


BIOCHAR FROM BIOMASS AND WASTE

FUNDAMENTALS AND APPLICATIONS

EDITED BY
YONG SIK OK, DANIEL C.W. TSANG,
NANTHI BOLAN, AND J.M. NOVAK

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YONG SIK OK

Korea Biochar Research Center, O-Jeong Eco-Resilience Institute (OJERI) & Division of Environmental Science and Ecological Engineering, Korea University, Seoul, Republic of Korea

DANIEL C.W. TSANG

Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, P.R. China

NANTHI BOLAN

Global Centre for Environmental Remediation (GCER), Faculty of Science, The University of Newcastle, Callaghan, NSW, Australia

J.M. NOVAK

U.S. Department of Agriculture, Agricultural Research Service, Coastal Plains Research Center, Florence, SC, United States

ELSEVIER

CHAPTER

5

Biochar for Mine-land Reclamation

James A. Ippolito[1], *Liqiang Cui*[2], *J.M. Novak*[3] *and Mark G. Johnson*[4]

[1]Department of Soil and Crop Sciences, Colorado State University, Fort Collins, CO, United States [2]School of Environmental Science and Engineering, Yancheng Institute of Technology, Yancheng, China [3]U.S. Department of Agriculture, Agricultural Research Service, Coastal Plains Research Center, Florence, SC, United States [4]U.S. Environmental Protection Agency, National Health and Environmental Effects Research Laboratory/ORD Western Ecology Division, Corvallis, OR, United States

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5.1 INTRODUCTION

Abandoned mine lands are those lands, waters, and surrounding watersheds where extraction, beneficiation, or processing of ores and minerals has occurred (US EPA, 2017a). Globally, abandoned mines number in the hundreds of thousands. Examples include:

- The United Kingdom, with more than 2000 abandoned mines (SRK Consulting, 2017);
- Italy, with approximately 3000 abandoned mines (Italy Europe 24, 2015);

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- France, with ~4000, Germany 100 s, Poland 1000–1500, Turkey > 700, and Korea >1000 abandoned mines (International Commission on Mine Closure, International Society for Rock Mechanics, 2008);
- Abandoned mines in Australia number >50,000 (Mining Technology, 2015);
- Canada, with ~13,000 abandoned mines (Mackasey, 2000);
- The United States is estimated to contain ~500,000 abandoned mines (BLM, 2016).

Furthermore, if the wastes contain sulfide ores, then oxidation reactions generate acid mine drainage, a large environmental concern because it leads to significant environmental impacts globally (Coetzee et al., 2010). In the western United States alone, approximately 33,000 mines sites generate acidity (Mittal, 2011), leading to increases in heavy metal bioavailability, degradation of mine-affected soils and surface waters (Ippolito et al., 2017), or contamination of shallow groundwaters (Ramontja et al., 2011). Thus, it is important that management strategies are available for reducing the continued environmental impact in mine lands with subsequent successful improvements in environmental quality.

Biochar may play a role in improving mine-land remediation by positively affecting changes in mine-land soil conditions. Biochar application has been shown to increase mine soil, tailings, and waste rock pH, cation-exchange capacity, water-holding capacity, organic matter content, nitrate concentration, biological *N*-fixation rates, and phosphatase and dehydrogenase activity (Fellet et al., 2011; Hanauer et al., 2012; Kelly et al., 2014; Kim et al., 2014; Reverchon et al., 2015). Biochar application to mine-land materials has also been shown to increase vegetative yield and cover (Aspen Center for Environmental Studies, 2011; Rodríguez-Vila et al., 2015). Reduction in bioavailable heavy metal concentration is speculated to produce a positive change in soil condition and improvement in plant growth. The following sections illustrate the important role biochar plays in sorbing, sequestering, precipitating, and ultimately reducing bioavailable metals in contaminated solutions, soils, and mine-land situations.

5.1.1 Cadmium

Exposure to Cd can lead to a variety of health effects, such as flu-like symptoms (short-term exposure to high Cd levels), kidney, bone, lung disease, and cancer (long-term exposure to low-level Cd levels) (US DOL-OSHA, 1993). Thus, reducing Cd exposure/ingestion by humans and animals is an important health concern. Biochars have been shown to play a role in reducing heavy Cd bioavailability in a variety of environmental settings.

Sekulić et al. (2018) showed that crushed apricot seeds, pretreated with phosphoric acid prior to pyrolysis, could almost linearly remove Cd from the aqueous phase as associated with increasing solution pH from 2 to 7. The authors attributed Cd removal to adsorption mechanisms up to ~pH 7 and Cd-hydroxide precipitation above pH 7. Karunanayake et al. (2018) used six different biochars (i.e., douglas fir biochar, magnetized douglas fir and switchgrass biochars, two different commercial biochars, pine wood biochar) to remove Cd from solution over a pH range of 2–7. Cadmium adsorption increased with increasing biochar surface area and, similar to the findings of Sekulić et al. (2018), sorption increased with increasing pH. Karunanayake et al. (2018) suggested that as solution pH increases, deprotonation of biochar surface carboxylic acid and other acidic hydroxyl groups leads to lower net positive charge, thus enhancing Cd sorption at negative biochar sites. Deng et al. (2017) used activated rice straw biochar to determine removal capabilities on solution-borne Cd. The authors reported that Cd sorption results at low pH values were similar to those reported by Karunanayake et al. (2018) and to Sekulić et al. (2018). Aslam et al. (2017) compared a low- and high-temperature biochar (350°C and 650°C, respectively) for removal of Cd from solution, and found that the lower temperature biochar was more effective at removal. It was speculated that this reduction was due to cation-exchange capacity and functional groups present. Shen et al. (2017a) used algae-derived biochar to effectively sorb and remove Cd from aqueous solution, with biochar sorbing up to 217 mg Cd g^{-1}. The authors attributed sorption to electrostatic interactions, ion exchange, and surface complexation.

In China, Cd accumulation in rice grown in Cd-contaminated soil from mining/smelting operations has been documented (Hu et al., 2016). As a remediation example, Cui et al. (2011) added wheat straw biochar at 0, 10, 20, and 40 Mg ha^{-1} to a rice paddy soil containing ~22 mg kg^{-1} total Cd. The amended biochar raised soil pH, decreased bioavailable soil Cd content by 5.5%–52%, and lowered rice Cd content by 17%–62%. Bian et al. (2013) found a similar response when adding wheat straw-derived biochar to rice paddies. Qi et al. (2018) showed that within soils containing greater sorption capacity, biochar made from wood shavings or chicken litter had no effect on bioavailable Cd concentrations. Under acidic conditions, however, the authors observed a decrease in soluble Cd content, attributing the reduction to soil pH increases. Yin et al. (2017) added rice straw biochar to a contaminated paddy soil, showing porewater Cd concentration reductions, which was likely due to immobilization via surface complexation and precipitation of insoluble Cd mineral phases. Ouyang et al. (2017) added increasing corn straw biochar applications (0%–5% by weight) to a soil containing elevated Cd concentrations from long-term use of Cd-containing phosphate fertilizers. Cd was found to be immobilized rather than transported offsite, likely due to Cd immobilization by biochar. In their study, a 3% application rate caused the greatest Cd reductions. Qian et al. (2017) added rice straw biochar to a soil slurry and a hydroponic system containing 5.6 mg Cd L^{-1}. Root growth was inhibited by the presence of Cd by 20%–50%, but when biochar was added root inhibition was only 4%–25%. Biochar was speculated by the authors to cause the positive root growth in the presence of Cd.

5.1.2 Copper

Long-term Cu exposure can irritate mucous membranes, cause headaches, dizziness, nausea, and diarrhea; drinking water containing excess Cu can lead to nausea, vomiting, diarrhea, and if taken intentionally, can cause liver and kidney damage, and even death (ATSDR, 2004). Since the greatest chance of ingesting excess Cu is via drinking water, it is important to reduce Cu release from piping, industrial applications, or from acid mine drainage. Again, biochar has been proven to remove Cu from various sources.

Biochar use for removing Cu from solution has been well studied. Ippolito et al. (2012) used a KOH-steam-activated pecan shell biochar to sorb Cu from solution. The authors noted that biochar could retain >42,000 mg Cu kg^{-1} biochar, and that under acidic conditions, Cu sorbed onto biochar as humic-like substances. In contrast, while under alkaline conditions, Cu oxide and carbonate precipitates were the dominate sequestration mechanisms. Deng et al. (2017) used activated rice straw biochar to remove Cu from solution over varying pH values. The authors showed that Cu removal rate increased with increasing pH up to ~pH of 5, likely due to deprotonation of functional groups leading to greater Cu removal. Furthermore, Cu removal capacity equaled between 36,000 and 47,000 mg Cu kg^{-1} biochar, within a range similar to Ippolito et al. (2012). Likewise, Batool et al. (2017) showed that farmyard manure biochar and poultry litter biochar could remove ~44,000 mg Cu kg^{-1} biochar. Tran et al. (2017) created biochar from several types of mono- or polysaccharides to remove Cu from solution. Similar to the previous findings, the authors showed that Cu removal was highly pH dependent and could sorb a maximum of ~57,000 mg Cu kg^{-1} biochar. He et al. (2017) created a microscale bagasse biochar/polysulfone membrane to remove Cu from water over varying pH values. Copper sorption was maximized at pH > 4.5 with a sorption capacity of ~14,000 mg Cu kg^{-1} membrane. The authors attributed the sorption to the membrane surface charge becoming negative above pH 4.4, along with biochar functional groups becoming deprotonated. Zhou et al. (2017) used Fe- or Zn-doped sawdust biochar to effectively remove Cu from solution, suggesting that hydrophobic and hydrophilic sites on the biochar caused a reduction in solution Cu content.

Biochar use for removing Cu from soils has been studied less. Cárdenas-Aguiar et al. (2017) spiked a soil with 1000 mg Cu kg^{-1}, then added 10% biochar derived from urban waste or biochar + compost. The authors then attempted to grow various plant species (i.e., mustard, cress, ryegrass). Mustard and cress growth was severely affected by Cu-contaminated soil alone. However, when biochar was added alone, there was positive mustard growth. Similarly, biochar + compost had a positive effect on cress productivity. Cárdenas-Aguiar et al. (2017) attributed these positive plant growth responses to biochar and/or compost immobilizing Cu. Rodríguez-Vila et al. (2017) amended Cu-contaminated mine soil with 0%, 20%, 40%, 80%, and 100% of a 95:5 part mixture of technosol:holm oak wood biochar. As with the biochar-Cu-solution removal findings above, the authors showed a decrease in Cu availability with increasing soil pH. They also observed an increase in plant growth using higher mixture application rates. Meier et al. (2017) added chicken manure or oat hull biochar to a Cu-contaminated soil at 0%, 1%, and 5% (w/w). Biochars increased soil pH, decreased Cu availability, and increased Cu associated with the organic and residual soil fraction. The authors also showed that microbial respiration increased, suggesting that biochars improved their habitat. Ippolito et al. (2017) added lodgepole pine or tamarisk-derived biochars (0%, 5%, 10%, and 15% by weight) to four mine-land soils containing elevated Cu concentrations. As with Meier et al. (2017), the authors observed a significant increase in pH and a decrease in Cu availability, with increasing Cu concentrations in the oxyhydroxide and carbonate soil phases.

However, the above biochar responses are not always observed. Ippolito (unpublished) utilized soils spiked with 0, 250, 500, and 1000 mg Cu kg^{-1} from a previous study (Ippolito et al., 2011), and then added increasing amounts (0%, 0.5%, 1%, and 2% by weight) of hardwood biochar. Their concern was to observe the effects on alfalfa growth and Cu uptake, and potential reductions in soil extractable Cu content (Fig. 5.1). Although increasing Cu content significantly decreased plant yield ($P < .001$), increasing the biochar application rate had no effect ($P = .293$) on improving plant growth. Increasing the biochar application rate decreased plant Cu concentrations ($P = .003$) but had no effect on available

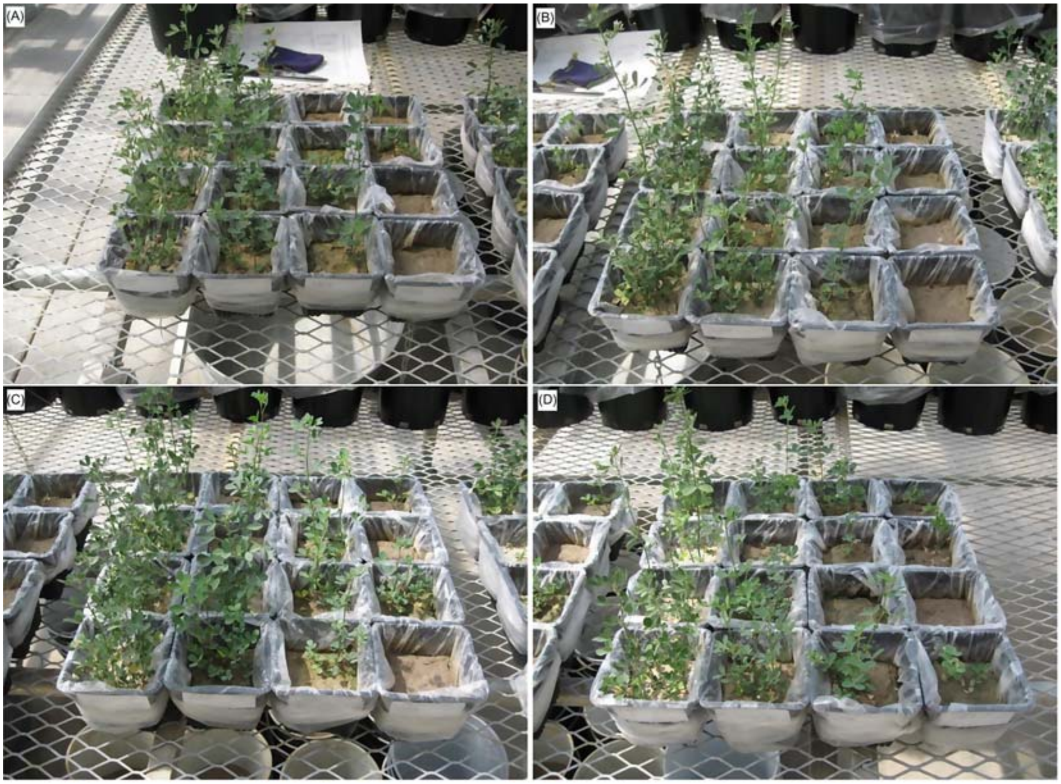

FIGURE 5.1 Four replicates (front to back) of, from left to right in each image, increasing Cu concentrations of 0, 250, 500, and 1000 mg kg^{-1}. Fast pyrolysis hardwood biochar was added to all pots at (A) 0%, (B) 0.5%, (C) 1.0%, and (D) 2% by weight and then alfalfa was grown over a period of approximately 30 days. *Photos courtesy of Jim Ippolito.*

soil Cu concentrations ($P = .348$). This is an example of employing a biochar that has not been vetted for soil Cu removal. Thus, some caution exists in terms of using any type of biochar for remediation purposes.

5.1.3 Lead

Widespread extraction, processing, and use of Pb has resulted in extensive environmental contamination, human exposure, and significant health problems globally (World Health Organization, 2017). Issues with long-term human Pb exposure include distribution to the brain, liver, kidneys, and bones; Pb release from bones during pregnancy, which subsequently leads to developing fetus exposure; it is particularly harmful to young children; and there is no known level of Pb exposure that is considered safe (World Health Organization, 2017). Short-term Pb exposure can lead to abdominal pain, constipation, headaches, irritability, loss of appetite or memory, and weakness (Centers for Disease Control and Prevention, 2017).

As with other heavy metals described above, scientific reports have established that biochar can sorb Pb. Aslam et al. (2017) compared biochars (350°C and 650°C, respectively) for Pb removal from solution. The authors found approximately 70%−95% Pb removal from solution after shaking with the low-temperature biochar, compared to only 39%−60% removal with the high-temperature biochar over the same shaking period. The authors suggested that Pb was bound to a greater extent with low-temperature biochars due to Pb attraction to oxygen-containing functional groups or precipitation with different compounds present on biochar surfaces. Deng et al. (2017) used activated rice straw biochar to remove solution-borne Pb, noting that Pb removal may have been mainly due to functional groups present on the biochar. Lee et al. (2017) suggested that Pb sorption onto palm oil sludge biochar was due to cation-exchange mechanisms. He et al. (2017) used a bagasse biochar to remove Pb from water over varying pH values. As with their Cu observations, Pb sorption was maximized at pH > 4.5, with sorption attributed to negative surface charge development above pH 4.4 and functional groups becoming deprotonated. Karunanayake et al. (2018) found a similar Pb−pH response with two douglas fir biochars. Sekulić et al. (2018) showed that crushed apricot seed biochar could sorb approximately 179 mg Pb g^{-1}. The authors speculated that solution Pb removal occurred via a number of pathways, including a quick surface sorption phenomenon, then followed by a slow sorption via intraparticle diffusion, and finally maximum sorption was reached since intraparticle diffusion reached a minimum. Shen et al. (2017b) utilized four biochars (i.e., hardwood, wheat straw pellets, rice husk, soft wood pellets) to remove Pb from solution, followed by sequential extraction to identify Pb phases present. Lead was sorbed onto the biochars predominantly as potentially bioavailable phases. This Pb phase could possibly be released back into the environment.

Biochar has been added to various Pb-contaminated soils with varying degrees of success in terms of reducing bioavailable Pb concentrations. Fellet et al. (2011) added increasing orchard pruning biochar (0%, 1%, 5%, and 10%, w/w) to a Pb-contaminated mine tailing. The authors observed a significant reduction in bioavailable Pb concentrations with increasing biochar application rate. Jain et al. (2017) added lemongrass biochar to acidic coal field overburden material in order to study the effects of herb growth and Pb uptake. The results suggested that biochar applied at 15% or 20% (by weight) reduced Pb translocation from roots to aboveground plant tissue by 81%, and aboveground plant Pb accumulation was reduced by ~94% as compared to controls. Kelly et al. (2014) added pine wood biochar to acidic mine-land soils at rates of 0%, 10%, 20%, and 30% (v/v). Biochar application increased soil pH and decreased solution Pb leachate concentrations by 63% in one mine soil, but did not affect Pb leachate concentrations from another mine soil. Biochar produced from tobacco was used to successfully increase soil cation-exchange capacity, reduce soil bioavailable Pb concentrations, increase Chinese cabbage yield, and decrease plant Pb uptake in heavily contaminated Pb soils from China (Lahori et al., 2017). Moreno-Barriga et al. (2017) added 1% and 2% hog waste biochar and $CaCO_3$ waste to a Pb-contaminated, acidic mine tailing to assess growth effects of proso millet. Biochar rate increased soil pH, reduced Pb in a relatively bioavailable form, and increased Pb in a more recalcitrant form. However, the highest biochar application rate negatively affected plant growth likely by limiting other nutrients essential for plant growth. This is another example of prevetting biochar before its field use. Thus, as with the Cu observations by Ippolito (above; unpublished), a need for caution exists when utilizing biochars for remediation purposes.

5.1.4 Zinc

Most Zn enters the environment as a result of mining activities; purifying of Zn, Pb, and Cd ores; steel production; coal burning; and waste-burning or reutilization (e.g., biosolids land application) (Agency for Toxic Substances and Disease Registry, 2005). Only exposure to high Zn doses has toxic effects, and long-term high-dose Zn supplementation interferes with human Cu uptake; thus Zn toxic effects typically induce human Cu deficiency symptoms (Plum et al., 2010). However, at the cellular level, excess endogenous Zn can act on several molecular regulators of programmed cell death, which sometimes occurs in the brain (Plum et al., 2010). Areas that have been mined for other elements (e.g., Pb, Au, Ag) typically produces waste mine tailings with elevated Zn concentrations (i.e., Zn is not released during the mining/smelting process); these are specific locations where excess Zn may become toxic to microorganisms and plants.

Recent biochar studies have specifically targeted Zn issues in soils. Kumar et al. (2018) spiked a sandy soil with 880 mg Zn kg^{-1}, aged the soil for 60 days, applied 1%, 3%, and 5% (by weight) using either grain husk or cattle manure biochar, and then grew Ficus over a 180 day period. In general, leaf Zn content decreased with increasing biochar rate, and pot leachate Zn concentrations were lower than the control, by a factor of $\sim 1-2$. The authors also showed that biochar acted as a Zn-sink via chemical extraction of separated biochar particles. Xu et al. (2017) added 0%, 0.5%, 1%, and 2% (w/w) wine lees (i.e., dead yeast and other particulates remaining after the wine-making process) biochar to a topsoil containing elevated Zn concentrations (1580 mg kg^{-1}) contaminated from nearby industrial processes; rice was grown throughout the study. The percentage of soil-exchangeable Zn decreased with increasing biochar application rate, over various rice growth stages, and rice yield increased at the two highest biochar application rates as compared to the control. The authors attributed positive results to biochar increasing soil properties such as pH and cation-exchange capacity, as well as containing functional groups that sorb Zn and reduce bioavailability.

The addition of 1% or 2% hog waste biochar to a heavily contaminated Zn-containing mine tailing ($>$1000 mg total Zn kg^{-1}) caused Zn to shift from exchangeable to Fe/Mn oxide-bound phases (Moreno-Barriga et al., 2017). Shifts in metal phases were attributed to an increase in mine-tailing pH associated with biochar application. In addition, changes in pH and shifts in Zn soil fractions were similar to that found by Ippolito et al. (2017). Lahori et al. (2017) added 1% tobacco biochar to a Zn-contaminated soil (225 mg total Zn kg^{-1}; 29 mg plant-available Zn kg^{-1}) and observed a significant reduction in plant-available Zn concentration as compared to control soil. The addition of a liming source along with biochar caused further reductions in plant-available Zn, with results likely explained by shifts in Zn form toward oxide-bound phases (e.g., see Moreno-Barriga et al., 2017; Ippolito et al., 2017). Fellet et al. (2011) added increasing orchard pruning biochar (0%, 1%, 5%, 10% weight:weight) to a Zn-contaminated mine tailing ($>$11,500 mg total Zn kg^{-1}). As with their Pb findings, the authors observed a significant reduction in Zn bioavailability with increasing biochar application rate, likely attributed to shifts in soil Zn pools as observed by others.

Although most studies have shown significant reductions in soil Zn availability associated with biochar application, others have shown no change or significant negative effects on soil Zn concentrations. Peltz and Harley (2016) provided a case study for biochar use in the Upper Animas Mining District of southwestern Colorado, USA. Findings from a 2-year trial, with mine-affected soils receiving 30% biochar (by volume), showed soil leachate concentrations with little change in total Zn. Kelly et al. (2014) added pine wood biochar (0%, 10%, 20%, 30% volume:volume) to a heavily contaminated mine soil ($>$2700 mg total Zn kg^{-1}) and repeated leaching the soil over a 2-month period. Results showed that biochar application actually caused significant increases in leachate Zn concentrations near the end of the study period in one of two spoil materials investigated.

5.1.5 Recent Case Study—Biochar Use in Multielement-Contaminated Mine Waste

Utilizing mine spoils with mixed heavy metal contamination, Ippolito et al. (2017) recently reported that increasing lodgepole pine or tamarisk biochar application (0%, 5%, 10%, and 15% by weight) to several acid generating mine-land soils could increase soil pH and decrease metal bioavailability. Furthermore, the authors showed via a sequential extraction procedure that biochar addition caused shifts in soil metal pools toward Cd, Cu, Pb, and Zn-associated carbonate and oxyhydroxide phases. Similar results were found in a recent parallel study by Ippolito using mine-land soils amended with increasing switchgrass biochar (unpublished). Switchgrass biochar (pH = 9.4) was added at 0%, 5%, 10%, and 15% (by weight) to four different acidic mine-land soils from Creede and Leadville, Colorado, USA, and from near Coeur d'Alene, Idaho, USA. Increasing biochar application rate increased soil pH (Fig. 5.2A), and concomitantly decreased soil Cu, Pb, and Zn bioavailability (Fig. 5.2B–D, respectively). Following switchgrass biochar application, soil phases shifted toward carbonate bound and organically complexed heavy metal phases and were likely responsible for the reduction in heavy metal bioavailability.

5.1.6 Recent Case Study—Biochar Use in Cd- and Zn-Contaminated Paddy Soil

Cui (unpublished) recently studied biochar application effect on a heavy metal-contaminated soil in China. Specifically, wheat straw biochar was applied to a Cd and Zn-contaminated paddy soil (total Cd and Zn = 22.6 and 186 mg kg^{-1}, respectively) at 0%, 5%, and 15% by weight, with soil mixtures shaken in 0.01 M $CaCl_2$ solution over a 240 day incubation period. Samples were destructively sampled at various time intervals, and mixture pH and 0.01 M $CaCl_2$ extractable Cd and Zn concentrations were determined. After 240 days, the solid phase was allowed to air dry, and then subject to the European Community Bureau of Reference (BCR) sequential extraction procedure according to Ure et al. (1993); additional BCR extraction information can be found in Ippolito et al. (2017).

Increasing biochar application rate increased soil-biochar mixture pH over the 240-day study (Fig. 5.3A), and based on previously published work (above), it was anticipated that heavy metal concentrations would decrease. Indeed, the author observed significant decreases in bioavailable Cd and Zn concentrations with increasing biochar application rate at all sampling times (Fig. 5.3B and C). Bioavailable Cd and Zn concentrations

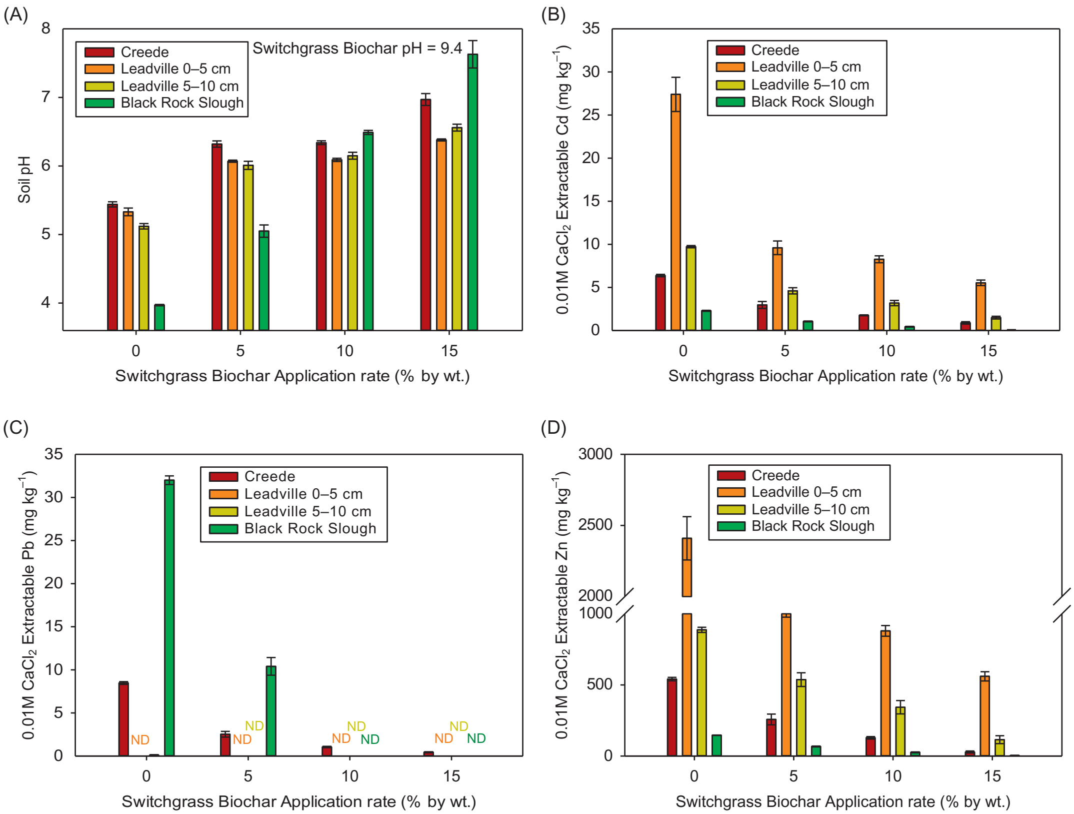

FIGURE 5.2 The effect of increasing switchgrass biochar rate on (A) pH and 0.01 M $CaCl_2$ extractable (B) Cd, (C) Pb, and (D) Zn concentrations in four mine-land soils. ND = nondetectable.

decreased by 53%–97% and 66%–98%, respectively, as compared to the control. Based on the BCR extraction procedure, Cui (unpublished) showed that Cd and Zn phases shifted toward carbonate and Fe/Mn oxyhydroxide phases. As shown and suggested by others (e.g., Ippolito et al., 2017; Ahmad et al., 2016; Park et al., 2011), these phases were likely responsible for the reduction in heavy metal bioavailability. Furthermore, these findings support the contention that biochars have the potential to be used to improve heavy metal-contaminated soils.

5.1.7 Recent Case Study—Designing Biochar Production and Use for Mine-Spoil Remediation

The Formosa mine site was established in Southwest Oregon, USA for silver, gold, and copper extraction from sulfide-containing rock deposits of the Rouge Formation. Mine spoils were discarded on the surface and ensuing oxidation of the sulfide ores caused their extreme acidification (Fig. 5.4A; $pH_{H2O} = 2.44$). Additionally, the spoils contained

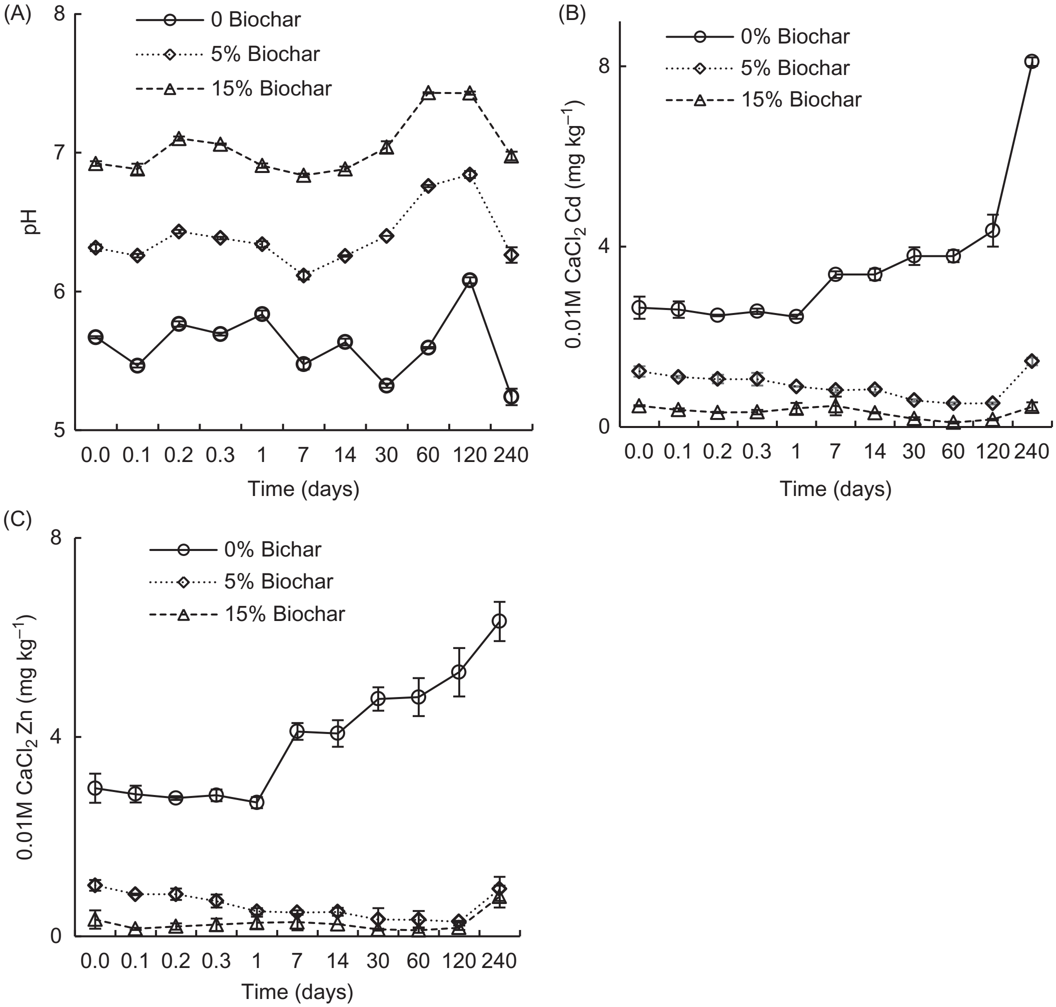

FIGURE 5.3 The effect of increasing wheat straw biochar application rate (0%, 5%, and 15% by weight) on Cd- and Zn-contaminated soil (A) pH and 0.01 M $CaCl_2$ extractable (i.e., bioavailable) (B) Cd and (C) Zn concentrations over a 240 day shaking/incubation period.

unextracted heavy metals such as Cu and Zn. Mine-spoil metal analysis revealed that the total, salt, and Mehlich-3 extractable Cu and Zn concentrations ranged between 609−651, 64−78, and 61−68 mg kg^{-1}, respectively. These spoil conditions have limited site revegetation and have probably stressed soil health characteristics (i.e., soil enzymatic and microbial activity). Thus, a reclamation plan should involve neutralizing the acid conditions, followed by reducing plant-available Cu and Zn concentrations. Additionally, restoring mine-spoil health characteristics could be facilitated by adding biochar, compost, and/or manure that increases spoil organic carbon (OC) content and enhances microbial growth conditions.

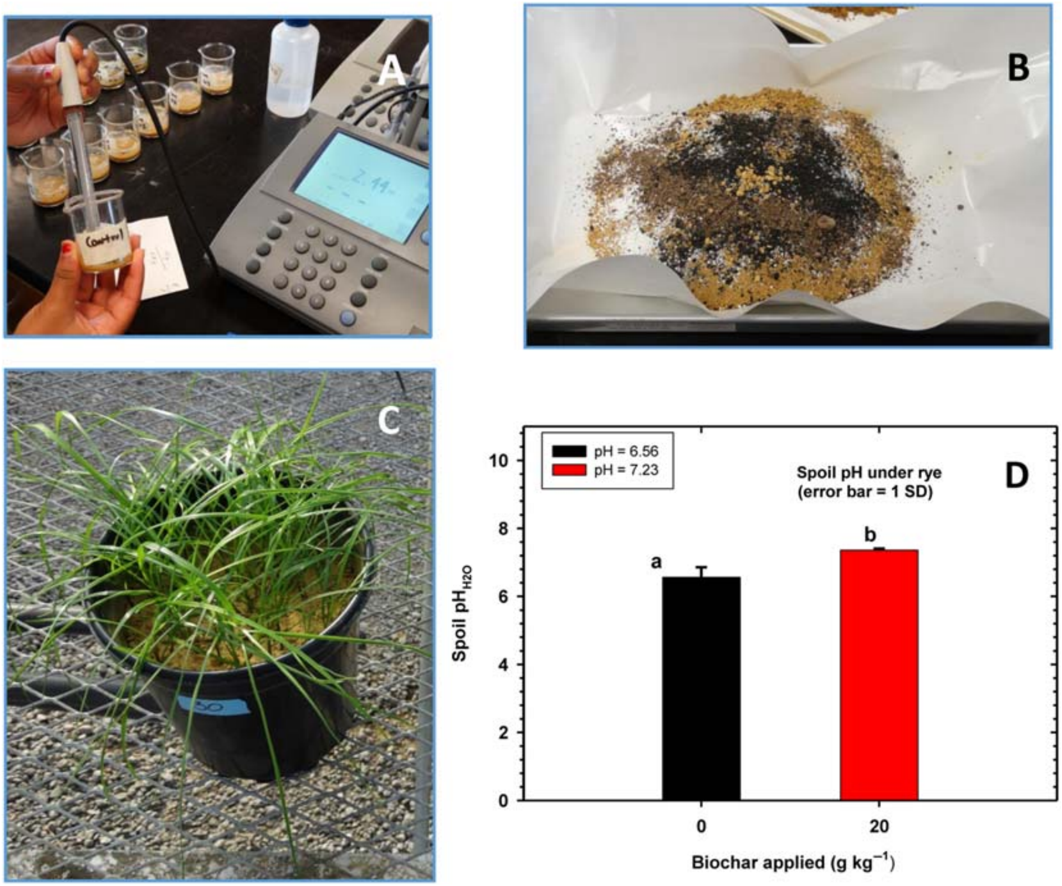

FIGURE 5.4 (A) pH of the Formosa mine spoil (located in southwest Oregon, USA). (B) Mixing 2% dairy manure biochar, 1% lime, and 0.5% poultry litter into the Formosa mine spoil. (C) Ryegrass grown in the amended Formosa mine spoil. (D) Average mine spoil pH values after the 100 day ryegrass experiment (the blue line in Fig. 5.4D signifies the upper pH threshold for cereal rye production). *Photos courtesy of Jeff Novak.*

A designer biochar was selected for addition to the Formosa mine spoil to assist with neutralizing the acidic pH and sequester both Cu and Zn concentrations. A manure feedstock and high pyrolysis temperature was selected since biochars produced from manures, at high temperature, are aklaline (Novak et al., 2009, 2012) and have an ash composition that can bind metals (Ehsan et al., 2014; Ippolito et al., 2017). Here, a dairy manure feedstock gasified at 800°C produced a designer biochar with a high ash content 52% (w/w) and an alkaline pH (10.2 in H_2O). These biochar characteristics have been implicated as key biochar traits for metal sequestration and as a lime source (Lehmann and Joseph, 2015).

The dairy manure biochar's ability to remediate the mine spoil was tested in a greenhouse experiment growing cereal rye (*Secale cereale*) as a test crop. Dairy manure biochar at 0 and 20 g kg^{-1} along with 10 g kg^{-1} of lime and 5 g kg^{-1} of fresh poultry litter manure were mixed into pots containing the Formosa mine spoil (Fig. 5.4B). The lime was added in case the acid-neutralization capability of this biochar was insufficient to effectively neutralize the Formosa mine-spoil acidic potential. Additionally, fresh poultry manure was added as an OC stimulant for microbial activity. Deionized H_2O was added to each mixture to bring the spoil moisture content to 10% (w/w). Each mine spoil was treated with 100 kg N ha^{-1} as a supplemental N source. Plant phosphorus (P) and potassium (K) nutritional requirements were assumed to be supplied by the dairy manure biochar because it contained 57 and 13 g kg^{-1} (by weight), respectively.

Rye was allowed to grow for 100 days (Fig. 5.4C). On the 72, 84, and 99 days of incubation, the rye was manually trimmed using scissors to a 6 cm height above the mine-spoil surface. The rye clippings were placed in beakers, oven-dried overnight at 60°C, and then weighed. Rye stubble (plant part below 6-cm trim height) was removed on day 100, dried and weighted in a similar fashion. Rye roots were separated from mine spoils by washing with deionized H_2O. Roots were placed in a beaker, dried in a similar manner and weighed. All rye material (cuttings, stubble, and roots) was later digested in concentrated HNO_3 and 30% H_2O_2. The digestate was filtered, and analyzed for Cu and Zn using ICP. A subsample of the mine spoil was collected for pH measurement in H_2O.

The greenhouse incubation revealed good rye growth after treatment without biochar (e.g., with lime alone; 0 g/kg biochar treatment) and with 20 g/kg biochar (Table 5.1). However, only the first plant cutting mean rye aboveground biomass yield was significantly different when compared to the control (Table 5.1). Although ryegrass grew well in the control (lime alone, 0 biochar), the benefits of adding the biochar can be observed in terms of plant metal uptake. Rye Cu uptake was reduced only in the third cutting and the root material. In contrast, biochar significantly reduced rye Zn uptake during all cuttings (and in roots) except at the first cutting. These results illustrate that the lime and biochar were capable of reducing plant uptake of Cu and Zn, although the results were mixed.

Mine-spoil mean pH values measured at the experiment end are shown in Fig. 5.4D. The blue line on Fig. 5.4D represents a soil pH of ~6.2, which is adequate for cereal growth. In both treatments, the pH at the end of the experiment exceeds this optimum pH range. The control treatment has a pH of 6.56 (spoil + lime alone) while the spoil treated with lime and biochar had a pH of 7.23. Thus, the amount of lime used in this experiment could be slightly reduced to < 10 g kg^{-1}. The results do show that there was a significant difference in the mean pH value between the control (0% biochar) and treated mine spoil. Raising the mine spoil pH to > 7 suggests that lime amounts can be reduced when used with this calcareous dairy manure biochar. It is important that the amount of lime and designer biochar addition be determined in preliminary experiments to ensure that the spoil pH is in a range that does not reduce the uptake of critical plant nutrients such as P and trace metals (i.e., B, etc.). One may also wish to consider the utility of lime and biochar when determining and neutralizing acid-generating potential in mine spoils containing sulfide-bearing mineral phases.

These results suggest that lime was important for raising the mine-spoil pH and the dairy manure biochar showed promise in minimizing both Cu and Zn uptake by rye. It is speculated that the reduced plant uptake of Cu and Zn may be through sequestration by components in the biochar ash, or by metal sorption or precipitation reactions associated with pH shifts as mentioned previously.

TABLE 5.1 Mean Rye Aboveground Biomass, Plant Cu and Zn Uptake at Different Cutting Days, and Cu and Zn in Roots at End of Study (Standard Deviation in Parentheses; odw = Oven Dry Weight; Data Not Published)[a]

	Biochar Treatment (g kg^{-1})	
Aboveground Biomass at Day of Cutting:	0	20
	Oven Dry Weight (g)	
1st cutting (d 72)	0.62(0.07)[a]	0.73 (0.06)[b]
2nd cutting (d 84)	1.23 (0.13)[a]	1.24 (0.17)[a]
3rd cutting (d 99)	2.15 (0.05)[a]	2.05 (0.16)[a]
Stubble (d 100)	5.73 (0.16)[a]	5.75 (0.48)[a]
Cu uptake in:	0	20
	mg kg^{-1}	
1st cutting (d 72)	26.7 (2.0)[a]	25.4 (1.5)[a]
2nd cutting (d 84)	25.4 (6.7)[a]	28.3 (8.5)[a]
3rd cutting (d 99)	22.3 (8.4)[a]	12.8 (0.9)[b]
Stubble (d 100)	10.2 (1.0)[a]	10.2 (2.4)[a]
Roots	205 (44)[a]	164 (14)[b]
Zn uptake in:	0	20
	mg kg^{-1}	
1st cutting (d 72)	79.5 (7.1)[a]	77.6 (6.1)[a]
2nd cutting (d 84)	87.9 (3.2)[a]	72.7 (6.0)[b]
3rd cutting (d 99)	73.6 (3.6)[a]	42.8 (3.6)[b]
Stubble (d 100)	73.7 (4.9)[a]	53.9 (4.2)[b]
Roots	202 (45)[a]	154 (16)[b]

[a]*Means compared between columns followed by a different letter are significantly different using a* t-test *at* $P < 0.05$ *level of significance.*

5.2 CONCLUSIONS

Over half a million abandoned mines exist globally. Many of these abandoned mine sites are capable of generating acidity, increasing metal solubility, and subsequently degrading environmental quality. Based on the current literature, biochar has been proven to play a role in alleviating acidity and heavy metal contamination through a number of reactions. Biochar reactions include the material acting as a liming source and raising soil pH. This allows for bioavailable metal concentrations to be reduced via precipitation, oxide, hydroxide, carbonate, and organic phase interactions. Understanding the on-site, heavy metal contamination conditions the initial metal forms present and the proper biochar application required for metal transformations is of paramount importance. Furthermore, understanding the potential for biochar-induced chemical reactions to occur, or lack thereof, prior to biochar land application, may save time and money during mine-land reclamation. Several examples were presented whereby biochar use did not affect soil heavy metal reductions, suggesting that caution exists in terms of haphazardly using any type of biochar for remediation purposes.

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