saito et al., 2011). Zheng et al. (2010) reported that biochar (produced from greenwaste at 450 °C) exhibited a high sorption affinity to atrazine and simazine, and was effective at removing these pesticides from aqueous solution (Zheng et al., 2010). Xu et al. (2012) proposed that biochar made from bamboo added to soil at 5% (ww) could be used as possible *in situ* sorbent for pentachlorophenyl and thus minimize the contaminants' bioavailability to earthworms (Xu et al., 2012). Thus the addition of biochar to soil or sediment has potential to function as a mitigation technology for a variety of POPs.

The sorption of organic contaminants by biochar is a result of two separate processes – i) relatively weak and linear *ab*sorption into amorphous organic matter, and ii) relatively strong and non-linear *ad*sorption onto the biochar surface (Chen et al., 2008; Cornelissen et al., 2005a, 2005b; Huang and Chen., 2010; Koelmans et al., 2006; Smernik., 2009). The sorption and subsequent immobilization of POPs to carbon materials would control their toxicity and fate, and decrease the potential adverse health effects associated with their bioaccumulation through the food web (Cho et al., 2009; Cornelissen et al., 2011; Ghosh et al., 2011; Langlois et al., 2011; Xu et al., 2012).

Soil and sediment contamination of PCBs in particular, is widespread as a result of extensive use, improper storage facilities and accidental releases (Safe, 1994). Traditionally, the remediation of PCBs involved soil excavation and transport, prior to off-site treatment by solvent extraction, thermal desorption, incineration, or landfilling

(Campanella et al., 2002). However, these techniques themselves can be detrimental to the environment, extremely costly and in some cases infeasible, due to the extent of contamination (Gerhardt et al., 2009). The use of phytoextraction, a volume reduction technology in which plants (e.g. *Cucurbita pepo* spp. *pepo*) are used to mobilize and accumulate significant amounts of the contaminant from the soil, has been a successful *in situ* green remediation strategy for POPs (Ficko et al., 2010; Huelster et al., 1994; Low et al., 2011; White., 2009; Whitfield Åslund et al., 2007, 2008; Zeeb et al., 2006). However phytoextraction has been shown to have limited effectiveness as contaminant concentration increases (Chaudhry et al., 2005; Vila et al., 2007; Zeeb et al., 2006) and the high cost of traditional remediation technologies usually dictates that low concentrations of PCBs are left on site. Despite many successes in both high cost traditional and low cost green remediation technologies, there are still concerns that significant PCB contamination remains in the soils at Brownfield sites, and consequently PCBs continue to enter the food chain and pose environmental and human health risks (Smith., 2012).

The current greenhouse study provides an evaluation of the ability of biochar to minimize the uptake of PCBs by the known PCB phytoextractor *C. pepo* ssp. *pepo* cv. Howden (pumpkin) and a common invertebrate species, *Eisenia fetida* (redworm). The reduced uptake of organic contaminants due to biochar soil additions would provide significant social benefits by reducing or eliminating the potential adverse effects of these substances entering the food chain. In addition, minimizing the bioavailability of organic contaminants in soil may alleviate some of the financial burden associated with the remediation of contaminated sites while reducing greenhouse gas emissions and improving soil quality.

2. Materials and methods

2.1. Greenhouse soil preparation

Weathered soils contaminated with commercial Aroclors 1254 and 1260 were collected from a contaminated site in Etobicoke, Ontario (Canada). The site is a former manufacturing facility for electrical transformers. Soils were collected from two areas on site, and were determined to have PCB concentrations of 136 ± 15.3 and 3.1 ± 0.75 μg/g, respectively. Using the sodium acetate method for cation exchange capacity (CEC) described by Laird and Fleming (2008), the PCB-contaminated soil had an average CEC of 10.22 cmol/kg ($n = 3$) and the pH of the soil was 7.72. Previously this soil was characterized (Whitfield Åslund et al., 2007, 2008) as being coarse-grained and sandy with a total organic carbon content of 3.5%. The soils were dried, sieved to 16 mm, and then homogenized separately using the Japanese pie-slab mixing method (Pitard., 1993).

2.2. Experimental design and sample collection for C. pepo tissue

The two soils (136 and 3.1 μg/g) were amended in triplicate (A, B, and C) with 0, 0.2, 0.7, 2.8 or 11.1% (w/w) biochar obtained from Burt's Greenhouses in Odessa, ON. The biomass feedstock of this biochar consisted of wood waste, mostly from used shipping pallets and construction. The temperature within the pyrolysis equipment reached 700 °C, and occurred over ~30 min. Each treatment ($n = 10$) was tumbled at 30 rpm for 24 h in a leachate soil tumbler at the Analytical Services Unit located at Queen's University. Vermiculite (density = 0.11 g mL^{-1} Schultz™, Bratford, ON,) was added to all treatments in a 2:1 v/v soil:vermiculite ratio to increase soil aeration. The soil/biochar/vermiculite mixture (total weight per planter of 2.25 kg) was placed in bottom perforated 8-inch diameter planting pots ($n = 30$) lined with aluminum foil.

Each planter received three pumpkin (*C. pepo* ssp. *pepo* cv. Howden) seeds purchased from the 'Ontario Seed Company' (Waterloo, ON), however extra seedlings were removed such that each planter
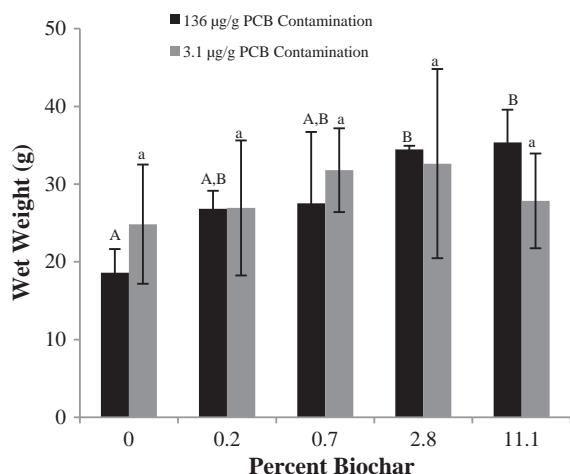
Fig. 1. Harvested wet weight of *Cucurbita pepo* shoots in unamended PCB-contaminated industrial soil and soil amended with a range of biochar concentrations. Error bars represent one standard deviation. Upper-case (136 μg/g PCB-contaminated soil) and lower-case letters (3.1 μg/g PCB-contaminated soil) indicate statistically significant differences between treatments ($p < 0.05$).

contained only one growing plant. Pumpkin plants were grown in the greenhouse located at the Royal Military College of Canada (RMC), measured on a weekly basis and harvested in 50 days. Greenhouse temperature was maintained at 27 °C (± 6 °C) and the pumpkins were grown under a 14:10 h (day:night) fluorescent photoperiod. Planters were top and bottom watered to maintain ~35% soil moisture.

A 30 g composite soil sample was collected from replicates for all treatments both immediately after soil tumbling with and without (i.e. control) biochar and after 50 days. All soils remained frozen until analysis. Particle size distribution by sieving performed on oven-dried samples (95 to 125 °C, 16 h) and pH of freshly tumbled treatments were analyzed by the Analytical Sciences Group at the Royal Military College of Canada (SI Fig. 1, Table 1). Cation exchange capacity of Burt's biochar, PCB-contaminated soil, and PCB-contaminated soil with biochar additions, all aged 50 days was calculated via the sodium acetate method outlined by Laird and Fleming (2008).

After 50 days, plants were harvested by cutting the shoot of the pumpkin with acetone rinsed scissors as close to the soil surface as possible. The soil in the planter was then emptied onto a tray (cleaned and rinsed with acetone between samples) and the root tissues collected. Air-monitoring of the greenhouse indicated that PCB
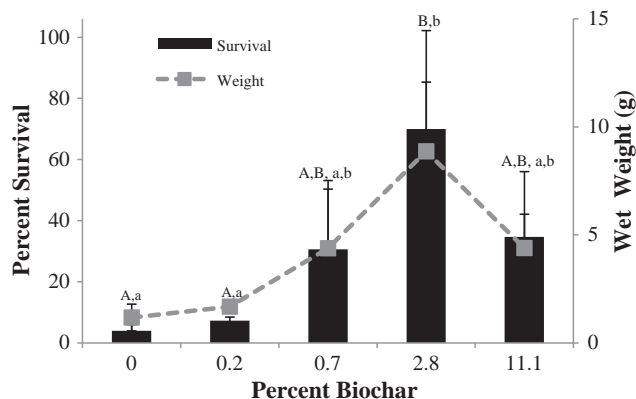
Fig. 2. Percent survival and wet weight of *Eisenia fetida* after 50 days of exposure to 136 μg/g unamended PCB-contaminated soil and soil amended with a range of biochar concentrations. Error bars represent one standard deviation. Upper case letters indicate statistically significant differences in worm survival between treatments and lower case letters indicate significant difference in worm weights between treatments ($p < 0.05$).

concentrations were below detectable limits (< 0.01), therefore aerial deposition on the plant tissues was considered insignificant. Plant tissues (root and shoot) were washed using running water, patted dry, and weighed to the nearest hundredth of a gram. They were then placed in individually labeled Whirlpak® bags and frozen until analysis.

2.3. Experimental design and sample collection for E. fetida tissue

Following plant harvest, redworms (*E. fetida*) (n = 50 worms, average weight = 20 ± 1.0 g) purchased from 'The Worm Factory' (Westport, ON), were added to the biochar treatments (i.e. 0, 0.2, 0.7, 2.8, 11.1%) in the 136 μg/g PCB-contaminated soil. The planters were covered with perforated aluminum foil and the worms were removed from the soil after 50 days. Soil moisture was maintained at ~35% moisture. Deceased earthworms were not included for PCB analysis as they could not be depurated.

Surviving worms were collected by emptying the soil from each planter onto a tray (cleaned and rinsed with acetone between samples). Collected worms were then counted, washed using a container of clean water, weighed, depurated for 72 h at 4 °C, dried for 24 h at 25 °C and stored in individually labeled Whirlpak® bags and frozen until analysis.

2.4. Analytical procedures

2.4.1. PCB Aroclors in soil, plant, and worm samples

Plant root and shoot samples were analyzed by microwave-assisted extraction (MAE) at the RMC. Microwave-assisted extraction was performed at a temperature of 120 °C for 35 min in 30 mL of 1:1 hexane:acetone mixture using a Milestone Ethos SEL microwave extraction system. Following extraction, sample extracts were concentrated using a Syncore, the solvent exchanged for hexane, and then extracts were applied to a Florisil column for cleanup.

PCB concentrations in soil and worm tissues were analyzed via Soxhlet extraction, based on the methods described by (Whitfield Åslund et al., 2007) and performed at the Analytical Services Unit located at Queen's University. Briefly, worm samples were finely chopped using metal scissors (rinsed with acetone between samples) and homogenized. Soil and chopped worm samples were dried overnight in a vented oven at 25 °C for approximately 12–18 h, and then ground with sodium sulfate and Ottawa sand. Decachlorobiphenyl (DCBP) was used as an internal surrogate standard. All soil and worm samples were extracted in a Soxhlet apparatus for 4 h at 4–6 cycles per hour in 250 mL of dichloromethane. The use of both extraction methods was validated by (Whitfield Åslund et al., 2008).

Plant, worm and soil extracts were analyzed for total Aroclors, using an Agilent 6890 Plus gas chromatograph equipped with a micro-[63]Ni electron capture detector (GC/μECD), an SPB™-1 fused silica capillary column (30 m, 0.25 mm ID × 0.25 μm film thickness) and HPChem station software. The carrier gas was helium, at a flow rate of 1.6 mL/min. Nitrogen was used as the makeup gas for the electron capture detector (ECD). Detection limits were 0.1 μg/g. All values were reported as μg/g dry weight.

2.4.2. Quality assurance/quality control (QA/QC)

One analytical blank, one control and one analytical duplicate sample were prepared and analyzed for every nine samples analyzed by Soxhlet or MAE. The control sample was spiked with a known amount of either Aroclor 1254 or 1260. Decachlorobiphenyl (DCBP) was added to each sample as a surrogate standard prior to extraction. None of the analytical blanks contained any PCB congeners at concentrations above detection limits (0.1 μg/g for total Aroclors) and all control samples were between 80 and 110% of the expected value. Relative standard deviations between the samples and their

analytical duplicate were below 24% for all results and the average surrogate recovery for samples analyzed for total Aroclor was 98%.

2.5. Statistical analyses

PCB concentrations (soil and tissue) are reported on a dry-weight basis. The tissue concentration data were analyzed by one-way analysis of variance (ANOVA) (dependant variable: shoot, root or worm PCB concentration; independent variable: percent biochar) followed by a post hoc Tukey comparison (levels of: percent biochar). Shoot and worm wet weights were compared between soil types (i.e. high or low level of PCB contamination) using a two-way ANOVA. Percent reductions in shoot, root and worm tissue among biochar percentages were also compared between types of biochar using a two-way ANOVA. All residuals of the data were determined to be normally distributed as determined by a Kolmogorov Smirnov test for normality. When data failed to meet the assumptions, data were $\log_{10}$-transformed. A significance level of $\alpha = 0.05$ was used for all tests, and results were recorded with the standard error of the mean. All statistical analyses were performed using SPLUS 8.0.

3. Results and discussion

3.1. Plant shoot and worm harvestable biomass

PCB concentrations in both control soils did not vary from the beginning (136 ± 15.3 and 3.1 ± 0.75 µg/g) to the end (153 ± 3.4 and 3.4 ± 0.29 µg/g) of the experiment. Traditionally, biochar amendments have been used as a method to increase plant productivity in agriculture (Chan et al., 2007; Lehmann et al., 2003). Pumpkin shoot weights significantly increased in size by 85 and 90% in the 136 µg/g PCB-contaminated soil, with biochar additions of 2.8 and 11.1%, respectively ($p < 0.05$) (Fig. 1). Pumpkin shoot wet weights did not differ among the two levels (136 µg/g and 3.1 µg/g) of soil contamination at any biochar application rate (Fig. 1). Whitfield Åslund et al. (2007, 2008) documented that *C. pepo* accumulated significant concentration of PCBs in plant shoots without jeopardizing plant health. Increase in shoot biomass could be due to biochar's ability to maintain soil moisture (Busscher et al., 2010; Novak et al., 2009a; Novak et al., 2009b) and provide macronutrients (potassium, phosphorous) and micronutrients (copper) (Lehmann et al., 2003; Novak et al., 2009a). Also oxidation of the biochar surface creates carboxyl groups which contribute to a higher cation exchange capacity (CEC) than in unamended control soil (Chan et al., 2007; Cheng et al., 2008; Liang et al., 2006). CEC is a measure of the negatively charged sites on a biochar or soil particle and is important as soil with a high CEC is better able to retain nutrients (e.g. Ca^{2+}, K^+, and Mg^{2+}) to replenish those removed from the soil water by plant uptake (Liang et al., 2006). The Burt's biochar used in this study had a CEC (NaOAc) of 24.2 cmol/kg, whereas, the PCB-contaminated soil (136 µg/g) had a CEC of 10.4 cmol/kg. Upon addition of 2.8 and 11.1% Burt's biochar to the 136 µg/g PCB-contaminated soil the CECs were only slightly higher at 12.8 and 10.8 cmol/kg, respectively after 50 days. The small difference could be due to the short duration of our experimental design (i.e. 50 days) as well as the soil and biochar heterogeneity. Future studies should analyze the CEC of the soil after several months or many years of biochar amendment to determine the long term benefits to soil CEC and seek further statistical significance.

Another soil improvement ability of biochar is that it can reduce the overall tensile strength of the soil (Lehmann et al., 2011). Reductions in tensile strength may be especially important for revegetation of contaminated sites where the soil quality is often intensely degraded (Lunney et al., 2010). Biochar addition to soils at contaminated sites to lower tensile strength may alleviate root elongation and proliferation problems, allow seeds to germinate more easily, and allow invertebrates to move more readily through the soil. After 50 days of pumpkin growth, the 136 µg/g PCB-contaminated soil in the

control treatment had become hard and thus it was more difficult to harvest the root tissue. Roots were easily harvested with gentle force from the soil treated with 2.8% and 11.1% biochar. Biochar additions to the 3.1 µg/g PCB-contaminated soil did not significantly increase plant growth. This area of the PCB-contaminated site has been revegetated for many years and subsequently is not as degraded as the soil collected in the area of higher contamination. It is not uncommon to observe greater yield improvements as a result of biochar soil amendments in degraded soils, as was the case in this study (Kimetu et al., 2008; Major et al., 2010; Novak et al., 2009b).

The presence of earthworms is considered a useful indicator of soil health (Snapp and Morrone., 2008). When collecting the 136 µg/g PCB-contaminated soil it was observed that earthworms of any species were absent from the site, however there were some occupying the area contaminated with 3.1 µg/g PCBs. Thus, the soil contaminated with the higher amount of PCB contamination was selected for the earthworm study. If biochar is to improve soil functions at Brownfield sites it must allow for re-habitation of the earthworm population and not have an adverse effect on the earthworms that occupy the soil. *E. fetida* were specifically chosen for this study because Langlois et al. (2011) reported no significant differences in worm weights between those
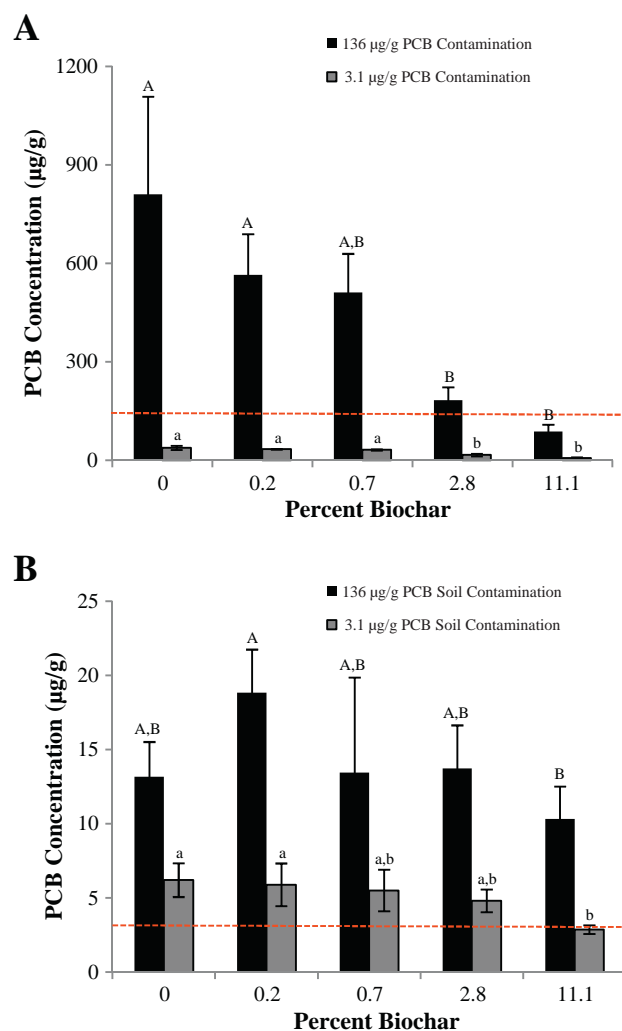

Fig. 3. Polychlorinated biphenyl (PCB) concentrations in root (a) and shoot (b) tissue of *Curcurbita pepo* grown in unamended PCB-contaminated industrial soil and soil amended with a range of biochar concentrations. Error bars represent one standard deviation. Upper-case (136 µg/g PCB-contaminated soil) and lower-case letters (3.1 µg/g PCB-contaminated soil) indicate statistically significant differences between treatments ($p < 0.05$). The line represents (a) the high PCB-contaminated soil concentration of 136 µg/g and (b) the low PCB-contaminated soil concentration of 3.1 µg/g.

exposed to PCB-contaminated soil (>50 μg/g), or PCB-contaminated soil amended with GAC after 2 months. The PCB concentration used in this study (136 μg/g) is not acutely toxic to *E. fetida*, which has an Aroclor 1254 LD_{50} of 4500 μg/g (Fitzpatric et al., 1992). However, soil at Brownfield sites are typically intensely degraded (i.e. lack essential nutrients, substrate quality, and/or vegetative cover) which may not allow for earthworm habitation. *E. fetida* in this study exposed to the control treatment had only a $4 \pm 2\%$ survival rate (n=3). In this greenhouse experiment, the addition of 2.8% biochar to industrial PCB-contaminated soil (136 μg/g) was optimal, significantly increasing the rate of worm survivorship by 17.5 times the control (Fig. 2) ($p<0.5$). It is noteworthy to also mention that addition of 0.7 and 11.1% biochar to the PCB-contaminated soil also increased worm survivorship by 7.7 and 8.8 times the control, respectively. Increases in worm survivorship resulted in up to 2.1 times greater worm weights (at 2.8% biochar addition) at harvest time (50 days) compared to the controls (Fig. 2).

Thus biochar additions can improve the health of soil invertebrates even in Brownfield soil highly contaminated with PCBs. This result, along with the significant increases in plant growth provide optimism for contaminated sites – in that with biochar additions, revegetation and the return of mesofauna are probable and thus the overall soil health and functionality may also be restored.

3.2. PCB concentrations in C. pepo

C. pepo was chosen to study the effects of biochar on the phytoavailability of PCBs because it has been widely documented as an efficient species at phytoextracting PCBs and other organic pollutants (Huelster et al., 1994; Low et al., 2011; White., 2009; Whitfield Åslund et al., 2007, 2008; Zeeb et al., 2006). The translocation and deposition of PCB congeners through the shoot tissue of *C. pepo* occur via transport in the xylem sap (Greenwood et al., 2011). Whitfield Åslund et al. (2008) reported that contaminant transfer pathways such as direct soil contamination, atmospheric deposition and volatilization from soil and subsequent redeposition on shoot tissue were negligible. Thus, if the addition of biochar to the soil reduced PCB uptake by *C. pepo*, it is likely to also reduce uptake by other plant species. As expected, root and shoot tissue of *C. pepo* accumulated substantial amounts of PCBs in the two control treatments (Fig. 3a and b). The extent of PCB bioaccumulation, as determined by a bioaccumulation factor ($BAF = [PCB]_{tissue}/[PCB]_{soil}$) in this study (0.11) was comparable to

Fig. 4. Bioaccumulation factor of polychlorinated biphenyls (PCBs) into *Eisenia fetida* exposed to an unamended (control) 136 μg/g PCB-contaminated industrial soil and soil amended with a range of biochar concentrations. Error bars represent one standard deviation. Upper-case letters indicate statistically significant ($p<0.05$) differences between treatments.

that of Whitfield Åslund et al. (2007) (0.15) who determined that there was potential for *in situ* phytoextraction of PCBs (Whitfield Åslund et al., 2007). Generally shoot BAFs decrease as the soil concentration increases (Zeeb et al., 2006). The soil concentration in the current study was roughly three times higher than that of Whitfield Åslund et al. (2007).

In both soils, the addition of biochar significantly reduced PCB levels in the plant roots. In soil with 136 μg/g PCB-contamination, the PCB concentration in root tissue decreased by 77% and 89% ($p<0.05$) with 2.8% and 11.1% biochar amendment, respectively (Fig. 3a). In soil with 3.1 μg/g PCB-contamination, biochar amendment at 2.8% and 11.1% reduced the concentration of PCBs in *C. pepo* root tissue 58% and 83%, respectively; $p<0.05$ (Fig. 3a).

The addition of biochar had less of an effect on PCB uptake into the plant shoots. At an 11.1% rate of biochar amendment in 3.1 μg/g PCB-contaminated soil, a significant 54% reduction in shoot tissue was observed ($p<0.05$) (Fig. 3b). Although not significant ($p=0.058$), biochar amendment at a rate of 11.1%, to 136 μg/g PCB-contaminated soil, reduced the shoot concentration of *C. pepo* by 22%. Significant reductions were not seen for plant shoots in soil amended with lower concentrations of biochar. These results are consistent with a study by Langlois et al. (2011) which determined that 12.5% AC amendment reduced the PCB concentration (Aroclor 1254) in root tissue of *C. pepo* by 97%, but only by 63% in shoot tissue (Langlois et al., 2011). Lunney et al. (2010) demonstrated that uptake of DDT into shoots and roots was eliminated with the addition of high levels of AC to soils contaminated with 1100 ppb DDT (Lunney et al., 2010).

The significant reductions in PCB concentrations into *C. pepo* root and shoot tissue observed, are consistent with Graber et al. (2011), Mesa and Spokas (2011), Nag et al. (2011) and Yu et al. (2009), which have stated that biochar soil amendment may also lead to decreased efficacy of soil-applied herbicides. Thus, although biochar amendment to minimize the phytoavailability of organic compounds such as PCBs has a profound positive effect from a remediation point of view; it may have a negative effect from an agricultural standpoint. Hence, careful consideration of site specific characteristics is necessary before applying biochar amendment, on a large scale.

3.3. PCB concentrations in E. fetida

The greatest reductions in PCB uptake by *C. pepo* were observed in the 136 μg/g PCB-contaminated soil, thus biochar treatments at this concentration were chosen for worm exposure. Worms exposed to 136 μg/g PCB-contaminated soil had PCB concentrations of 2440 μg/g. This 18-fold (Fig. 4) increase in tissue concentration illustrates the ability of PCBs to bioaccumulate within an organism ($BAF = 18.0 \pm 2.9$), and the potential for them to biomagnify through the food chain (Beckingham and Ghosh., 2011; Ghosh et al., 2011; Millward et al., 2005). Treatment of 136 μg/g PCB-contaminated soil with 2.8% and 11.1% biochar, significantly ($p<0.05$) reduced the bioaccumulation of PCBs into the worm tissue by 53% and 88%, respectively. Worms in the 0.2% and 0.7% amendments had PCB concentrations that were not significantly different from the control. Biochar is a porous material consisting mostly of micropores (<2 nm) that provide surface area for contaminant binding (Cornelissen et al., 2005a, 2005b; Kasozi et al., 2010; Spokas et al., 2009; Yu et al., 2010; Zheng et al., 2010). It is possible that biochar adsorbed the PCB molecules so strongly that the contaminant-biochar complex cannot be broken down by digestive enzymes and microbial flora as it passes through the gut of *E. fetida* (Langlois et al., 2011), resulting in reduced worm PCB concentrations.

These large reductions of the bioavailability of PCBs to the earthworm *E. fetida* are consistent with Xu et al. (2012) who used a chemical extraction method using methanol to represent bioavailability of pentachlorophenyl to earthworms. In this study the authors found that compared to the control, the concentration of pentachlrophenyl extracted by methanol decreased by 56% in the soil amended with 5%
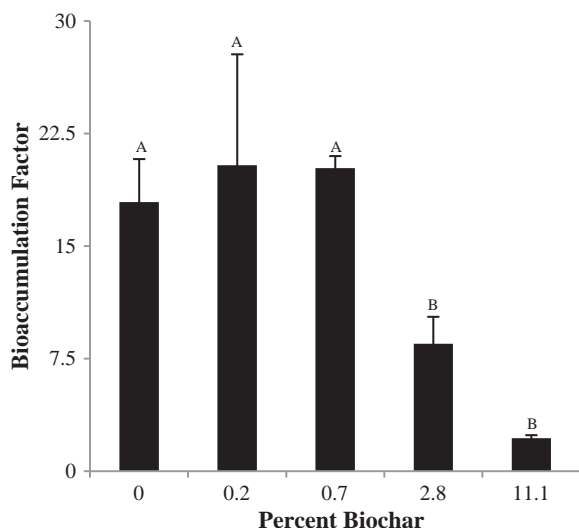
(w/w) bamboo biochar. The high efficacy of biochar to reduce PCB bioaccumulation in invertebrates can be compared to the efficiency of activated carbon. Langlois et al. (2011) determined that an addition of 12.5% AC to soil significantly reduced PCB bioaccumulation in *E. fetida* by 99% (Langlois et al., 2011). It will be useful in future studies to include activated carbon as a positive control to directly compare the efficiency of biochar and activated carbon to minimize the bioavailability of organic contaminants.

Sorption of contaminants is a key process that controls the toxicity, transport and fate of non-polar organic compounds such as PCBs (Cornelissen et al., 2005a, 2005b; Ghosh et al., 2011; Koelmans et al., 2006). In the past few years much work has been published as a result of laboratory kinetic testing, that organic contaminants are adsorbed onto the surfaces and absorbed into the organic matter of biochar (Cornelissen et al., 2005a, 2005b; Kasozi et al., 2010; Spokas et al., 2009; Yu et al., 2010; Zheng et al., 2010). In comparison, this study demonstrates sorption and hence immobilization of PCBs by biochar in a complex scenario with biological components such as weathered PCB-contaminated soil, earthworms and plants. This study provides evidence that biochar has significant potential to serve as a mechanism to sequester PCBs in the soil, thereby, minimizing their bioavailability and potential to enter the food chain. This technology, possibly in combination with bioaccessibility assays to determine appropriate cleanup levels, based on environmental and human health risks (e.g. Dean and Ma, 2007), could be used during Brownfield site closure, where traditional remediation approaches or phytoextraction have been exhausted, yet levels of residual contamination remain.

Biochar is produced by the pyrolysis of organic matter; however, many types of organic matter can be used, varying from sawdust to corn stalks to chicken manure to construction wastes, under different pyrolysis conditions. These differences are expected to alter the biochar's physiochemical properties and its sorption capabilities (Yao et al., 2011). Care must be taken to ensure that the biomass itself does not contain any contaminants (e.g. heavy metals, PAHs, PCBs). Thus, before this technology can be implemented *in situ*, careful characterization of the biochar including, contaminants, sorption capacity, specific surface area, cation exchange and those suggested by the International Biochar Initiative (IBI) should be conducted.

In this greenhouse experiment biochar produced the greatest percent reductions in *C. pepo* shoot and root material as well as *E. fetida* tissue when added at 11.1% (w/w). However, statically significant reductions in PCB concentration in root and worm tissues were achieved at 2.8% (w/w), which is a much more realistic application rate for large-scale experiments such as at a PCB-contaminated Brownfield sites, and this concentration is currently recommended by some researchers for activated carbon amendment (Langlois et al., 2011, McLeod et al., 2007, Zimmerman et al., 2005). Thus, future work should focus on field-relevant application rates and direct comparisons between the efficiency of different biochars with activated carbon at ca. 3%. Many groups have investigated the potential of activated carbon to sorb PCBs in aquatic sediments and terrestrial soils; this study is the first to present reductions in PCB phytoavailability and bioavailability in weathered PCB-contaminated soil. Given that biochar costs are typically 50–75% less than the cost of the activated carbon, and the additional agricultural and environmental benefits, this is a promising new application of biochar.

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Acknowledgements

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In situ application of activated carbon and biochar to PCB-contaminated soil and the effects of mixing regime

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ARTICLE INFO

ABSTRACT

The *in situ* use of carbon amendments such as activated carbon (AC) and biochar to minimize the bioavailability of organic contaminants is gaining in popularity. In the first *in situ* experiment conducted at a Canadian PCB-contaminated Brownfield site, GAC and two types of biochar were statistically equal at reducing PCB uptake into plants. PCB concentrations in *Cucurbita pepo* root tissue were reduced by 74%, 72% and 64%, with the addition of 2.8% GAC, Burt's biochar and BlueLeaf biochar, respectively. A complementary greenhouse study which included a bioaccumulation study of *Eisenia fetida* (earthworm), found mechanically mixing carbon amendments with PCB-contaminated soil (i.e. 24 h at 30 rpm) resulted in shoot, root and worm PCB concentrations 66%, 59% and 39% lower than in the manually mixed treatments (i.e. with a spade and bucket). Therefore, studies which mechanically mix carbon amendments with contaminated soil may over-estimate the short-term potential to reduce PCB bioavailability.

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1. Introduction

Polychlorinated biphenyls (PCBs) are a group of chlorinated organic contaminants characterized as being persistent, bioaccumulative and anthropogenic in nature. Recent studies have shown that both plants and earthworms can accumulate up to six and eighteen times the soil PCB concentration, respectively (Denyes et al., 2012). In Canada, soils containing PCBs are regulated and may require remedial action, including costly techniques such as soil excavation and incineration (Environment Canada, 1999). Therefore, there is a considerable need for cost effective alternative remediation strategies which also minimize the bioavailability of PCBs.

The use of carbon-rich, charcoal like materials such as biochar and activated carbon (AC) for the *in situ* stabilization of organic contaminants in sediments and soils has received increasing attention in recent years (Denyes et al., 2012; Beesley et al., 2011; Ghosh et al., 2011; Paul and Ghosh, 2011; Kupryianchyk et al., 2013). The addition of these materials to soils has been shown to immobilize organic contaminants thereby reducing their bioavailability to plants (Denyes et al., 2012; Jakob et al., 2012; Langlois et al., 2011; Lunney et al., 2010), invertebrates (Denyes et al., 2012; Paul and Ghosh, 2011; Langlois et al., 2011; Sun and Ghosh, 2007) and fish (Kupryianchyk et al., 2013). Biochar is a charcoal like material produced from the pyrolysis of organic matter under very low oxygen conditions (Verheijen et al., 2010), while AC is a more processed form of charcoal which has higher associated costs. Both biochar and AC have high sorptive capacities as a result of their chemical structures, high porosity and large surface areas (Hale et al., 2011; Marsh and Rodríguez Reinoso, 2006; Oleszczuk et al., 2012a).

In recent years, Europe and the United States have implemented pilot testing of the *in situ* use of AC as a sediment amendment (Ghosh et al., 2011). Many studies (Ghosh et al., 2011; Beckingham and Ghosh, 2011; Cho et al., 2009; Cornelissen et al., 2011; Oen et al., 2011, 2012; Kupryianchyk et al., 2013) have shown that as a result of high AC sorption capacity, the porewater hydrophobic organic contaminant (HOC) concentration and the bioaccumulation of HOCs in benthic organisms are decreased. Additionally, studies by Hale et al. (2011) and Langlois et al. (2011) suggested that AC may be suitable for soil remediation of pyrene and PCBs, respectively.

While AC research has focused on soil and sediment remediation as this product was considered to have the strongest sorption potential (Ghosh et al., 2011; Oleszczuk et al., 2012b), biochar research has focused on soil quality improvements and carbon sequestration potential. Biochar offers additional agronomic and environmental benefits such as increases in soil cation exchange capacity (CEC) (Liang et al., 2006), water holding capacity (Karhu et al., 2011) and decreased fertilizer requirements, leading to increased crop yields at lower costs. Additionally, the carbon component of biochar is stable, and thus may sequester atmospheric carbon (Lehmann, 2007; Zimmerman et al., 2011) and function in the mitigation of climate change. Biochar is quickly gaining in popularity, however there are still only a limited number of studies published examining the use of biochar to minimize the bioavailability of contaminants (Denyes et al., 2012; Gomez-Eyles et al., 2011; Hossain et al., 2010; Saito et al., 2011; Yu et al., 2010) and most of these studies are laboratory based. Similarly, there are studies available in which AC is applied to soils in the greenhouse (Langlois et al., 2011; Lunney et al., 2010) and also in the field (Ghosh et al., 2011; Jakob et al., 2012; Beckingham and Ghosh, 2011; Hale et al., 2012) for sorption of contaminants. However, very few studies compare the *in situ* efficiency of biochar and AC directly (Hale et al., 2011; Marchal et al., 2013) and most have utilized laboratory based sorption methods (Chai et al., 2012; Chen and Yuan, 2011; Cornelissen et al., 2005a,b; Xu et al., 2012; Zheng et al., 2010).

The present study investigates and compares the performances of two types of biochar and granular activated carbon (GAC) as *in situ* stabilization amendments for PCB-contaminated Brownfield soils under both field and greenhouse conditions. In addition, the effects of an agronomic/environmentally-relevant mixing regime on the ability to reduce PCB uptake of both biochar and AC are compared to standard sorption literature mixing methods.

2. Methods

2.1. Soil and materials

The *in situ* experiments were carried out at a Brownfield site in Etobicoke, Ontario (Canada) that was a former manufacturing facility for electrical transformers. The soil was contaminated with commercial Aroclors 1254 and 1260, and has weathered in place over a period of approximately 50 years. It was determined to have a PCB concentration of 71.4 ± 10.8 μg/g ($n = 5$). Using the sodium acetate method for cation exchange capacity (CEC) described by Laird and Fleming (2008), the PCB-contaminated soil had an average CEC of 9.5 ± 1.3 cmol/kg ($n = 2$) and a pH of 7.7. Previously this soil was characterized (Whitfield Åslund et al., 2007) as being coarse-grained and sandy with a total organic carbon content of 3.5%. Soil was collected from the Brownfield site for both greenhouse experiments.

Two types of biochar and one GAC were used for all field and greenhouse experiments. Cation exchange capacity for all carbon amendments were determined using the sodium acetate method for CEC described by Laird and Fleming (2008). The Brunauer–Emmett–Teller (BET) surface area of the GAC and biochars were measured by N_2 gas sorption analysis at 77 K in a relative pressure range from 0.01 to 0.10 using an ASAP 2000 surface area analyzer (Micromeritics, USA) after degassing at 120 °C for a minimum of 2 h. Burt's biochar (Burt's Greenhouses, Odessa ON) was produced from used shipping pallets and construction waste. The temperature within the pyrolysis equipment reached 700 °C over 30 min. BlueLeaf biochar (BlueLeaf Inc., Drummondville, QB) was created via pyrolysis of softwood material at a temperature of 450 °C for 2.5 h. GAC obtained from A.C. Carbone Inc. (St. Jean sur Richelieu, QC) was produced from bituminous coal. The percent organic matter and moisture of the carbon amendments were determined using the loss on ignition procedure outlined by Nelson and Sommers (1996), and pH was determined as outlined in Ahmedna et al. (1997). Burt's biochar was determined to have a moisture content of 20%, be 63% organic matter as determined by loss on ignition and have a pH of 9. BlueLeaf biochar was determined to have a moisture content of 3.8%, be 97% organic matter as determined by loss on ignition and have a pH of 10. The GAC used in this study had a moisture content of 6.8%, be 39% organic matter as determined by loss on ignition and had a pH of 9. Particle size distribution of all materials was determined via progressive dry sieving (in triplicate) adapted from ASTM D5158-98 (American Society for Testing and Materials (ASTM), 2005) using seven U.S. Standard sieves (4.7, 2.0, 1.0, 0.50, 0.25, 0.15, and 0.0075 mm).

2.2. Field design

PCB-contaminated soil was tilled extensively using a 22″ garden tiller. The four treatments included in this experiment were i) control (0% carbon amendment), ii) 2.8% (w/w) GAC, iii) 2.8% (w/w) Burt's biochar, and iv) 2.8% (w/w) BlueLeaf biochar. The amendment percentage of 2.8% (w/w) was based on the work of Langlois et al. (2011) and Denyes et al. (2012). Four plots, 400 cm long by 50 cm wide were dug to a depth of 30 cm, spaced 50 cm apart from each other. The carbon treatments were mixed into their corresponding plot using the following method. Half of the amount of carbon material needed for each plot was added into the plot, covered with half the soil and tilled four times. The remainder of the measured carbon material and soil were added to the plot and tilled another four times. This method ensured thorough mixing and mimicked agronomic practices.

Each plot received nine pumpkin (*Cucurbita pepo* ssp. *pepo* cv. Howden) seeds purchased from the 'Ontario Seed Company' (Waterloo, ON), however extra seedlings were removed at ca. three weeks, such that each plot contained only three growing plants, evenly spaced at one per square meter. Pumpkin plants were measured on a weekly basis and harvested at 50 days. Average daily temperatures and total precipitation in this region for the duration of the experiment (i.e. June–August 2011), were 21.8 °C and 163.6 mm, respectively (Environment Canada (EC), 2012). Plants were watered three times a week regardless of precipitation.

2.3. Greenhouse experiments

2.3.1. Initial greenhouse experiment

PCB-contaminated soil was collected from the field site immediately prior to initiation of the field experiment for both this greenhouse experiment and the subsequent one described below. The soil was dried, sieved to 16 mm, and then homogenized using the Japanese pie-slab mixing method (Pitard, 1993). The soil was amended in triplicate (A, B, and C) with 0% and 2.8% (w/w) GAC, Burt's biochar, or BlueLeaf biochar as in the field experiment. Treatments were manually mixed together (10 turns/replicate/treatment) using a bucket and spade, then the amendment mixture was placed in bottom perforated 6-inch diameter planting pots (total soil weight per planter of 1000 g).

2.3.2. Greenhouse comparison of mechanically tumbled vs. manually mixed carbon amendments

For this second greenhouse experiment, PCB-contaminated soil was either manually mixed or mechanically tumbled in triplicate (A, B and C). Manual mixing was identical to that performed in the initial greenhouse experiment as described above (Section 2.3.1). Mechanical tumbling occurred at 30 rpm for 24 h (Denyes et al., 2012). The soil/carbon amendment mixture was placed in the same sized planting pots as the initial greenhouse experiment (Section 2.3.1), however the mixture was half the weight (total soil weight per planter of 500 g).

For both greenhouse experiments, each planter received three pumpkin seeds (*Cucurbita pepo* ssp. *pepo* cv. Howden) and extra seedlings were removed such that each planter contained only one growing plant. Pumpkin plants were grown in the greenhouse located at the Royal Military College of Canada (RMC), measured on a weekly basis and harvested at 50 (2.3.1) or 36 days (2.3.2). Greenhouse temperature was maintained at 27 °C (± 6 °C) and the pumpkins were grown under a 14:10 h (day: night) fluorescent photoperiod. Planters were top and bottom watered to maintain sufficient moisture.

A 30 g composite soil sample was collected from replicates for all treatments for both greenhouse and field experiments, immediately after mechanically mixing or manual mixing with each carbon amendment and after the pumpkins were harvested. A 200 g soil sample was collected from each of the mechanically or manually mixed treatments and analyzed for particle size distribution via progressive dry sieving (in triplicate) adapted from ASTM D5158-98 (American Society for Testing and Materials (ASTM), 2005) using seven U.S. Standard sieves (4.7, 2.0, 1.0, 0.50, 0.25, 0.15, and 0.0075 mm). All soils were frozen until analysis. Plants were harvested by cutting the shoot of the pumpkin with acetone rinsed scissors as close to the soil surface as possible. Root samples were then collected and rinsed clean with water. Both shoot and root tissues were patted dry, and weighed to the nearest hundredth of a gram. They were then placed in individually labeled Whirlpak® bags and frozen until analysis. Air-monitoring of the greenhouse and field site indicated PCB concentrations were below detectable limits (<0.01), therefore, aerial deposition on the plant tissues was considered negligible.

2.4. Experimental design and sample collection for Eisenia fetida tissue

The worm experiment was performed in the RMC greenhouse, post pumpkin harvest. Twenty-five redworms (*Eisenia fetida*) purchased from 'The Worm Factory' (Westport, ON) were added to each pot for 36 days in both the mechanically and manually mixed treatments. The pots were covered with perforated aluminum foil. Soil moisture was maintained ~35% moisture (Paul and Ghosh, 2011; Chai et al., 2012; Angell et al., 2012).

Surviving worms were collected by emptying the soil from each planter onto a tray (cleaned and rinsed with acetone between samples). Worms were counted,

washed using a container of clean water, weighed, depurated for 72 h at 4 °C, dried for 24 h at 25 °C and stored in individually labeled Whirlpak® bags and frozen until analysis.

2.5. Analytical procedures

2.5.1. PCB Aroclors in soil, plant, and worm samples

All samples were dried at 25 °C for 24 h immediately prior to analysis. Plant root and shoot samples were analyzed by microwave-assisted extraction (MAE) at RMC. Microwave-assisted extraction was performed at a temperature of 120 °C for 35 min in 30 mL of 1:1 hexane: acetone mixture using a Milestone Ethos SEL microwave extraction system. Following extraction, sample extracts were concentrated using a Syncore, the solvent exchanged for hexane, and then extracts were applied to a Florisil column for cleanup (Whitfield Åslund et al., 2008).

PCB concentrations in soil and worm tissues were analyzed via Soxhlet extraction, based on the methods described by Whitfield Åslund et al. (2007) and performed at the Analytical Services Unit located at Queen's University. Briefly, worm samples were finely chopped using metal scissors (rinsed with acetone between samples) and homogenized. Chopped worm samples were dried overnight in a vented oven at 25 °C for approximately 12–18 h, and then soil and worm samples were ground with sodium sulfate and Ottawa sand. Decachlorobiphenyl (DCBP) was used as an internal surrogate standard. All soil and worm samples were extracted in a Soxhlet apparatus for 4 h at 4–6 cycles per hour in 250 mL of dichloromethane. The use of both extraction methods was previously validated by Whitfield Åslund et al. (2008)

Plant, worm and soil extracts were analyzed for total Aroclors, using an Agilent 6890 plus gas chromatograph equipped with a micro-^{63}Ni electron capture detector (GC/μECD), a SPB™-1 fused silica capillary column (30 m, 0.25 mm ID × 0.25 μm film thickness) and HPChem station software. The carrier gas was helium, at a flow rate of 1.6 mL/min. Nitrogen was used as the makeup gas for the electron capture detector (ECD). Detection limits were 0.1 μg/g. All values were reported as μg/g dry weight.

2.5.2. Quality assurance/quality control (QA/QC)

One analytical blank, one control and one analytical duplicate sample were prepared and analyzed for every nine samples analyzed by Soxhlet or MAE. The control sample was spiked with a known amount of either Aroclor 1254 or 1260. Decachlorobiphenyl (DCBP) was added to each sample as a surrogate standard prior to extraction. None of the analytical blanks contained PCBs at concentrations above detection limits (0.1 μg/g for total Aroclors) and all control samples were between 80 and 110% of the expected value. Relative standard deviations between the samples and their analytical duplicate were below 18% for all results and the average surrogate recovery for samples analyzed for total Aroclor was 98%.

2.6. Statistical analyses

PCB concentrations (soil and tissue) are reported on a dry-weight basis. The tissue concentration data were analyzed by one-way analysis of variance (ANOVA) (dependant variable: shoot, root or worm PCB concentration; independent variable: carbon amendment) followed by a post hoc Tukey comparison (levels of: carbon amendment). The particle size distribution of the i) PCB-contaminated soil, ii) the carbon amendments and iii) the 2.8% soil/carbon mixtures were compared between manually mixed and mechanically mixed treatments using a one-way ANOVA. All residuals of the data were determined to be normally distributed as determined by a Kolmogorov Smirnov test for normality. A significance level of $\alpha = 0.05$ was used for all tests, and results were recorded with the standard error of the mean. All statistical analyses were performed using SPLUS 8.0.

3. Results and discussion

3.1. Field and greenhouse experiment

In the field experiment all carbon amendments significantly reduced the uptake of PCBs into the root tissue of *C. pepo* ($p < 0.05$). Activated carbon reduced *C. pepo* root PCB uptake by 74%, and Burt's biochar and BlueLeaf biochar reduced PCB uptake by 72% and 64%, respectively (Fig. 1a). There were no significant differences between the GAC, Burt's biochar and BlueLeaf biochar treatments in either tissue type implying that all carbon amendments performed equally in terms of their ability to minimize PCB phytoavailability *in situ* (Fig. 1a and b). When this experiment was replicated in the greenhouse, the results were quite different with only the GAC amendment significantly reducing the PCB uptake into *C. pepo* root tissue (Fig. 1a). In the field experiment, *C. pepo* shoot tissue PCB concentration was not significantly reduced as a result of any carbon amendment (Fig. 1b) whereas in the greenhouse the addition of
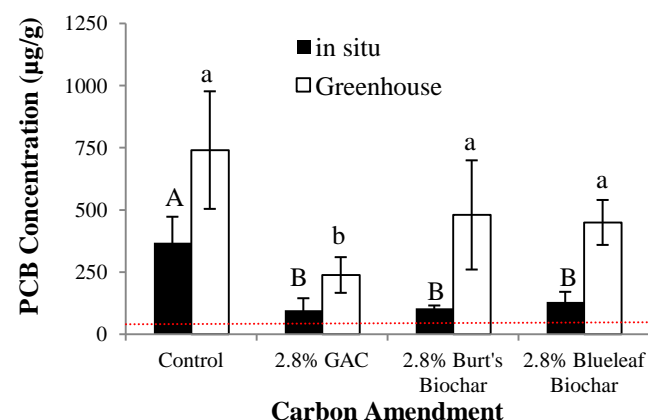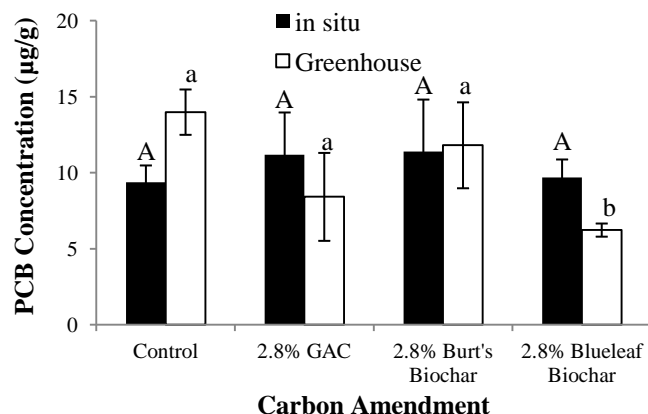

Fig. 1. Polychlorinated biphenyl (PCB) concentrations in root (a) and shoot (b) tissue of *Curcubita pepo* grown in unamended PCB-contaminated Brownfield soil and Brownfield soil amended with 2.8% GAC or biochar, carbon amendments. Error bars represent one standard deviation. Upper-case (*in situ*) and lower-case letters (greenhouse) indicate statistically significant differences between treatments ($p < 0.05$). The line represents (a) the high PCB-contaminated soil concentration of 71 μg/g.

BlueLeaf biochar did significantly reduce shoot uptake (55%). As in Denyes et al. (2012) and Langlois et al. (2011), *Cucurbita pepo* spp. *pepo* were chosen to study PCB phytoavailability because this species has been widely documented to accumulate significant amounts of organic contaminants (Whitfield Åslund et al., 2007; Huelster et al., 1994; Low et al., 2011; Whitfield Åslund et al., 2008; Zeeb et al., 2006), including PCBs from the soil into root and shoot tissues via transport in the xylem sap (Greenwood et al., 2011).

The shoot tissue of *C. pepo* plants grown *in situ* in the control treatment, i.e. PCB-contaminated soil alone, grew well, being on average 2.5 m long and weighing 1013 g. This result was expected as Whitfield Åslund et al. (2007, 2008) demonstrated that that *C. pepo* can accumulate significant concentration of PCBs in plant shoots without jeopardizing plant health. In the greenhouse, pumpkins grown in PCB-contaminated soil amended with 2.8% Burt's or BlueLeaf biochar grew even larger (97% and 100%, respectively) than the control pumpkins ($p < 0.05$). These treatments also produced *C. pepo* plants that were 72% and 75% larger than the *C. pepo* plants grown in the 2.8% GAC amendment. These greenhouse results are expected as one of the agronomic benefits of adding biochar to soil is that it can reduce the overall tensile strength of the soil (Lehmann et al., 2011) which will in turn alleviate root elongation and proliferation problems, allow seeds to

germinate more easily, and invertebrates to move more readily through the soil (Atkinson et al., 2010; Chan et al., 2007). Pumpkin plants grown *in situ* in PCB-contaminated soil amended with BlueLeaf biochar were 92% larger than the controls and 28% larger than the *C. pepo* plants grown in GAC amendment, however due to large standard deviations that are often associated with field data, these results are not significant. These results are further discussed in Section 3.2.2.

Decreases in contaminant uptake and increases in plant growth can be explained by strong sorption of the PCB molecules onto the AC/biochar particles and the relative improvements to substrate quality these materials offer to the intensely degraded Brownfield soil. Results of *in situ* carbon amendment showed that AC and biochar statistically performed equally in terms of their abilities to minimize the phytoavailability of PCBs to *C. pepo*. However, biochar outperformed AC with respect to improving substrate quality and increasing plant growth. These results are consistent with the recent findings of Oleszczuk et al. (2012a, 2012b), who reported that AC was more effective than biochar in reducing sewage sludge toxicity, while biochar was more effective in improving *Lepidium sativum* growth. Given that in this study, the biochars offered additional agronomic and environmental benefits and performed statistically as well as AC in terms of ability to minimize PCB uptake, biochar may offer a lower cost, greener alternative to AC amendment for soil remediation.

Although substantial, the effects of all carbon soil amendments observed both *in situ* and in the greenhouse were less than expected and there were significant differences in the greenhouse and field results. Upon careful review of the literature, and comparison to our previous study (Denyes et al., 2012), one difference between this study and others, that report up to 99% reductions in PCB bioavailability (Paul and Ghosh, 2011; Langlois et al., 2011; Beckingham and Ghosh, 2011), is the mixing strategy. The study described here attempted to mimic agronomic methods which are relevant from an engineering perspective for the *in situ* stabilization of PCBs, however most published studies mix the carbon amendment and soil mechanically for hours or days (Denyes et al., 2012; Langlois et al., 2011; Chai et al., 2012; Hale et al., 2011). Mass kinetic modeling has also been used to explain PCB immobilization in sediments as a result of AC amendments using different mixing approaches (Werner et al., 2006; Cho et al., 2012). Generally *in situ* mixing has lower short term efficiencies compared to laboratory based experiments, as it may result in spatially heterogeneous AC particles, minimizing PCB contact and delaying treatment benefits (Cho et al., 2007, 2009). Using passive sampling efforts and kinetic modeling however, it has been suggested that overtime even poorly mixed systems will achieve significant PCB immobilization by AC (Cho et al., 2012).

To quantify the effect of mixing at our PCB-contaminated Brownfield site, an additional greenhouse experiment to directly compare mixing methods was performed in which the carbon amendments were either manually mixed with a spade and bucket, or mechanically mixed in a soil tumbler for 24 h at 30 rpm.

3.2. Manual versus. mechanical mixing regimes

3.2.1. Particle size distribution

In this study, particle size distribution was analyzed in an effort to understand differences in sorption and growth between manually and mechanically mixing carbon amendments with soil. Amendment of AC/biochar to Brownfield soils alters the particle size distribution which in turn may change the soil structure, texture, and porosity. These changes are expected to improve Brownfield substrate quality by altering tensile strength and oxygen content, water storage capacity, and nutritional status of the soil within the plant rooting zone (Atkinson et al., 2010). Currently, few studies are available linking biochar sorption potential with particle size distribution (Zheng et al., 2010; Cabrera et al., 2011; Kasozi et al., 2010; Chai et al., 2012), while even fewer report on soil substrate effects (Borchard et al., 2012; Zimmerman, 2010). From a sorption potential perspective, smaller particle sizes of biochar/AC are favorable as this is expected to increase the external surface area, and thus ability of the contaminant to access pore space for binding (Sun and Ghosh, 2007). Additionally smaller particle sizes are favored for sorption as there are then a greater number of particles per unit volume of soil (Hale and Werner, 2010). However, larger particle sizes may favorably increase soil aeration and prevent biochar/AC movement into the subsoil over time. Kasozi et al. (2010), Cabrera et al. (2011) and Chai et al. (2012) reported higher sorption of catechol, fluometuron and polychlorinated dibenzo-p-dioxins/dibenzofurans, respectively, to fine particle sized biochar versus coarse biochar.

Activated carbon is generally available as two types, powdered (PAC) or granular (GAC). These two types of AC have different particles sizes and generally PAC particles are around 20 μm in size while GAC particles are in the range of 300–1700 μm (Jakob et al., 2012; Langlois et al., 2011; Hale et al., 2011; Oen et al., 2012; Chai et al., 2012; Amstaetter et al., 2012). Studies examining biochar sorption often homogenize the biochar to pass through a 250 μm sieve (or similar size) (Chen and Yuan, 2011; Chai et al., 2012; Sun et al., 2012; Uchimiya et al., 2012) which may enhance sorption potential, however, not be feasible for large scale application and may overestimate the inherent sorption potential.

Based on the studies by Kasozi et al. (2010) and Cabrera et al. (2011) which defined fine particle sizes as those <0.25 mm and <0.2 mm, respectively in this study, fine particles are defined as those ≤0.25 mm and coarse particles as ≥0.5 mm. The carbon amendments used increased in their relative proportions of coarse particles from Burt's biochar (52%) < BlueLeaf biochar (86%) < GAC (96%) (Table 1). Burt's and BlueLeaf biochars were more uniformly distributed among all sieve sizes, while 95% of the GAC particles were retained in the 1 mm and 0.5 mm sieves only. Although GAC is considered the most 'coarse' carbon amendment in this study, both Burt's and BlueLeaf biochar contain higher proportions of larger particle sizes (4.7 and 2 mm).

When the carbon amendments were manually mixed into the contaminated soil, the average percent of fine particles in the soil/carbon mixture were 32%, 32% and 31%, for the amendments of

Table 1
Origin and characteristics of GAC, Burt's biochar and BlueLeaf biochar.

Treatment	Source material	Pyrolysis temperature (°C)	Moisture (%)	Loss on ignition (%)	pH	Cation exchange capacity (cmol/kg)	Specific surface area (m²/g)	Coarse particles (%)	Fine particles (%)
GAC	Bituminous coal	700	6.8	39	9.2	5.0	808.5	96	4
Burt's biochar	Shipping pallets/ Construction waste	700	20	63	9.0	34	373.6	52	48
BlueLeaf biochar	Softwood	450	3.8	97	10	18	54.7	86	14

GAC, Burt's biochar and BlueLeaf biochar, respectively (Fig. 3a). However these percentages significantly increased for all carbon amendments to 47%, 50% and 49%, respectively, when the soil was mechanically mixed ($p < 0.05$).

3.2.2. The effect of mixing regime on plant and worm PCB concentrations

When AC and biochar were manually mixed into PCB-contaminated soil there were no significant reductions in PCB concentration in *C. pepo* root and shoot tissues (Fig. 2a and b), and the only significant reduction in *E. fetida* tissue was seen in AC-

A Root

B Shoot

C Worm
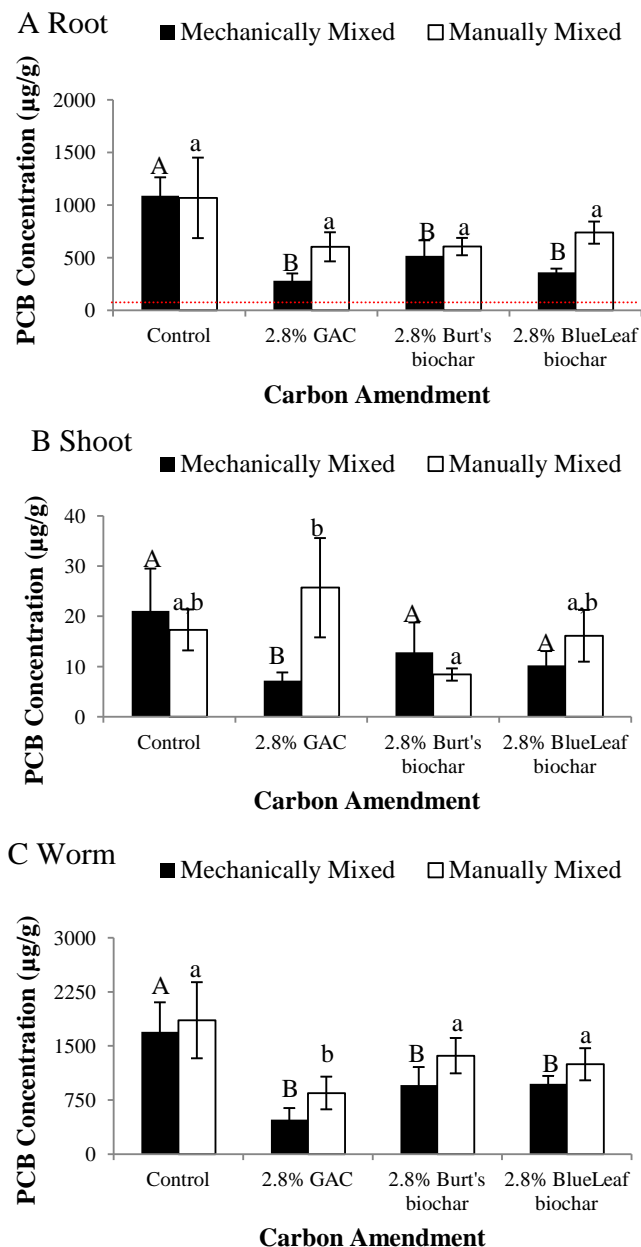
Fig. 2. Polychlorinated biphenyl (PCB) concentrations in root (a) shoot (b) and worm (c) tissue of *Curcubita pepo* and *Eisenia fetida* grown in unamended PCB-contaminated Brownfield soil and Brownfield soil amended with 2.8% GAC or biochar, carbon amendments. Error bars represent one standard deviation. Upper-case (mechanically mixed) and lower-case letters (manually mixed) indicate statistically significant differences between treatments ($p < 0.05$). The line represents (a) the high PCB-contaminated soil concentration of 71 μg/g.

A Fine Particles
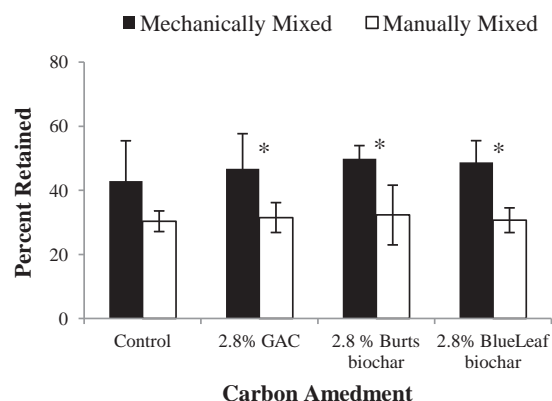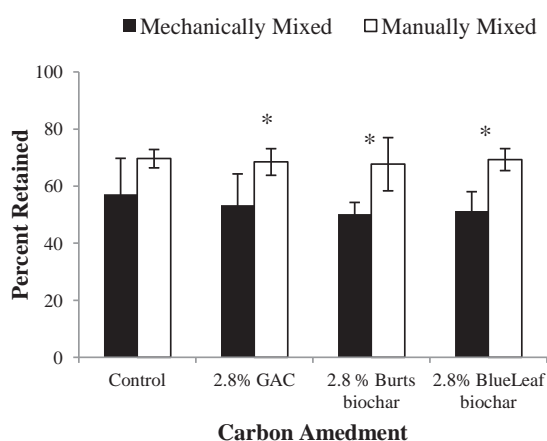

B Coarse Particles

Fig. 3. Particle size distribution of biochar and activated carbon amendments mechanically or manually mixed with PCB-contaminated Brownfield soil at 2.8% (by weight). Fine particles (A) are those 0.25 mm and smaller and coarse particles are 0.5 mm or larger (B). Error bars represent one standard deviation. *Indicate statistically significant differences between mixing methods ($p < 0.05$).

amended soil (54% reduction) (Fig. 2c). This result is similar to the initial greenhouse study where only GAC and BlueLeaf reduced root and shoot uptake, respectively. However, when the same treatments were mechanically mixed (i.e. 24 hrs at 30 rpm) PCB uptake became significantly reduced. Activated carbon mechanically mixed into soil at 2.8% reduced the PCB concentration in *C. pepo* root and shoot tissue by 74% and 66%, respectively ($p < 0.05$) (Fig. 2a and b) and *E. fetida* tissue by 72% (Fig. 2c). Burt's biochar amendment at 2.8% reduced the uptake of PCBs into *C. pepo* root tissue and *E. fetida* tissue by 53% and 44%, respectively ($p < 0.05$). BlueLeaf biochar amendment (2.8%) also reduced the uptake of PCBs into *C. pepo* root tissue by 66% and *E. fetida* tissue by 44%. These results are more consistent with our previous work (Denyes et al., 2012) which found that 2.8% Burt's biochar addition to PCB-contaminated soil decreased the uptake of PCBs to *E. fetida* by 53% and *C. pepo* roots by 77%.

This is the first study demonstrating PCB bioavailability reductions in soils under environmentally relevant mixing methods. On average, when PCB-contaminated soil was mechanically mixed for 24 h with biochar or AC, PCB concentrations in shoot, root and worm tissues were 66%, 59% and 39% lower than the manually mixed treatments (i.e. with a spade and bucket). In our work the percent reductions in earthworm PCB concentration after AC amendment increased from 54% (manual mixing) to 72% (mechanical mixing), respectively. This is consistent with an earlier

study by Sun and Ghosh (2007), which showed larger PCB reductions (14%) in *L. variegatus* after mixing AC and sediment for longer times, compared to short-term mixing. These authors also stressed that under identical conditions with the same GAC dosage and mixing time, reduction in AC particle size decreased PCB bioaccumulation. In the current study, particle size decreased by as much as 18% as a result of mechanical mixing, offering an explanation for the greater PCB reductions. This 24 h mixing strategy increased the soil/carbon amendment contact time, improved the homogeneity of the mixture and offered a greater number of particles per unit volume of soil.

A biota to sediment/soil accumulation factor (BSAF) (BSAF = [PCB$_{tissue}$]/[PCB]$_{soil}$) is often used to quantify the bioavailability of organic contaminants to plants and earthworms. The mean BSAF reduction for all mechanically mixed carbon amendments in earthworms was $90 \pm 3\%$ and $58 \pm 13\%$ in plants (roots and shoots). The mean BSAF reductions for all manually mixed carbon amendments for earthworms ($38 \pm 15\%$) and plants (roots and shoots) ($21 \pm 38\%$) (Table 2), observed in this study was closely related to the results of Jakob et al. (2012). These authors performed *in situ* amendment of GAC to PAH-contaminated soils using an excavator, which may be considered an agronomic mixing method similar to that in our study. The study reported that GAC (particle size range: 300–800 μm) reduced BSAFs of PAHs by an average of $47 \pm 44\%$ in earthworms and $46 \pm 35\%$ in plants. These authors also found that powdered activated carbon (PAC), i.e. AC with particles smaller than 45 μm, performed better than GAC, reducing earthworm BSAF by on average $72 \pm 19\%$.

It appears from the large reductions in PCB uptake by both plants and worms as a result of mechanical mixing, that mixing regime and particle size may explain the differences in contaminant uptake reported in literature (Denyes et al., 2012; Langlois et al., 2011; Beckingham and Ghosh, 2011; Paul and Ghosh, 2011) and in the present study. Based on the shift towards smaller grain sizes as a result of mechanical mixing, it is evident that this type of mixing achieved a more homogeneous distribution of AC/biochar in the soil and increased the accessible surface area (Werner et al., 2006), again resulting in lower PCB uptake by plants and worms. This effect was demonstrated by Werner et al. (2006) using passive samplers and Sun and Ghosh (2007) using worms, but this is the first study to report on the effects in soils on plant and worm uptake. Both the *in situ* and mixing experiments presented were conducted over a relatively short periods of time (60 and 40 days, respectively). Based on mass transfer kinetic modeling and a five year field study of PCB-contaminated sediment in California, it has been suggested that overtime the lower treatment effects of poorly mixed systems will diminish and treatment goals will eventually be achieved, although it may take many years longer than in a homogeneous system (Cho et al., 2012; Werner et al., 2006). Therefore, a monitoring component should be included in future work to determine if this phenomenon also holds true in soil systems. Also, from a soil remediation perspective to achieve the desired reduction in risk, carbon amendments with larger particle size distributions should be ground and thoroughly mixed into the soil with agronomic methods in mind.

Mixing regime also affected the biomass of both *C. pepo* shoot and *E. fetida* tissues. On average, *C. pepo* plants grown in soil that was manually mixed with biochar had 28% more biomass than plants grown in soil that was mechanically mixed, a result likely linked to improved substrate texture due to larger particle sizes. However, as in the *in situ* experiment, GAC amendment which was manually mixed did not increase *C. pepo* biomass. Soil amendment with GAC is not expected to offer comparable soil quality improvements to biochar. The slow oxidation of the biochar surface increases soil cation exchange capacity (Cheng et al., 2008), while its macroporosity (>50 nm) decreases nutrient and water leaching losses (Atkinson et al., 2010). Activated carbon is produced with the objective of maximizing microporosity (<2 nm), which is important for contaminant sorption and allows it to remain stable over long periods of time. The average biomass increase of *E. fetida* as a result of AC/biochar soil additions was significantly larger in the mechanically mixed treatment ($34 \pm 11\%$) than the manually mixed treatment ($1 \pm 7\%$) ($p < 0.05$). In all mechanically mixed treatments and all but GAC manually mixed treatments, earthworm biomass increased over the respective controls, suggesting that biochar amendments did not cause adverse ecotoxicological effects. The reduction in particle size and subsequent increase in external surface area and mixture homogeneity as a result of mechanically mixing likely explain why AC/biochar treatments were more effective at minimizing the uptake of PCBs to *C. pepo* and *E. fetida* than when manually mixed and the ensuing reduced toxicity may then explain why *E. fetida* biomass was greater in the mechanically mixed treatments.

4. Conclusions

This is the first study to investigate and directly compare the effects of *in situ* biochar and AC amendments to a PCB-contaminated Brownfield soil. It was determined that both biochars performed equally to GAC at decreasing phytoavailability of PCBs to pumpkin roots. When biochar was added to the degraded PCB-contaminated Brownfield soil, pumpkin *C. pepo* plants grew larger than plants grown in the controls and AC treatments and neither biochars caused adverse ecotoxicological effects to soil invertebrates. This study also shows that laboratory based mixing may exaggerate the sorptive capacities of both AC and biochar, at least in the short-term. Although similar work has been conducted using kinetic modeling or passive samplers in PCB-contaminated sediment systems, our work is novel in approaching the effects of mixing in PCB-contaminated soil systems to both plants and earthworms. Reductions in *E. fetida* tissue as a result of biochar addition were only significant when the soil was mechanically mixed for 24 h at 30 rpm, and under greenhouse conditions. Neither AC nor biochar when manually mixed were capable of significantly reducing PCB uptake by *C. pepo*. Sorption and subsequent reductions in bioavailability of organic contaminates as a result of carbon amendments, are important in mitigating risks posed to both environmental and human health. Thus although AC and biochar show significant potential to serve as sorbents for the *in situ* stabilization of organic contaminants, future research should focus on environmentally relevant application methods to better determine the actual remediation potential of these materials.

Table 2
Bioaccumulation factor of polychlorinated biphenyls (PCBs) into *Cucurbita pepo* and *Eisenia fetida* grown in/exposed to unamended PCB-contaminated Brownfield soil and Brownfield soil amended with 2.8% GAC or biochar, carbon amendments with two mixing methods.

Mixing type	Treatment	Biota to soil accumulation factors		
		C. pepo ssp pepo		*E. fetida*
		Root	Shoot	
Manually Mixed	Control	15 ± 5.1	0.2 ± 0.1	26 ± 7.4
	2.8% GAC	8.6 ± 1.9	0.4 ± 0.1	12 ± 3.2[a]
	2.8% Burt's biochar	8.5 ± 1.2	0.1 ± 0.0	19 ± 3.4
	2.8% BlueLeaf biochar	10 ± 1.5	0.2 ± 0.1	17 ± 3.1
Mechanically mixed	Control	15 ± 2.5	0.3 ± 0.1	25 ± 5.7
	2.8% GAC	3.9 ± 1.0[a]	0.1 ± 0.0	6.1 ± 2.3[a]
	2.8% Burt's biochar	7.2 ± 2.1[a]	0.2 ± 0.1	13 ± 3.5[a]
	2.8% BlueLeaf biochar	5.0 ± 0.5[a]	0.1 ± 0.0	14 ± 1.5[a]

[a] Indicate statistically significant differences from the corresponding control.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2013.07.016.

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