5-2019

The Impact of Wood Biochar on the Plant Uptake of Pharmaceuticals and Personal Care Products from Reclaimed Wastewater

Jeffrey Flashinski
Utah State University

THE IMPACT OF WOOD BIOCHAR ON THE PLANT UPTAKE OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS FROM RECLAIMED WASTEWATER

by

Jeffrey Flashinski

A thesis proposal submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Environmental Engineering

Approved:

William J. Doucette, Ph.D. Environmental Chemistry Major Professor	Bruce Bugbee, Ph.D. Plant Physiology Committee Member
Darren McAvoy, M.S. Forestry Committee Member	Laurie S. McNeill, Ph.D. Civil Engineering Committee Member

Richard S. Inouye, Ph.D.
Vice Provost for Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2019

ABSTRACT

THE IMPACT OF WOOD BIOCHAR ON THE PLANT UPTAKE OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS FROM RECLAIMED WASTEWATER

by

Jeffrey Flashinski, Master of Science

Utah State University, 2019

Major Professor: Dr. William J. Doucette
Department: Civil and Environmental Engineering

Reclaimed water is increasingly used in drier regions for non-potable purposes. When used for irrigation, wastewater contaminants such as pharmaceuticals and personal care products (PPCPs) can accumulate in exposed crops. The US Environmental Protection Agency (US EPA) considers PPCPs contaminants of emerging concern due to their near universal presence in the environment and their potential for endocrine disruption. Biochar, a byproduct of pyrolysis of biological material, may be an effective sorbent for PPCPs.

The main objective of this study was to investigate the impact of wood biochar soil amendments on the plant bioavailability of PPCPs in reclaimed water. PPCPs were selected as target contaminants because of their widespread usage and their frequent detection in reclaimed water. The biochars used were produced from western US trees

that often require removal to reduce potential forest fire fuel (pinyon and juniper) or have been damaged by insect attack (lodgepole pine). The impact of biochar on the bioavailability was tested by growing corn for 28-days in non-amended and biochar amended growth media (soil and sand) irrigated with reclaimed water supplemented with PPCPs (1 mg/L). Measured leaf concentrations of PPCPs were used as a proxy for root uptake and translocation.

PPCP sorption coefficients (Kd's) were determined for the growth media mixtures that were used in the corn experiment to examine the relationship between sorption and corn leaf concentrations. A hydroponic corn uptake study was also conducted to determine transpiration stream concentration factor (TSCF) for the target compounds.

Results from the corn experiment showed that the corn leaves grown in biochar amended soils were significantly lower in concentrations ($p<0.05$) than those grown in non-amended soil for 4 out of the 5 compounds of interest. In the sand, the corn grown in pinyon juniper (PJ) biochar amended sand had significantly lower leaf concentrations compared to the control corn leaves in sand for 4 of the 5 compounds of interest, however the lodgepole pine (LP) biochar amended sand only reduced leaf concentrations for 1 of the 5 compounds. The biochar amendments did not negatively impact plant growth.

(103 pages)

PUBLIC ABSTRACT

THE IMPACT OF WOOD BIOCHAR ON THE PLANT UPTAKE OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS FROM RECLAIMED WASTEWATER

Jeffrey Flashinski

Reclaimed water (treated water discharged from wastewater treatment plants (WWTPs)) is increasingly used in drier regions for irrigation purposes. This effectively increases the water supply and reduces the amount of WWTP discharge into surface waters but it creates the potential for contaminants in the reclaimed water, such as pharmaceuticals and personal care products (PPCPs), to accumulate in exposed crops. The US Environmental Protection Agency (US EPA) considers PPCPs contaminants of emerging concern due to their near universal presence in the environment and their potential for endocrine disruption. Biochar is gaining attention as a soil amendment and could potentially be used to sequester contaminants in the soil thereby reducing the contaminant uptake in crops.

The main objective of this study was to investigate the impact of wood biochar on the corn uptake of PPCPs originating from reclaimed water. Biochars derived from regional trees were chosen because they are rapidly expanding and represent a source of forest fire fuel (pinyon and juniper trees) or because they are frequently attacked by insects (lodgepole pine). The impact of biochar on contaminant uptake was tested by growing corn in non-amended soil and soil amended with biochar while being watered with reclaimed water supplemented with PPCPs (1 mg/L). Sand was also used for comparison since it is a less sorptive growth media. After a 28-day growing period, the corn leaves were dried, extracted, and analyzed for PPCPs.

ACKNOWLEDGMENTS

I would like to thank my program advisor Dr. William Doucette for his guidance and exceeding willingness to share his knowledge with me, always delivered with compassion and consideration for my own understanding of the research topics studied during my time at Utah State University. I feel immense gratitude for being accepted into this program and I have grown as a person through my course studies and lab work as a research assistant. His breadth of knowledge has increased my appreciation for chemistry and science which I will always continue to study.

I would also like to thank Dr. Bruce Bugbee, Dr. Laurie McNeill, and Darren McAvoy for their participation on my committee and their thoughtful comments in guiding this study. I'd like to thank Joe Stewart for helping me with analytical issues at the waterlab and for routinely inquiring if I was "pushing the frontiers of science." I'm also grateful to the following people for their assistance in conducting experiments: Alec Hay (USU Greenhouse), Debora Perez, Leila Ahmadi, Vivian Tsai, Brad Buswell, Autumn Slade, and Kevin Maughan (Hyrum WWTP).

And finally, a thank you to all my friends and family for their support and encouragement.

Jeffrey M. Flashinski

CONTENTS

Page

ABSTRACT iii

PUBLIC ABSTRACT v

AKNOWLEDGMENTS vi

LIST OF TABLES ix

LIST OF FIGURES xiii

INTRODUCTION 1

Literature Review 1
Biochar Properties 3
Sorption of PPCPs to Soil and Biochar 5
Plant Uptake of PPCPs 7

MATERIALS AND METHODS 8

Physicochemical Properties of Target Analytes 8
Biochar 10
Soil 12
Reclaimed Wastewater 13
Preliminary Corn Growth/Uptake Experiment 16
Corn Growth/Uptake Experiment 17
Follow-up Corn Experiment 20
Hydroponic Corn Experiment 20
Sample Extraction 21
Column Sorption Experiment 22
Liquid Chromatography/Mass Spectrometry Analysis 23
Statistical Analyses 24

RESULTS AND DISCUSSION 26

Overview of Experiments 26
Preliminary Corn Growth/Uptake Experiment 26
Corn Growth/Uptake Experiment 27
Follow-up Corn Experiment 38
Hydroponic Corn Experiment 40
Column Sorption Experiment 44

SUMMARY AND CONCLUSION 48

RECOMMENDATIONS FOR FUTURE WORKS 52

ENGINEERING SIGNIFICANCE 55

REFERENCES 56

APPENDICES 62

APPENDIX A - Corn Growth/Uptake Experiments 63

LIST OF TABLES

Table Page

1: Target analyte abbreviations, formulas, structures, molecular weights, and corresponding uses. 9

2: Physicochemical properties of target analytes, including pK_a, K_H, log K_{ow}, log D at pH=8, water solubility, and charge of major species at pH = 8. 10

3: Properties of Biochar (carbon %, EC, pH, liming, butane activity, bulk density, water holding capacity, and total ash). 11

4: Soil properties (organic matter %, EC, pH, P, K, N). 12

5: PPCP concentrations in Hyrum WWTP effluent based on triplicate samples from September 2017. 13

6: Hyrum WWTP effluent properties from a sample from Sep. 2017 used in the corn column growth/uptake experiment. 14

7: Hydrosol nutrient solution constituents based on dissolving 130 ounces into 1000 gallons (approx. 1 g/L). 15

8: Constituents of Logan City tap water from 2014 analysis. 16

9: Different experiment matrices for the corn experiment with the number of columns and purpose of each growth media. 18

10: Composition of hydroponic nutrient solution. 21

11: Corn growth based on stem and leaf fresh weight on days 8, 15, 22, 28 with averages and standard deviation calculated for day 8 and day 28 values. 30

12: Average total transpiration volume (mL) with dry leaf weight (g) for the Fall 2017 corn experiment. 31

13: Average chlorophyll (µmol/m2) for each growth media in the Fall 2017 corn experiment. 32

14: Leaf concentration averages (ng compound/g dry leaf wt.) for each growth media in the 2017 corn growth/uptake experiment not adjusted for deuterated recoveries. The full range is presented for samples <MDL with the detection limit as the upper bound. Std. dev. is for the detection limit concentrations. 34

Table Page

15: Corn leaf concentration (ng/g) comparison of amended to nonamended growth media. 35

16: Corn leaf uptake concentration per transpiration volume (ng/g/L). Averages listed for each growth media/experiment matrix. 37

17: Corn leaf concentration (ng/g/L) comparison of amended to non-amended media..... 37

18: Leaf concentration averages (ng compound/g dry leaf wt.) for non-amended soil and sand in the follow up July 2018 corn experiment. 39

19: Leaf concentration averages (ng compound/g dry leaf wt.) for non-amended soil and sand in the Fall 2017 corn experiment. 40

20: Leaf concentration (ng/g) variability (coefficient of variation) for the October 2017 and July 2018 corn experiments. 40

21: Leaf, stem, and above ground average concentrations in ng/g (dry wt.) and ng/g/L (mass compound/dry wt./volume transpired) for hydroponic corn grown in spiked nutrient solution (approx. 200 µg/L). 42

22: Average TSCF values for each target compound calculated for the spiked corn plants in the hydroponic experiment. 42

23: Estimated root exposure concentrations (µg/L) for the Fall 2017 corn experiment using the hydroponic corn leaf and exposure concentrations. 44

24: Irrigation solution concentrations (µg/L) for the Fall 2017 corn experiment which was applied onto the surface of the soil or sand. 44

25: Kd values (L/kg) determined in the column sorption experiment. 45

A1: Initial growth media weight for each PVC column in the main corn growth/uptake experiment. 63

A2: Method Detection Limit (MDL) values for the target compounds..... 64

A3: Chromatography gradient settings 64

A4: Corn above ground fresh weight (g) for the preliminary experiment in March 2017. 65

Table Page

A5: Tukey test results for above ground mass in the preliminary corn experiment (March 2017).. 65

A6: Total compounds added per column for each target compound based on total volume added over 28 days in the main corn growth/uptake experiment 65

A7: Amount of water remaining in each column (mL) and water per mass growth media (mL/g) after 28 days with averages and standard deviations. 66

A8: Tukey test results for water holding capacity between experiment matrices 67

A9: Corn growth based on stem and leaf fresh weight on days 8, 15, 22, 28. 68

A10: Anova results for corn growth in soil. 69

A11: Anova results for corn growth in sand. 69

A12: Tukey mean comparison results for corn growth in soil. 69

A13: Tukey mean comparison results for corn growth in sand. 70

A14: MANOVA test comparing corn growth from the preliminary and main experiment. The squares shaded in yellow implies significance ($p<0.05$). 70

A15: Total transpiration volume per column (mL) with dry leaf weight (g). Standard deviation for soil columns is 33.5 mL and for sand columns is 181.9 mL based on evaporation columns. 71

A16: Anova results for chlorophyll (µmol/m2) of corn leaves grown in soil. 72

A17: Tukey t-test results for chlorophyll (µmol/m2) of corn leaves grown in soil... 72

A18: Anova results for chlorophyll (µmol/m2) of corn leaves in sand. 72

A19: Tukey t-test results for chlorophyll (µmol/m2) of corn leaves in sand.. 73

A20: Tukey t-test results for chlorophyll (µmol/m2) of corn leaves grown in soil and sand media. 73

A21: Corn leaf concentration data (ng/g dry leaf wt.) of target analytes for 30 leaf samples grown 28 days for the Fall 2017 corn experiment. 74

A22: Recovery of deuterated compounds in corn leaf samples. 75

A23: Corn leaf concentration (ng/g) significant differences test with ANOVA. 75

Table Page

A24: Total compounds added per column for each target compound during the July 2018 corn experiment. 75

A25: Transpiration volume (mL) and above ground biomass (dry wt.) for each corn plant in the hydroponic experiment. 76

A26: Exposure concentrations (µg/L) for each corn plant which received the spiked hydroponic nutrient solution. 76

A27: Recovery of deuterated compounds in corn leaf samples for the hydroponic experiment. 76

A28: TSCF dimensionless ratio values for the hydroponic spiked corn plants using mass compound extracted from above ground biomass per transpiration volume over the exposure concentration for the hydroponic solution (ng/L). 77

A29: Recovery of target compounds for the column sorption experiment. 77

LIST OF FIGURES

Figure Page

1: Preliminary corn experiment above ground growth results (fresh weight). 27

2: Temperature (F) and relative humidity (RH) measurements every during the October 2017 corn experiment at the Utah State Research Greenhouse. 28

3: Corn growth curves based on fresh weight of stem and leaves for soil media at day 8, 15, 22, and 28. 29

4: Corn growth curves based on fresh weight of stem and leaves for sand media at day 8, 15, 22, and 28. 29

5: Corn growth based on fresh weight of stem and leaves for soil media. 30

6: Corn growth based on fresh weight of stem and leaves for sand media. 30

7: Dry leaf weight (g) vs. transpiration (mL) for corn grown in soil..... 32

8: Dry leaf weight (g) vs. transpiration (mL) for corn grown in sand. 33

9: Dry leaf weight (g) vs. chlorophyll (µmol/m^2) for corn grown in soil. 33

10: Dry leaf weight (g) vs. chlorophyll (µmol/m2) for corn grown in sand with or without amendments..... 33

11: Leaf concentrations (ng/g) for corn grown in non-amended soil vs. biochar amended soil. 36

12: Scatterplot of leaf concentration vs. Kd value for carbamazepine in non-amended, PJ biochar amended, and LP biochar amended soil. 47

13: Scatterplot of leaf concentration vs. Kd value for carbamazepine in non-amended, PJ biochar amended, and LP biochar amended sand. 47

A1: Setup for main corn growth/uptake experiment (Oct.-Nov. 2017). 78

A2: Preliminary corn experiment (March 2017) with LED panels at the waterlab (UWRL). 78

A3: Preliminary corn experiment (March 2017) with LED panels at the waterlab (UWRL). 78

A4: 28 day corn in LP biochar amended sand and LP biochar amended soil. 79

Figure Page

A5: 28 day corn in LP biochar amended soil and LP biochar amended sand. 79

A6: 28 day corn in LP biochar amended soil and PJ biochar amended sand. 79

A7: 28 day corn in PJ biochar amended soil and PJ biochar amended sand. 79

A8: 28 day corn in PJ biochar amended soil and PJ biochar amended sand. 80

A9: 28 day corn in PJ biochar amended soil and PJ biochar amended sand. 80

A10: 28 day corn in PJ biochar amended soil and non-amended spiked sand. 80

A11: 28 day corn in non-amended soil and non-amended unspiked sand. 80

A12: 28 day corn in non-amended soil and non-amended unspiked sand. 81

A13: 28 day corn in non-amended unspiked soil and sand. 81

A14: 28 day corn in perlite amended sand and perlite amended soil. 81

A15: 28 day corn in perlite amended sand and perlite amended soil. 81

A16: Follow-up corn experiment (July-Aug. 2018) of spiked soil and sand. 82

A17: Hydroponic unspiked corn (Sep. 2018). 82

A18: Hydroponic experiment (Aug. 2018) of spiked and unspiked corn..... 82

A19: Hydroponic experiment (Aug. 2018) of spiked and unspiked corn..... 82

A20: Hydroponic spiked corn (Sep. 2018). 83

A21: Hydroponic spiked and unspiked corn (Sep. 2018). 83

A22: Scatterplot of leaf concentrations vs. Kd value for atrazine in non-amended, PJ biochar amended, and LP biochar amended soil. 83

A23: Scatterplot of leaf concentrations vs. Kd value for atrazine in non-amended, PJ biochar amended, and LP biochar amended sand. 84

A24: Scatterplot of leaf concentrations vs. Kd value for carbamazepine in non-amended, PJ biochar amended, and LP biochar amended soil. 84

A25: Scatterplot of leaf concentrations vs. Kd value for carbamazepine in non-amended, PJ biochar amended, and LP biochar amended sand. 85

Figure Page

A26: Scatterplot of leaf concentrations vs. Kd value for fluoxetine in non-amended, PJ biochar amended, and LP biochar amended soil. 85

A27: Scatterplot of leaf concentrations vs. Kd value for fluoxetine in non-amended, PJ biochar amended, and LP biochar amended sand. 86

A28: Scatterplot of leaf concentrations vs. Kd value for sulfamethoxazole in non-amended, PJ biochar amended, and LP biochar amended soil. 86

A29: Scatterplot of leaf concentrations vs. Kd value for sulfamethoxazole in non-amended, PJ biochar amended, and LP biochar amended sand. 87

A30: Scatterplot of leaf concentrations vs. Kd value for triclosan in non-amended, PJ biochar amended, and LP biochar amended soil. 87

A31: Scatterplot of leaf concentrations vs. Kd value for triclosan in non-amended, PJ biochar amended, and LP biochar amended sand. 88

INTRODUCTION

Literature Review

Water shortages, especially in arid and semi-arid regions of the world, are likely to become more prevalent throughout the 21st century due to population growth, urbanization, and rising temperatures. Reclaimed water (also known as recycled or reused water) will increasingly be used for irrigation in water-stressed areas to decrease the diversion of water from sensitive ecosystems and to possibly reduce wastewater treatment plant (WWTP) costs. For example, the city of Hyrum, Utah started using reclaimed water for irrigation purposes (gardening and crops for animal feed) to save on the cost of alum coagulant used in the wastewater treatment process.

Reclaimed water can contain low levels of many contaminants including pharmaceuticals and personal care products (PPCPs) (Ong 2016). PPCPs represent myriad compounds that include pharmaceuticals such as antibacterials and antidepressants, personal care products such as soaps, lotions, and shampoos, and compounds used in sunscreens, plasticizers, toothpastes, etc. After use, PPCPs are often flushed down the drain or toilet within a household or enter surface waters through other pathways. PPCPs that make their way to WWTPs are usually not completely removed during treatment. WWTP effluents are a major source of PPCPs in the environment and their presence and impact has yet to be fully understood (Kaleniecka and Zarzycki 2015; Sima et al. 2014). PPCPs have been labeled contaminants of emerging concern because of their near universal presence in the environment and their potential impact on exposed organisms (US EPA 2016a).

When using reclaimed water for irrigation there's a potential for PPCPs to accumulate in food crops. For example, PPCPs have been detected at low levels in crops irrigated with reclaimed water (Wu et al. 2015) and Paltiel et al. (2016) found carbamazepine in human urine when subjects consumed agricultural products irrigated with reclaimed water.

A cost-effective method for reducing the uptake of PPCPs by plants irrigated with reclaimed water would reduce crop contamination concerns. Biochar has been gaining attention in recent years and studies have examined its effectiveness as a soil amendment and contaminant sorbent. Biochar soil amendments reduced the uptake of pesticides by spring onions (Yu et al. 2009) and copper by ryegrass (Karami et al. 2011). Solanki and Boyer (2017) found that coconut and wood biochars removed more than 90% of 7 different pharmaceuticals from synthetic urine suggesting that biochar applied to soil might also be capable of limiting PPCP bioavailability to plants.

The primary objective of this study was to investigate the impact of wood biochar amendments to soil on plant uptake and PPCP bioavailability. The hypothesis was that the biochar amendments would reduce the bioavailability of PPCPs while not negatively impacting plant growth. Corn was used in this study due to its commercial viability and because it has been irrigated with reclaimed water before (Hassanli et al. 2009). Leaf concentrations were measured to evaluate corn uptake and transport of PPCPs to above ground plant tissues. Sorption coefficients (Kd's) for PPCPs were also measured in the various growth media used in the corn experiment to examine the relationship between sorption and plant bioavailability.

Biochar Properties

Biochar has a long history of use as a soil amendment and was applied to Amazonian soil as early as 8000 BC (Lal 2016). Amazon *terra preta* was made by adding a mixture of biochar, bone, and manure to the otherwise relatively infertile soil (WinklerPrins 2014). Today this *terra preta* contains as much as 9% organic carbon compared to surrounding non-amended soils which have <0.5% organic carbon (Groot et al. 2017). Adding biochar restored the degraded soil, improved crop yields, and created a soil which could support a wide array of crops (Cornell 2006). Biochar has repeatedly been shown to improve plant growth especially when applied to acidic soils partly due to the typically high pH of biochar (Pudasaini et al. 2012; Yamato et al. 2006; Schultz et al. 2013; Uzoma et al. 2011).

Biochar is similar in properties to charcoal, although charcoal is often made with the intention to be used as a fuel. Biochar is highly porous and can increase the bulk surface area of the growth media when it is applied (Downie 2009). Biochar is generally produced to use as a soil amendment and can be adjusted to 'fit' a soil by changing pyrolysis temperature or feedstock. The increase in porosity and surface area often improves water and nutrient retention (Liu et al. 2017; Laird et al. 2010). Biochar produced at higher temperatures is less hydrophobic which allows for greater water retention (Gray et al. 2014).

Biochar is often produced from readily available biological waste that would otherwise decompose or combust. Limiting the transportation distance of biochar from production to use sites is an important to consideration for reducing costs and carbon

emissions. For example, mobile pyrolysis units have been developed to produce and use biochar on site to limit transportation costs. There are millions of acres of trees in Utah, Arizona, Wyoming, and Idaho that could serve as biochar feedstock and need removal because they are rapidly expanding and represent a source of forest fire fuel. This study used two biochars, one produced from lodgepole pines and the other produced from pinyons and junipers. Pinyon and juniper trees cover 8 million acres at 5,000 to 8,000 feet elevation in Utah, they occupy the driest forested sites, and burn at high temperatures which can threaten the health and longevity of the forest (McAvoy et al. 2012). Lodgepole pines cover nearly half a million acres in Utah and are often subject to beetle attacks (Amman and Schmitz 1988).

When using biochar as a soil amendment, the type of soil and the varying characteristics of the different feedstocks should be considered. The feedstock properties that play an important role in determining the biochar characteristics are: fractions of fixed carbon, caloric value, volatile components, fraction of cellulose, lignin, percentage of inorganic substance, particle size, and true density (Verheijen et al. 2010). Cellulose undergoes thermal degradation at temperature ranges of 240-350C while lignin undergoes thermal degradation at temperature ranges 280-500C (Brebu and Vasile, 2010).

The temperature and duration of pyrolysis will play an important role in the characteristics of the biochar as well. Pyrolysis done in a short time interval (<1 hr) at lower temperatures (<400C) will yield a greater mass of biochar from the original biomass (>80% biochar yield compared to the gas and bio-oil produced) but the percent carbon will be lower (<60%) compared to biochar produced at higher temperatures

(>600C) with longer pyrolysis time intervals (>2 hrs) which will have less biochar yield (<25% biochar) with a higher percent carbon (>90%) (Wannapeera et al. 2011; Ronsse et al. 2013). Feedstock characteristics will help determine the effect of pyrolysis temperature and residence time on biochar.

Sorption of PPCPs to Soil and Biochar

Sorption is an important factor in determining the environmental fate and plant uptake of organic contaminants. Sorption coefficients quantitatively represent the equilibrium distribution of a chemical between an environmental solid (i.e. soil, sediment) and the aqueous phase and depend on properties of the soil and chemical of interest. The key properties of the solid that determine this distribution include: organic matter, clay mineral content and type, clay to organic matter ratio, particle size distribution, surface area of the sorbent, and pH. For neutral organic compounds, hydrophobicity, often quantified by the octanol/water partition coefficient (Kow), is considered the main property governing the sorption to soils. For ionizable organics, charge and pKa also play a significant role.

Soils are complex mixtures which makes it difficult to identify specific sorption mechanisms and usually several mechanisms are occurring simultaneously in which compounds are sorbed on both organic and inorganic constituents. However, some general behaviors have been observed. For example, the sorption of neutral and hydrophobic organic compounds is often highly correlated with the organic carbon content of the solid and the hydrophobicity of the compound. In addition, cationic organics and weak bases are typically strongly sorbed to negatively charged soils while

anionic organics are weakly sorbed (Doucette et al. 2018).

The main sorption properties of biochar are the carbonized and non-carbonized fractions and the surface, pore, and bulk properties (Zhao et al. 2013). This will be affected by the biochar feedstock and pyrolysis temperature and residence time. Adsorption to biochar transitions from a polarity-selective process for biochar pyrolyzed below 450C to a porosity-selective process for biochar pyrolyzed between 500-600C and displays no selectivity for biochar pyrolyzed at 700C or activated carbon in which the adsorptive saturation capacities are comparable to predicted values based on the monolayer surface coverage (Chen et al. 2008). Sorption is assisted by π–π electron donor–acceptor interactions and occurs by sorption to exterior surfaces which continues further by a pore-filling mechanism (Nguyen et al. 2007). The pyrolysis of biological material has been shown to increase the specific surface area, aromaticity, pH and C/N ratio (Tang et al. 2018). For hydrophobic organic compounds sorption coefficients significantly increase with pyrolysis temperature, surface area and pore volume, aromaticity, and thermal stability, and decreased with H/C, O/C, (O + N)/C content of biochar (Kupryianchyk et al. 2016).

The sorption of PPCPs to biochar should reduce the bioavailability of PPCPs to plant roots. There are many possible mechanisms associated with the sorption of PPCP by biochars. In the Solanki and Boyer (2017) study, the sorption of pharmaceuticals to biochar could not be attributed to a single factor but rather was due to “a combination of superposing factors, e.g., pharmaceutical chemical structure and hydrophobicity, biochar

surface area, pyrolysis temperature and biopolymer makeup, and waste water pH and chemistry."

Plant Uptake of PPCPs

Root uptake of most organic contaminants is passive which means that the more water transpired, the greater the amount of organic contaminants that moves into the plant tissue. The TSCF is the ratio between a compound's concentration in the xylem to that in the solution adjacent to the roots and is commonly used to describe the relative ability of an organic compound to be passively transported from root to shoot. Dettenmaier et al. (2008) presented an empirical relationship between transpiration stream concentration factor (TSCF) values and log Kow that indicates that non-ionizable, polar, highly water-soluble organic compounds are most likely to be taken up by plant roots and translocated to shoot tissue. Xylem transport is directly related to transpiration rates, whereas phloem transport is determined by differences between synthesis and consumption sites (Marschner H. 1995). Xylem transport rates during the day are approximately 10 times greater than phloem transport rates (Lang, A. 1990). For neutral organic compounds, hydrophobicity, often expressed as log Kow, is considered the main physical chemical property impacting plant uptake whereas for ionizable compounds the pKa of the compound and pH of the water transpired must also be considered (Doucette et al. 2018).

MATERIALS AND METHODS

Physicochemical Properties of Target Analytes

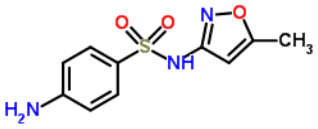
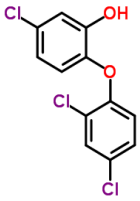
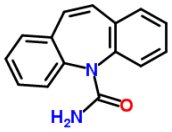
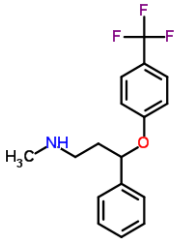
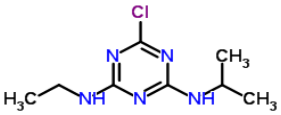
Four PPCPs and one herbicide (Table 1) were used as target analytes in this study. Gemfibrozil was also originally included but due to analytical issues and low recovery of the deuterated spikes (<10%) the data were not included. When analyzing various PPCPs it can be difficult to obtain sufficient recoveries for all target compounds but recoveries in this study were closely aligned with literature values (Wu et al. 2012).

The four PPCPs were chosen for this study based on their chemical properties (Table 2), widespread usage, potential risk to the environment, and frequent detection in WWTP effluent (Benotti et al. 2008). Atrazine was selected because it is an herbicide commonly used on corn and can be compared to the results of previous sorption studies with biochar. The range of average reported concentrations for these compounds in WWTP effluents is from 8.7 ng/L (fluoxetine) to 910 ng/L (sulfamethoxazole) (US EPA 2016b, Singer et al. 2002

The target PPCPs represent a range of therapeutic uses including an antibiotic linked to antibiotic resistance in bacteria (sulfamethoxazole), an antimicrobial used in handsoaps (triclosan), an anticonvulsant that prevents seizures and relieves nerve pain (carbamazepine), and an antidepressant used in Prozac (fluoxetine).

Analytical standards were purchased for atrazine (>99%), triclosan (>99%), and carbamazepine (>99%) from Sigma Aldrich, and for fluoxetine hydrochloride (>98%) and sulfamethoxazole (>99%) from Spectrum Chemical (Gardena, CA).

Table 1: Target analyte abbreviations, formulas, structures, molecular weights, and corresponding uses.

Compound	Molecular Weight	Structure	Class/Use
Sulfamethoxazole (SMZ) $C_{10}H_{11}N_3O_3S$	253		Antibiotic
Triclosan (TCS) $C_{12}H_7Cl_3O_2$	290		Antimicrobial
Carbamazepine (CBZ) $C_{15}H_{12}N_2O$	236		Anticonvulsant
Fluoxetine (FLX) $C_{17}H_{18}F_3NO•HCl$	346		Antidepressant
Atrazine (ATZ) $C_8H_{14}ClN_5$	216		Herbicide

The log D values at pH=8 were included in Table 2. Log D is the relative lipophilicity of a compound at the specific pH based on the charge of the compound whereas log K_{ow} values are useful at a pH where the compounds are in neutral form. In this study there were two compounds that were mostly neutral at pH=8 (CBZ and ATZ), one mainly positively charged compound with high water solubility (FLX), and two negatively charged compounds (SMZ and TCS) although only 55% of triclosan is negatively charged at this pH.

Table 2: Physicochemical properties of target analytes, including pK_a, K_H, log K_{ow}, log D at pH=8, water solubility, and charge of major species at pH = 8.

Compound	pK_a	K_H (atm-m^3/mole)	log K_{ow}	log D at pH=8	Solubility (mg/L) 25ºC	Charge at pH = 8
SMZ	1.6,5.7[1]	9.56E-13	0.79	-0.11	610	Negative
TCS	7.9[5]	4.99E-09	4.98	4.50	10	Negative[a]
CBZ	13.9[3]	1.08E-10	2.77	2.77	112[6]	Neutral
ATZ	1.60[2]	2.60E-09	2.20	2.20	35[2]	Neutral
FLX	9.8[4]	8.90E-08	4.17	2.38	14,000[5]	Positive

[1] Boreen et al. (2004); [2]PubChem CID: 2256; [3] Jones et al. (2002); [4]DrugBank: "Fluoxetine"; [5] O'Neil (2006); [6]Ferrari et al. (2003). Log Kow and log D values came from Chemicalize (July 2018) https://chemicalize.com/ developed by ChemAxon (http://www.chemaxon.com). All other values were obtained using EPI Suite (US EPA 2012).
[a]At pH = 8, the speciation of TCS is approximately 55% negatively charged and 45% neutral. All other major species listed are greater than 98% of that compound.

Biochar

Two commercially available wood biochars were chosen for this study based on their abundance and need for removal in the local region. The lodgepole pine (LP) biochar, pyrolyzed at 550C, was produced by Confluence Energy (Kremmling, Colorado). The pinyon and juniper (PJ) biochar was pyrolyzed at 500C and produced by Amaron Energy (Salt Lake City, Utah).

Biochar properties (Table 3) were determined by Utah State University Analytical Laboratories unless otherwise noted. Values for volatile matter and total ash were determined using a modified American Society for Testing and Materials (ASTM) Method D1762-84 for testing wood charcoal as follows. Approximately 200 mg of sieved biochar (0.850 mm) was oven dried for 24 h at 100C and cooled in a desiccator until a constant weight was obtained. Volatile matter content was determined as weight loss after combustion at 900–950C for 7 min. Ash content was determined as weight after combustion at 750C for 6 hours with no ceramic cap.

Table 3: Properties of Biochar (carbon %, EC, pH, liming, butane activity, bulk density, water holding capacity, and total ash).

Biochar Type:	Pinyon-Juniper (Dry Wt.)	Lodgepole Pine (Dry Wt.)
Carbon %	62.8%	63.9%
Electrical Conductivity (EC)	0.10 dS/m	0.08 dS/m
pH Value	9.4	9.2
Liming (Neutralizing)*	3.9%	2.9%
Butane Activity*	4.0 g/100 g	13.9 g/100g
Bulk Density*	261 kg/m^3	280 kg/m^3
Water Holding Capacity***	0.132 mL/g	0.597 mL/g
Volatile Matter %**	9.2%	16.0%
Total Ash**	6.1%	1.6%

Biochar properties were determined by Utah State University Analytical Laboratories. *Values reported by biochar company; **Values were determined in the lab using American Society for Testing and Materials (ASTM) Method D1762-84 for testing wood charcoal (percent by mass); ***Values determined by experimental data.

The amount of water remaining in each corn column after 28 days was used to determine the water holding capacity of the biochars. This was done by using the amount of water held in biochar amended soils compared to the amount in non-amended soil and dividing by the biochar dry weight (33 g) in each column.

The biochars used in this study have relatively high cellulose and lignin content compared to other commonly used feedstocks such as manure, plants, or grass. The two biochars had a similar percent carbon, pH, and bulk density. The main differences between them were the butane activity, the total ash content, and the LP-biochar had higher concentrations of Na, B, Zn, Fe, and Mn than the PJ-biochar. Butane activity measures total adsorption capacity above a relatively low adsorption energy threshold and basically estimates the total micropore volume of the porous adsorbent. The total ash percentage is important because this signifies the liming impact on the soil and how much the biochar will affect the soil pH.

Biochar can be "charged" by mixing it with compost or soaking it in nutrients before applying it to soil to make it more suitable for immediate application otherwise biochar amended soils can require extra fertilizer due to the increased nutrient holding capacity. The biochars used in this study were not pretreated or specifically matched to the soil that they were applied to.

Soil

Soil used in this study was obtained from a commercial supplier in Cache County, Utah. Corn growth and sorption experiments were conducted using soil with and without amendments. The soil was slightly alkaline, clay loam, pH=7.7, and 2.7% organic carbon (Table 4). The standard procedure for the determination of soil salinity is from an extract of a saturated paste of the soil, and the electric conductivity is then written as Ece. The addition of biochar was expected to only have a slight impact on pH which was already higher than the preferred pH range (5.8-7.0) for optimal corn yield (Espinoza and Ross 2003).

Table 4: Soil properties (organic matter %, EC, pH, P, K, N).

Soil Properties:	Clay Loam
% organic matter	2.7%
Ece (dS/m)	2.49
pH Value	7.7
P (mg/kg)	92
K (mg/kg)	667
NO_3-N (mg/kg)	75.6

Soil properties were determined by Utah State University Analytical Laboratories.

Reclaimed Wastewater

Reclaimed wastewater was obtained from the Hyrum (Utah) Wastewater Treatment Plant which uses effluent for secondary irrigation (and home gardening) during the summer months. The Hyrum WWTP treats almost exclusively domestic wastewater with very few industrial inputs. Ahmadi et al. (2018) determined the concentration of the 5 target PPCP compounds (Table 5) by liquid chromatography mass spectrometry (LC/MS) and the concentrations were below the EPA reported averages for WWTP effluents for each target PPCP (US EPA 2016b). In addition, an analysis of the reclaimed water was done by Utah State University Analytical Laboratory to determine pH, salinity, Total Dissolved Solids (TDS), hardness, and an elemental analysis (Table 6).

Table 5: PPCP concentrations in Hyrum WWTP effluent based on triplicate samples from September 2017.

PPCP compound:	Hyrum WWTP Effluent (ng/L)
Carbamazepine	11.43±0.47
Fluoxetine	4.23±0.29
Gemfibrozil	19.80±2.23
Sulfamethoxazole	708.17±31.83
Triclosan	5.40±0.95

PPCP concentrations were determined by Ahmadi et al. 2018.

Table 6: Hyrum WWTP effluent properties from a sample from Sep. 2017 used in the corn column growth/uptake experiment.

WWTP Effluent Properties	Hyrum Effluent
	Sep. 2017
Salinity – EC (umhos/cm)	1220
pH	7.7
Total Dissolved Solids (TDS) (ppm)	732
Hardness ($CaCO_3$ mg/L)	324
Nitrate-N (mg/L)	8.94
Chloride (mg/L)	149
Potassium (mg/L)	22.6
Magnesium (mg/L)	33.1
Phosphorus (mg/L)	3.1
Sodium (mg/L)	112.9
Sulfur (mg/L)	11.4
Calcium (mg/L)	75

The PPCP concentrations in the reclaimed water were too low to be reliably detected in corn leaves in a 20 day experiment. Preliminary experiments with 10 µg/L and 100 µg/L spikes indicated that not all compounds would be detected at these levels in the corn leaves. It was decided to increase the concentration of the target compounds in the fortified reclaimed water to 1 mg/L since the main objective of the study was to determine the impact of biochar amendment on plant uptake based on leaf concentrations. Conservatively assuming linear sorption isotherms, the impact of biochar on plant uptake at higher levels was assumed to be proportional to the impact at lower levels typically found in irrigation water. The spiked reclaimed water was remade every few days and kept in a dark cooler (4C) to avoid compound degradation or phototransformation. The water was tested every few days to make sure concentrations were near target levels.

To make sure that the plants received adequate nutrients over the duration of the various uptake studies, a nutrient solution was made by mixing Logan city tap water with Hydrosol (N-P-K=5-11-26; 1 g/L) and calcium nitrate (0.5 g/L) with a PPCP spike (1 mg/L). The composition of Logan city tap water can be viewed in Table 7 and composition of hydrosol nutrient solution can be viewed in Table 8. The soil columns received 46% nutrient solution and 54% reclaimed water and the sand columns received 53% nutrient solution and 47% reclaimed water. The different percentages were used based on visible growth deficiencies such as leaf scorch and striping. Unspiked reclaimed water and nutrient solution were used for one set of corn (experiment control blank) to determine the impact on uptake and growth.

Table 7: Hydrosol nutrient solution constituents based on dissolving 130 ounces into 1000 gallons (15pprox.. 1 g/L).

Hydrosol	Symbol	ppm
Constituent		
All Nitrate	N	50
Phosphorus	P	48
Potassium	K	216
Magnesium	Mg	30
Sulfate	SO_4	117
Iron	Fe	3
Manganese	Mn	0.50
Zinc	Zn	0.15
Copper	Cu	0.15
Boron	B	0.50
Molybdenum	Mo	0.10

Hydrosol constituents determined by Scotts Testing Laboratory (Scotts 2004).

Table 8: Constituents of Logan City tap water from 2014 analysis.

Logan City Tap Water	ppm
Constituent	
Nitrate (as Nitrogen)	0.20-0.50
Total Dissolved Solids (TDS)	193-314
Chlorine	0.300
Lead	0.0056
Barium	0.060-0.085
Fluoride	0.200
Selenium	0.0005
Sodium	5-34
Copper	0.156

Logan city: Water Quality Report (2014).

Preliminary Corn Growth/Uptake Experiment

A preliminary experiment was conducted in March 2017 growing corn in PVC columns for 30 days in the lab using Ultrathin 225 LED All White 3300LM Grow Light Panels. This study was conducted to determine appropriate exposure concentrations to enable reliable detection of the target compounds in corn leaves. The columns contained soil or soil amended with biochar or perlite at 2 different ratios (0.5 and 5% by mass). Perlite is inert, volcanic glass often used in potting soils due to its high porosity and it was included in this study to compare the impact of soil aeration and water retention on corn growth/uptake. Triplicate columns were used for each matrix and a total of 30 corn plants were grown. Corn was irrigated with tap water spiked with the target compounds at 10 µg/L however this concentration was too low to reliably detect target compounds in the corn leaves. The growth data were compiled using the stem and leaf weight (fresh and dry) and averages were compared from the different soil media to determine if biochar amendments impacted corn growth.

Results from this preliminary experiment indicated that a concentration of 10 ug/L in the irrigation water was too low to reliably detect target compounds in the corn leaves. It was also observed that the soil amendments did not negatively impact above ground biomass production.

Corn Growth/Uptake Experiment

Corn was grown in soil, sand, or soil and sand amended with biochars in polyvinylchloride (PVC) columns (599 cm^3) for 28 days (Oct. 21, 2017 to Nov. 17, 2017) at the Utah State Research Greenhouse (Figure A1). Corn grown in soil was compared with corn grown in soil amended with biochar (5% by mass, 17pprox.. 23% by volume) and corn grown in soil amended with perlite (perlite mixed at equivalent volume to biochar). In addition to soil, sand was used to grow corn and compared to sand amended with biochar (as well as perlite). Sand was used as comparison with a less sorptive growth media.

The soil was hand stirred in buckets so that larger clumps (17pprox.. >1" diameter) were broken down before filling the PVC columns (dimensions: inner diameter=5 cm; height from screen to top=30.5 cm). To avoid being left with only fine particles at the end, twice the amount of mass that was needed was stirred in each bucket. The biochars were air dried and sieved at ¼" to ensure uniform size before mixing with the sand or soil. Neither the soil or sand were washed or pretreated for the experiments in this study. The columns were packed to keep the volume of media similar in each column (17pprox.. 5 cm from media to top of column). The weight of the growth media in each of the 54 columns can be viewed in Table A1. Each column was placed in a

small plastic bucket that was used to collect the leachate. The leachate volume was measured and samples were collected to determine target analyte concentrations.

Two corn seeds (Syngenta 8590 GT 2006) were placed 1" below the media surface in each column and all columns had at least one seed sprout. For the columns in which both seeds sprouted, the shorter plant was cut at the base of the stem after 7 days. The weight was recorded and used to construct the growth curves. Four of the columns were left without seeds and watered to determine the amount of evaporation. This information was used to estimate the amount of transpiration by each plant at the end of 28 days. Five corn columns were used for each experiment matrix, but only 3 of the 5 corn plants were grown the entire 28 days (Table 9). The other two plants were cut earlier to create growth curves.

Table 9: Different experiment matrices for the corn experiment with the number of columns and purpose of each growth media.

Growth Media	# Columns	Purpose of Experiment
Sand – No corn	2	Measure evaporation (transpiration)
Sand – Unspiked water	5	Experiment control blank
Sand – Spiked water	5	Sand control matrix
Sand – Perlite amended	5	Sand aeration control
Sand – PJ Biochar amended	5	Examine PJ Biochar impact (growth, uptake)
Sand – LP Biochar amended	5	Examine LP Biochar impact (growth, uptake)
Soil – No corn	2	Measure evaporation (transpiration)
Soil – Unspiked water	5	Experiment control blank
Soil – Spiked water	5	Soil control matrix
Soil – Perlite amended	5	Soil aeration control
Soil – PJ Biochar amended	5	Examine PJ Biochar impact (growth, uptake)
Soil – LP Biochar amended	5	Examine LP Biochar impact (growth, uptake)
TOTAL # COLUMNS	54	(20 cut early for growth curves)

After the seeds were planted the columns were watered until the solid media was fully saturated. The plants were watered a minimum of every other day and irrigation was done with a pipette slowly applying the solution onto the growth media surface. Care was taken to avoid water contacting the leaves as biochar can only reduce uptake of compounds transported root to shoot. Light intensity was measured with an Apogee MQ-200 Quantum Flux at midday (12-1 PM) and the chlorophyll content was measured at the end of 28 days with an Apogee CCM-200 Plus for all 30 corn plants. The humidity and room temperature were measured every ten minutes using the Hobo Pro V2 Ext Temp/RH Onset. Transpiration was calculated as follows:

$$total\ volume\ of\ water\ added\ per\ column - (leachate\ volume + water\ remaining\ in\ growth\ media + avg.volume\ evaporated) = volume\ transpired.$$

The corn was grown for 28 days because this was the minimum required for the plants to transpire enough water and generate enough leaf material to detect all the compounds based on preliminary experiments. After 28 days the columns were weighed and the leaves and stems cut and dried in a desiccator. Once the leaves reached a constant weight they were ground with pestle and mortar using liquid nitrogen and dried in a desiccator. The ground leaves were placed in centrifuge tubes, weighed, and spiked with the deuterated compounds of interest. The leaves were dried again before extraction.

Follow-up Corn Experiment

A follow up experiment to the main corn growth/uptake experiment was done in July-August 2018 growing corn in 6 PVC columns using triplicates of soil and sand irrigated with spiked reclaimed water (1 mg/L). The purpose of this experiment was to compare leaf concentration data in the controls with the previous experiment, specifically the uptake of atrazine in soil/sand and the variability in the leaf concentrations. Results for atrazine in the previous experiment indicated that there was more leaf accumulation of atrazine in the soil than the sand. Corn grew until a similar plant mass as the main experiment was obtained. The extraction method was slightly altered and the CEM EDGE was used for extraction with methanol. After extraction the sample was concentrated and cleaned up using the same procedure as in the Oct.-Nov. 2017 corn growth/uptake experiment.

Hydroponic Corn Experiment

A hydroponic corn experiment was conducted with 5 corn plants receiving spiked hydroponic solution (20pprox.. 200 µg/L) and 5 corn plants receiving unspiked hydroponic solution. The concentration of the target compounds in the hydroponic solution used was selected to be similar to the pore water concentrations in the soil column experiments for most compounds. The composition of the hydroponic solution can be viewed in Table 10. The purpose of this experiment was to determine the transpiration stream concentration factor (TSCF) which describes the efficiency with which a compound translocates to the shoot from the root. Samples were collected from each hydroponic vessel daily, diluted 9:1, and analyzed with LC/MS to determine the

exposure concentrations. Corn leaves and stems were extracted and analyzed with the same procedure as was used in the corn column experiment. Corn growth was analyzed to determine whether the 200 µg/L spike had an impact. The spike was delivered from a stock of methanol so the final concentration in the hydroponic solution was 0.02% methanol (by volume). The same concentration of methanol was used in the unspiked hydroponic solution to ensure that growth differences were not from methanol.

Table 10: Composition of hydroponic nutrient solution.

Compound	Molar Conc. (M)
Ca(NO3)	1
K(NO3)	2
KH2PO4	0.2
MgSO4	0.5
K2SiO3	0.3
	21pprox.21ar (mM)
FeCl3	50
EDDHA	25
Fe-HEDTA	250
MnCl2	20
ZnCl2	30
H3BO3	400
CuCl2	40
Na2MoO4	1

Sample Extraction

Target compounds were extracted from the dry leaf samples by performing 3 separate extractions with 5 mL of methanol. After the first 5 mL was added, the tube was vortexed for 1 minute and stored overnight in the dark to maximize solvent contact with

the tissue. The following day the sample was vortexed again for 1 minute and centrifuged for 30 minutes at 5000 RPM. The supernatant was pipetted to a pre-weighed vial. The next 2 extractions were done by adding 5 mL methanol to the tube, vortexing for one minute, letting the samples sit for 30 minutes, and then centrifuging for 30 minutes at 5000 RPM. The supernatant from each extraction were combined.

The combined supernatant was dried with nitrogen gas and reconstituted in acetonitrile to less than 1 mL using a Biotage Turbovap Classic II. The reason for switching solvents was that preliminary experiments proved methanol was better at extracting the target compounds, while acetonitrile was better at removing chlorophyll during cleanup which can act as an analytical interference. The concentrated extracts were brought up to the same volume of 1 mL by adding acetonitrile (0.786 g/mL). The exact volume was determined and used in the leaf concentration analysis.

Sample cleanup was done by adding 0.6 mL of the concentrated samples into 2 mL Phenomenex roQ QuEChERs (7.5 mg graphitized carbon black, 150 mg $MgSO_4$, 25 mg primary/secondary amine) along with 0.3 mL acetonitrile and 0.3 mL of basic methanol (10<pH<11 by adding KOH). The QuEChER was vortexed for 30 seconds and centrifuged for 10 minutes at 4000 RPM. The supernatant was put into a 2 mL vial and analyzed using LC/MS. Extraction for the follow-up corn experiment was done with the CEM EDGE which used 15 mL of methanol at 100 F for 5 minutes.

Column Sorption Experiment

Column sorption studies were performed using glass columns (internal diameter = 2.3 cm, height from glass frit to top = 40 cm, vol = 382 cm3) with 0.5 g of the growth

media type used in the corn column experiment. Reclaimed water (100 mL) spiked with the target compounds (1 mg/L) was poured through the column. Water exiting the column was collected and analyzed for target compounds. Sorption equilibrium was assumed once the effluent compound mass was >90% of the initial mass added to the column. To maximize contact time with the media the flow of water through the growth media was stopped overnight by placing a rubber stopper in the top of the column. The target compounds were then extracted from the solid media by pouring 100 mL aliquots of methanol through the column (holding the methanol in the media overnight) until compounds were below method detection limit (MDL). Activated carbon (Sigma Aldrich, 12-20 mesh, CAS 7440-44-0) was included in this experiment as a comparison. Activated carbon (AC) is similar to biochar but is produced at higher pyrolysis temperatures and has a higher percentage of carbon. Sorption coefficients were determined by dividing the total mass of compound extracted by the mass of growth media over the concentration of the final pour leachate:

$$Kd = \left(\frac{compound\ ng}{0.5\ growth\ media\ g}\right) / \left(\frac{compound\ ng}{leachate\ mL}\right).$$

Liquid Chromatography/Mass Spectrometry Analysis

Individual standards were created by dissolving known masses of the compounds in LC/MS grade methanol. These standards were used to spike the reclaimed water for irrigation and to create calibration curve standards. Calibration curve standards ranged from 0.1 µg/L to 100 µg/L. All standard solutions were stored in the dark at 4ºC when not in use.

In addition, deuterated standards were made for each of the target contaminants in the same way as the non-deuterated standards. The deuterated standards were directly spiked into the dry leaf material before extraction to determine extraction efficiency. Deuterated standards of sulfamethoxazole-d4, carbamazepine-d10, fluoxetine-d5, gemfibrozil-d6, triclosan-d3, and atrazine-d5 were purchased from CDN Isotopes (Pointe-Claire, Quebec, Canada). The deuterated standards were analyzed separately from the non-deuterated standards. Laboratory blank samples (LBSs) were used to check for contamination issues and continuous calibration verification (CCV) samples were used every 7-10 samples during LC/MS analysis.

An Agilent 1290 Infinity LC system with an Agilent 6490 Triple Quadrupole MS system was used to analyze sample extracts for the target compounds. Method Detection Limits (MDLs) are listed in Table A2. Separation of the analytes was achieved with an Agilent Eclipse Plus C18 column (2.1 x 50 mm, 1.8 µm I.D, 0.45 mL/min flow rate, 10 min. run time, 10 µL injections). The LC/MS system utilized a binary pump with mobile phase A prepared with 0.1 % methanol and 0.1 % formic acid (by volume) in DI water and mobile phase B prepared with 0.1 % formic acid (by volume) in LC/MS grade acetonitrile. The gradient chromatographic settings are given in Table A3.

Statistical Analyses

Statistical analyses were conducted and one-way ANOVA with a significance level of 0.05 ($p < 0.05$) was performed to study the effect of biochar amendments on leaf concentrations and growth. Multivariate Analysis of Variance (MANOVA) was used to compare data for the different growth media and experiments. The detection limit was

used for results below MDL. This allowed a conservative estimate of the uptake reduction in biochar amended soils. Significant differences ($p < 0.05$) between the control and treatments were separated by the Tukey test using Rstudio 1.0.136.

RESULTS AND DISCUSSION

Overview of Experiments

The purpose of the preliminary experiment was to determine an appropriate concentration of target compounds to use in the irrigation solution so the compounds would be detected in the corn leaves. The corn growth/uptake experiment was conducted to compare uptake of compounds in corn leaves grown in non-amended vs. biochar amended media as well as to compare the impact of biochar amendments on corn growth. The follow-up experiment was done to compare the coefficient of variation values in the compound concentrations in the corn leaves grown in non-amended media. It was also used to evaluate atrazine uptake obtained in the main corn growth/uptake experiment. The hydroponic experiment was conducted to determine TSCF values. The column sorption experiment was conducted to determine Kd values for the target compounds in the different growth media used in the corn growth/uptake experiment.

Preliminary Corn Growth/Uptake Experiment

Corn were grown in columns with light measurements ranging from 54 to 85 $\mu mol/m^2s$ during the 30 days using LED panels for 16 hours per day. Target compounds were below detection limit except carbamazepine which was detected in a spiked nonamended soil leaf sample at a concentration of 1.21 ng/g (dry weight). The results indicated that the concentration of contaminants (10 µg/L) in the plant spiked solution

was too low to be accurately detected in the leaves for a short term (30 days) corn experiment using soil.

Results for above ground corn growth are displayed in Figure 1 with the values listed in Table A4. The average growth for PJ-biochar amended soil was 5.66 g (±1.00), for LP-biochar amended soil was 2.62 g (±0.49), and for the non-amended soil was 4.16 g (±1.40). There were no statistical differences ($p<0.05$) in growth between the amended and non-amended soil (Table A5) indicating that biochar did not negatively impact growth. Pictures of the preliminary corn experiment can be viewed in Figures A2-A3.

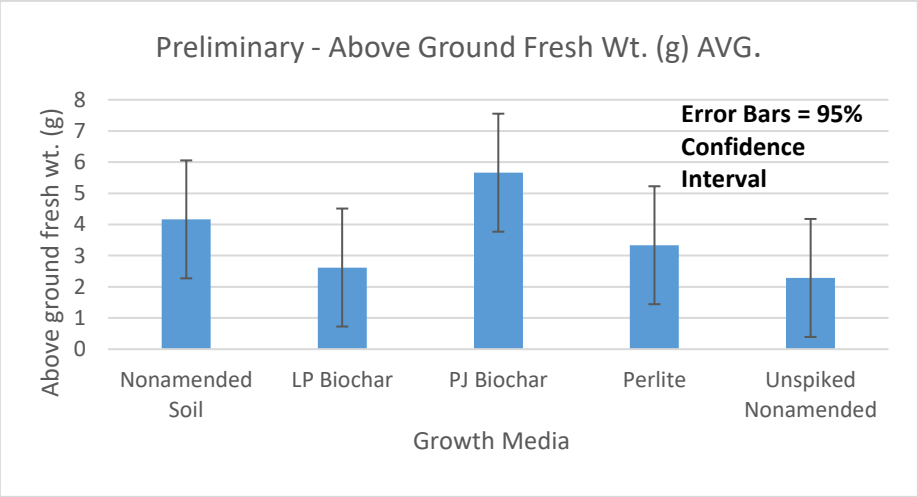


Figure 1: Preliminary corn experiment above ground growth results (fresh weight).

Corn Growth/Uptake Experiment

The average greenhouse temperature and relative humidity were 75.4 F (24.1 C) and 26.5%, respectively, during the 28-day study that occurred in Fall 2017 (Figure 2). The outside weather was mostly cloudy and light intensity in the greenhouse averaged 280 ±171 µmol/m^2s at mid-day (12-1 PM) based on 14 measurement events. Corn grown in soil media received 727.7 ± 6.2 mL total per column (based on calibration and

precision of pipette) and the corn in sand media received 980.3 ± 8.4 mL total per column over the 28 days. The total mass of target compounds added based on volume and irrigation sample concentrations are listed in Table A6.

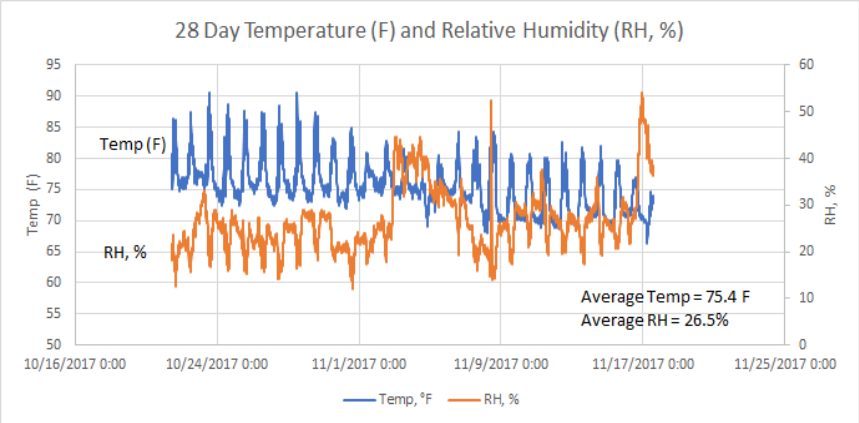
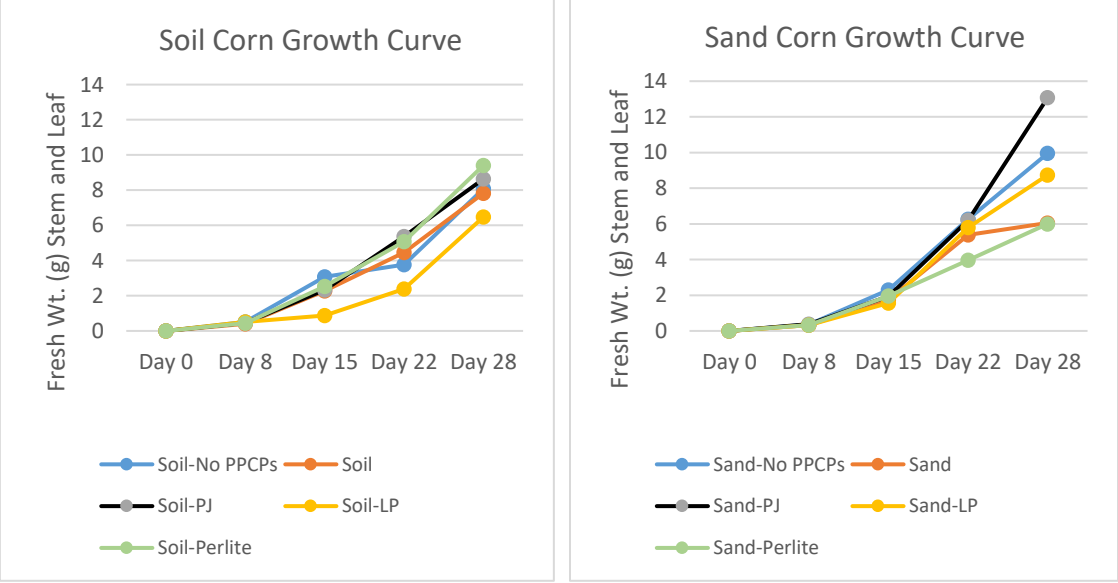


Figure 2: Temperature (F) and relative humidity (RH) measurements every 10 minutes during the corn experiment at the Utah State Research Greenhouse.

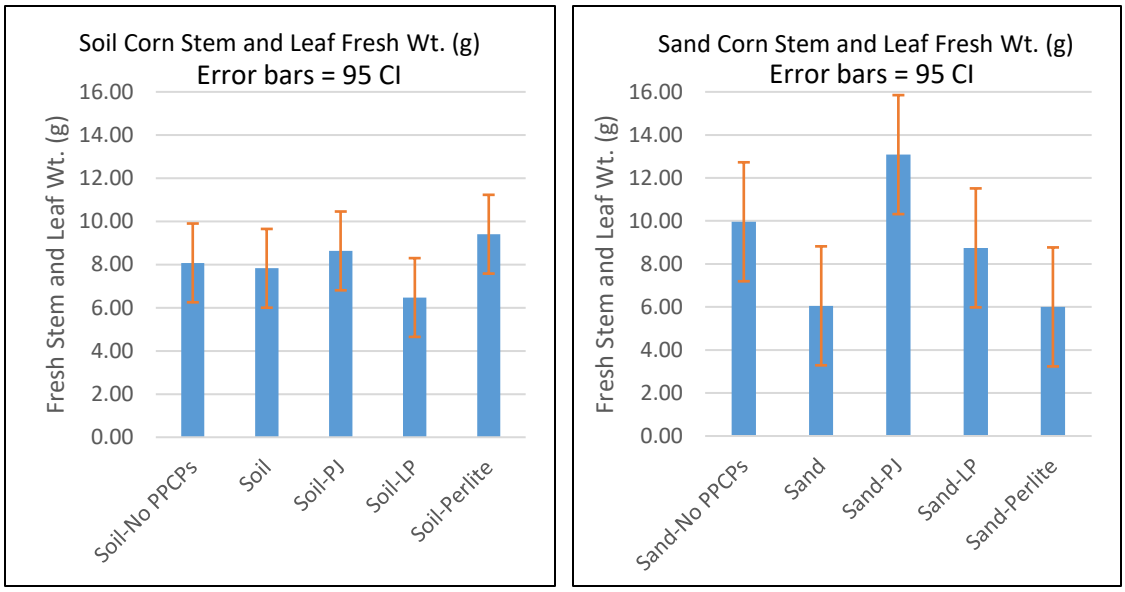
The amount of water held by the growth media in each column after 28 days is listed in Table A7 with the soil media columns having an average of 0.322 mL/g (±0.034) and the sand media columns having an average of 0.214 mL/g (±0.023). Trends were the same for average volume held in the columns for both soil and sand (perlite amended > LP-biochar amended > PJ-biochar amended > nonamended media (spiked) > unspiked nonamended media) and there were significant ($p<0.05$) differences for all groups except nonamended and unspiked nonamended media ($p<0.10$) (Table A8).

Growth curves based on above ground fresh weights are shown in Figures 3 and 4. The data used to generate the growth curves are provided in Table A9 with the averages listed in Table 11. Results for the ANOVA tests comparing growth are listed in Tables A10 and A11 and results for Tukey t-tests are listed in Tables A12 and A13 for

soil and sand. There were no statistical differences ($p<0.05$) in corn growth between the growth media using soil. The average growth for non-amended soil was 7.83 g (±0.50), for PJ-biochar amended soil it was 8.63 g (±2.36), and for LP-biochar amended soil was 6.47 g (±1.00). There were no statistical differences in corn growth between sand media except for sand-PJ biochar ($p<0.02$) which had more growth (13.08 g ±2.38) than the non-amended sand (6.05 g ±0.49) and the perlite amended sand (6.00 g ±0.92). The average growth for sand-LP biochar was 8.75 g (±0.78) (Figures 5-6). A MANOVA test was done comparing corn growth including data from the preliminary and main experiment and the PJ-biochar amended media had significant ($p<0.01$) improvements in growth compared to the non-amended, perlite amended, and LP-biochar amended media (Table A14). This suggests PJ-biochar may improve plant growth. Differences between the unspiked media were not significant ($p<0.19$) suggesting that there were no toxic effects to growth due to the presence of the target compounds.



Figures 3-4: Corn growth curves based on fresh weight of stem and leaves for each growth media type at day 8, 15, 22, and 28.



Figures 5-6: Corn growth based on fresh weight of stem and leaves for each growth media type. Error bars are 95% confidence interval.

Table 11: Corn growth based on stem and leaf fresh weight on days 8, 15, 22, 28 with averages and standard deviation calculated for day 8 and day 28 values. For day 8, n=3-5; day 15, n=1; day 22, n=1; day 28, n=3.

Matrix	Day 8		Day 15	Day 22	Day 28	
	Fresh Wt. (g)	stand. Dev.	Fresh Wt. (g)	Fresh Wt. (g)	Fresh Wt. (g)	stand. Dev.
Soil-No Spike	0.52	0.19	3.07	3.77	8.08	1.42
Soil	0.40	0.11	2.28	4.45	7.83	0.50
Soil-PJ	0.45	0.08	2.33	5.36	8.63	2.36
Soil-LP	0.51	0.14	0.88	2.38	6.47	1.00
Soil-Perlite	0.44	0.13	2.53	5.08	9.41	0.62
	Day 8	stand. Dev.	Day 15	Day 22	Day 28	stand. Dev.
Sand-No Spike	0.36	0.10	2.30	6.27	9.96	3.72
Sand	0.32	0.12	1.75	5.38	6.05	0.49
Sand-PJ	0.37	0.12	1.94	6.21	13.08	2.38
Sand-LP	0.32	0.09	1.57	5.80	8.75	0.78
Sand-Perlite	0.34	0.14	1.95	3.97	6.00	0.92

The average amount of transpiration for each experiment matrix (mL) is displayed in Table 12 along with the corresponding average dry leaf weight (g) and the individual values are listed in Table A15 for each growth media. Scatterplots of dry leaf weight (g)

vs. transpiration (mL) for corn grown 28 days with or without amendments in soil and sand (Figure 7-8). Chlorophyll averages are listed in Table 13 and there were no significant differences between chlorophyll in corn leaves grown in soil media (Tables A16-A17) or sand media (Tables A18-A19). When comparing chlorophyll using both soil and sand data there were significant differences ($p<0.04$) between LP-biochar and unspiked non-amended media (Table A20). This suggests that the corn grown in LP-biochar amended media was iron deficient since there is a correlation between iron deficiency and low chlorophyll content (Terry and Low 1982). Scatterplots for dry leaf growth vs. chlorophyll were constructed for soil media (Figure 9) and sand media (Figure 10).

Table 12: Average total transpiration volume (mL) with dry leaf weight (g) for the Fall 2017 corn experiment.

Growth Media	Transpired (mL)		Dry Leaf Wt. (g)	
	AVERAGE	st. dev.	AVERAGE	st. dev.
Soil No PPCPs	107.7	24.8	0.308	0.039
Soil	82.3	4.4	0.295	0.018
Soil Perlite	82.0	5.9	0.302	0.013
Soil PJ	87.5	23.3	0.323	0.048
Soil LP	73.9	6.6	0.240	0.037
Sand No PPCPs	228.3	27.6	0.350	0.071
Sand	186.0	10.3	0.226	0.025
Sand Perlite	147.3	29.0	0.195	0.035
Sand PJ	194.4	47.6	0.437	0.069
Sand LP	184.1	15.2	0.257	0.013

Table 13: Average leaf chlorophyll (µmol/m^2) for each growth media.

Growth Media	AVG Chlorophyll	ST DEV
	µmol/m^2	
Soil No PPCP	292.0	41.1
Soil	269.4	44.5
Soil Perlite	257.8	48.9
Soil PJ	267.8	58.0
Soil LP	173.5	21.7
Sand No PPCP	293.9	47.0
Sand	273.1	16.9
Sand Perlite	274.9	19.1
Sand PJ	260.9	17.0
Sand LP	239.8	51.9

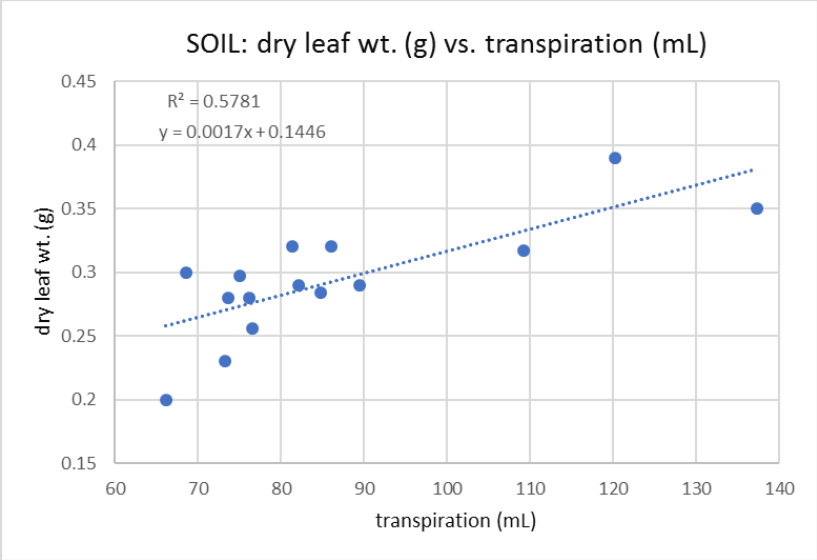


Figure 7: Dry leaf weight (g) vs. transpiration (mL) for corn grown in soil with or without amendments.

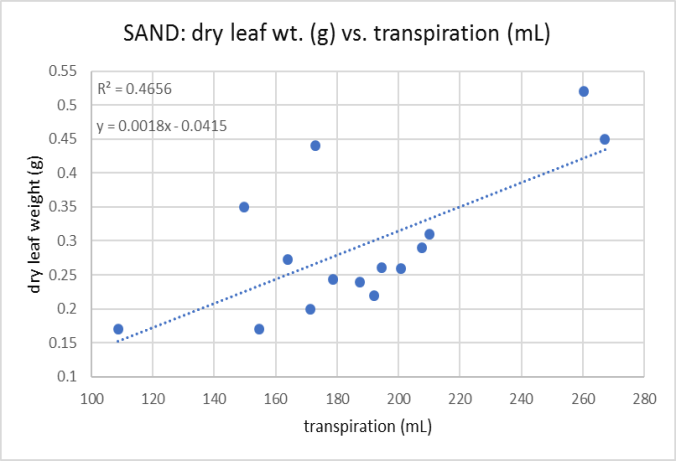


Figure 8: Dry leaf weight (g) vs. transpiration (mL) for corn grown in sand.

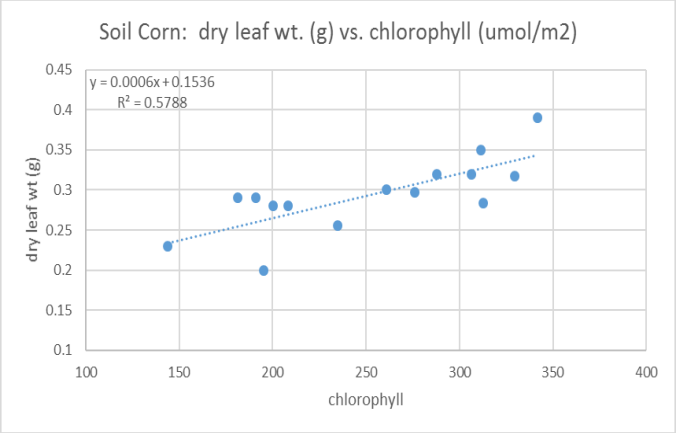


Figure 9: Dry leaf weight (g) vs. chlorophyll (µmol/m2) for corn grown in soil with or without amendments.

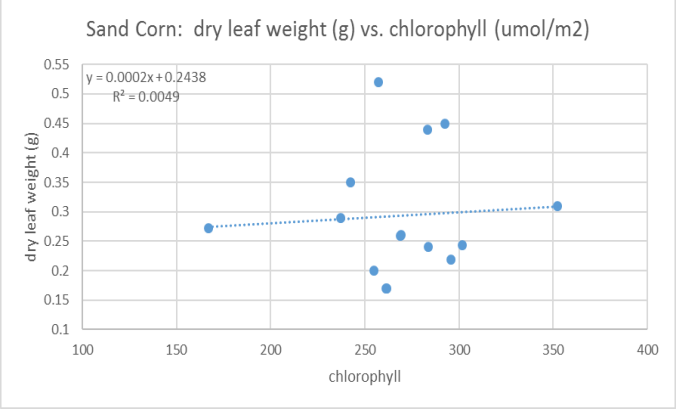


Figure 10: Dry leaf weight (g) vs. chlorophyll (µmol/m2) for corn grown in sand with or without amendments.

Leaf concentration averages for each experiment matrix are displayed in Table 14 and all values are listed in Table A21. Concentration data was not adjusted for recoveries or solvent loss in the plant tissue. Deuterated compound recoveries are listed in Table A22 with recoveries of target analytes ranging from 43% (SMZ) to 87% (CBZ). The corn plants that were irrigated with unspiked water were <MDL for all leaf samples in both soil and sand.

Table 14: Leaf concentration averages (ng compound/g dry leaf wt.) for each growth media in the 2017 corn growth/uptake experiment not adjusted for deuterated recoveries. The full range is presented for samples <MDL with the detection limit as the upper bound. Std. dev. is for the detection limit concentrations.

	ATZ	std. dev.	CBZ	std. dev.	FLX	std. dev.	SMZ	std. dev.	TCS	std. dev.
Media	ng/g		ng/g		ng/g		ng/g		ng/g	
Soil No PPCPs	0-0.9	0.2	0-0.9	0.3	0-0.7	0.2	0-0.9	0.3	0-0.9	0.2
Soil	88.6-88.9	65.5	4956	2175	42.3-42.5	42.7	11.1-11.4	7.8	173.2	54.7
Soil Perlite	107.2-107.4	77.9	4226	1585	92.5	101.1	0-0.8	5.8	174.1	115.9
Soil PJ Biochar	0-0.8	0.1	836	285	36.0	12.2	0-0.8	0.1	24.4	10.4
Soil LP Biochar	14.6-14.9	19.8	1302	598	11.0-11.2	13.5	1.1-1.5	0.3	35.5	39.1
Sand No PPCPs	0-0.7	0.1	0-0.8	0.1	0-0.6	0.1	0-0.8	0.1	0-0.8	0.1
Sand	18.7	18.6	40609	3857	909	307	33.2	7.7	942.3	76.1
Sand Perlite	9.0	3.7	57415	11897	2120	430	23.2	4.9	1020.4	176.4
Sand PJ Biochar	3.1-3.5	6.4	2172	828	177	107	1.2-1.5	1.4	87.0	41.8
Sand LP Biochar	12.8	4.2	38364	2480	860	196	19.6	3.1	325.1	231.9

Leaf concentration comparisons of the target compounds are listed in Table 15. The ANOVA test results can be viewed in Table A23. Biochar amended soils significantly reduced corn leaf concentrations for 4 out of 5 compounds (not FLX) compared to non-amended soil (Figure 11). PJ-biochar amended sand significantly reduced corn leaf concentrations for 4 out of 5 compounds (not ATZ) compared to non-amended sand while LP-biochar amended sand significantly reduced concentrations for 1 out of 5 compounds (TCS). Perlite amended soil had no impact on leaf concentrations and perlite amended sand significantly increased concentrations for 1 out of 5 compounds (FLX) compared to non-amended sand. A MANOVA analysis of all target compounds indicated the PJ-biochar amended soil significantly ($p<0.006$) reduced leaf concentrations and the LP-biochar amended soil significantly ($p< 0.015$) reduced leaf concentrations compared to the non-amended soil. The PJ-biochar amended sand significantly reduced ($p<0.000$) leaf concentrations and the LP-biochar amended sand did not significantly ($p<0.531$) reduce leaf concentrations compared to the non-amended sand.

Table 15: Corn leaf concentration (ng/g) comparison of amended to nonamended growth media. Shaded squares are statistically significant ($p<0.05$).

% Diff. in Conc.	ATZ	CBZ	FLX	SMZ	TCS
Soil	0%	0%	0%	0%	0%
Soil Perlite	21%	-15%	118%	-7%	1%
Soil PJ	-99%	-83%	-15%	-93%	-86%
Soil LP	-83%	-74%	-74%	-87%	-80%
Sand	0%	0%	0%	0%	0%
Sand Perlite	-52%	41%	133%	-30%	8%
Sand PJ	-81%	-95%	-81%	-95%	-91%
Sand LP	-32%	-6%	-5%	-41%	-65%

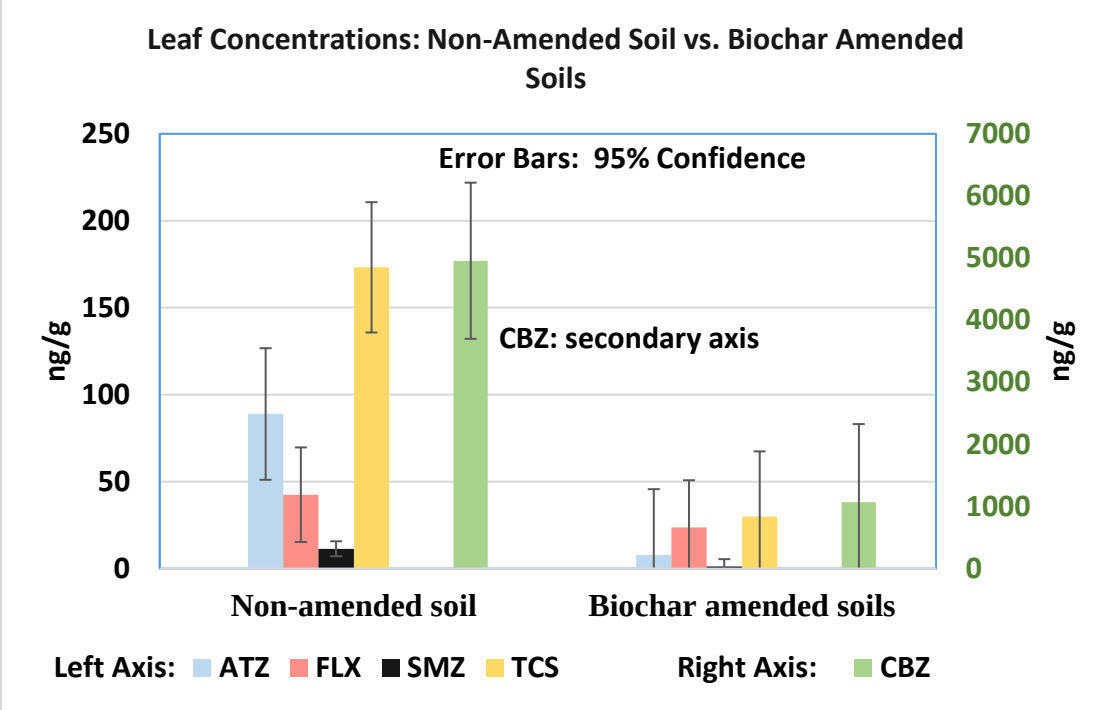


Figure 11: Leaf concentrations (ng/g) for corn grown in non-amended soil vs. biochar amended soil. Carbamazepine concentrations are listed on the secondary axis.

Averages for corn leaf concentration per transpiration volume (ng/g/L) are listed in Table 16 with percentage reduced and significant differences ($p<0.05$) listed in Table 17. The ng/g/L concentration was included because it can be a useful comparison for experiments conducted in different environmental conditions by incorporating both leaf mass and transpiration volume. This data was used to compare with the leaf and exposure concentration data from the hydroponic experiment. Pictures of the corn at 28 days can be seen in Figures A4-A15.

Table 16: Corn leaf uptake concentration per transpiration volume (ng/g/L). Averages listed for each growth media/experiment matrix with standard deviations using detection limit for compounds <MDL.

Growth Media	ATZ ng/g/L	Std. dev.	CBZ ng/g/L	Std. dev.	FLX ng/g/L	Std. dev.	SMZ ng/g/L	Std. dev.	TCS ng/g/L	Std. dev.
Soil No PPCPs	9.0	4.7	10	5	7	4	9.4	4.9	9	5
Soil	1118.5	848.6	61826	30834	546	566	140.6	94.9	2139	761
Soil Perlite	1251.8	891.6	50433	15493	1055	1115	124.5	60.3	2054	1373
Soil PJ	9.4	3.1	10290	4953	465	234	9.8	3.3	278	106
Soil LP	223.9	299.6	18449	9950	167	206	20.4	4.2	526	598
Sand No PPCPs	3.3	0.9	4	1	3	1	3.5	0.9	3	1
Sand	106.7	110.2	218649	19211	4994	1968	181.4	53.3	5078	434
Sand Perlite	58.2	14.7	411346	124635	15139	4397	159.5	27.3	7025	912
Sand PJ	20.0	24.3	11006	3467	1081	779	8.7	8.2	519	294
Sand LP	72.8	41.2	209841	21898	4676	1001	105.6	9.9	1755	1223

Table 17: Corn leaf concentration (ng/g/L) comparison of amended to nonamended media. Shaded squares are significant ($p<0.05$).

% difference (ng/g/L)	ATZ	CBZ	FLX	SMZ	TCS
Soil	0%	0%	0%	0%	0%
Soil Perlite	12%	-18%	93%	-11%	-4%
Soil PJ Biochar	-99%	-83%	-15%	-93%	-87%
Soil LP Biochar	-80%	-70%	-69%	-86%	-75%
Sand	0%	0%	0%	0%	0%
Sand Perlite	-45%	88%	203%	-12%	38%
Sand PJ Biochar	-81%	-95%	-78%	-95%	-90%
Sand LP Biochar	-32%	-4%	-6%	-42%	-65%

Follow-up Corn Experiment

The follow up experiment to the main corn growth/uptake experiment was conducted in July 2018 with 3 non-amended soil corn columns and 3 non-amended sand corn columns receiving spiked irrigation water (1 mg/L). The corn in soil grew 15 days and the corn in sand grew for 20 days with the purpose of obtaining a similar mass as the main corn growth/uptake experiment. Corn was able to grow faster during this experiment due to the increase in sunlight (midday average = 1271 µmol/m^2s ± 422). The average above ground plant fresh weight in soil was 10.6 g (± 0.56) and the average above ground plant fresh weight in sand was 5.6 g (± 1.40). The total amount of water/nutrient solution added to the soil columns was 627 mL (± 54.8) and to the sand columns was 1567 mL (± 137.0). The total average amount of compounds added to each column can be viewed in Table A24.

A revised method was used in this experiment to reduce the variability of the transpiration measurements observed in the previous experiment. One column was covered at the top and a similar amount of leachate that was in the corn column buckets each day was added to the bucket holding the covered column. Two other columns were used, one filled with sand and one filled with soil and they were saturated with water without leachate. The amount of water evaporated from each of these columns was measured daily and a final average was calculated to measure evaporation. This method measured leachate evaporation and growth media evaporation separately and was used to estimate transpiration. The average transpiration for the soil columns was 253.3 mL (± 11.2) and the average transpiration for the sand columns was 360.9 mL (± 3.8).

The average leaf concentrations and recoveries are listed in Table 18 with a comparison to the Fall 2017 data in Table 19. In this experiment, the leaf concentration of atrazine was higher for sand than for the soil suggesting that the atrazine results in the Fall 2017 corn growth/uptake experiment (soil>sand) was an anomaly. It was expected that compounds would have lower leaf concentrations in the non-amended soil compared to the non-amended sand due to the lower sorption values of the sand. In the July 2018 experiment the leaf concentrations were <MDL for sulfamethoxazole and recoveries for 4 of the 5 compounds were lower than the main corn growth/uptake experiment suggesting that the EDGE extraction was not as efficient for these compounds as the extraction in the Oct.-Nov. 2017 corn experiment. This could be due to the shorter extraction time (5 minutes) of the EDGE compared to the other method used (39pprox.. 24 hours). Variability in leaf concentrations was determined as standard deviation over average leaf concentration (coefficient of variation) and was similar in both experiments but differed for each compound and growth media (Table 20). A picture of this experiment can be viewed in Figure A16.

Table 18: Leaf concentration averages (ng compound/g dry leaf wt.) for nonamended soil and sand in the follow up July 2018 corn experiment not adjusted for deuterated recoveries.

Growth Media	ATZ	CBZ	FLX	SMZ	TCS
	ng/g	ng/g	ng/g	ng/g	ng/g
Soil	3.0	330.7	108.6	<MDL	34.4
Sand	18.6	1724.8	1743.7	<MDL	166.3
Recovery	42%	54%	98%	59%	47%
Std. dev. Soil	1.3	27.0	122.3	n/a	27.8
Std. dev. Sand	7.6	226.8	299.3	n/a	112.2

Table 19: Leaf concentration averages (ng compound/g dry leaf wt.) for nonamended soil and sand in the Fall 2017 corn experiment not adjusted for deuterated recoveries.

Growth Media	ATZ	CBZ	FLX	SMZ	TCS
	ng/g	ng/g	ng/g	ng/g	ng/g
Soil	88.9	4956.2	42.5	11.4	173.2
Sand	18.7	40609.5	909.0	33.2	942.3
Recovery	59%	87%	73%	43%	73%
Std. dev. Soil	65.5	2175	42.7	7.8	54.7
Std. dev. Sand	18.6	3857	307	7.7	76.1

Table 20: Leaf concentration (ng/g) coefficient of variation (standard deviation/average leaf concentration) for the October 2017 and July 2018 corn experiments.

2017 Experiment	ATZ	CBZ	FLX	SMZ	TCS
Variability	(SD/AVG)	(SD/AVG)	(SD/AVG)	(SD/AVG)	(SD/AVG)
Soil	74%	44%	100%	68%	32%
Sand	99%	9%	34%	23%	8%
2018 Experiment	ATZ	CBZ	FLX	SMZ	TCS
Variability	(SD/AVG)	(SD/AVG)	(SD/AVG)	(SD/AVG)	(SD/AVG)
Soil	44%	8%	113%	n/a	81%
Sand	41%	13%	17%	n/a	67%

Hydroponic Corn Experiment

The hydroponic corn experiment was split into two different growing rounds with 3 spiked (200 ug/L) and 3 unspiked hydroponic solutions used in each round. In the second round, one plant from each experiment matrix died due to lack of air flow through the tubes supplying air bubbles to the hydroponic solution. The first round began July 31, 2018 and the corn was grown for 15 days with average sunlight at midday of 1250 µmol/m^2s (± 451.3). The second round began September 1, 2018 and the corn was grown for 19 days with average sunlight at midday of 1227 µmol/m^2s (± 515.4). The

average above ground dry weight in the first round was 0.751 g (± 0.043) for the corn with spiked solution and 2.010 g (± 0.307) for the corn with unspiked solution. The average above ground dry weight in the second round was 0.613 g (± 0.063) for the corn with spiked solution and 1.592 g (± 0.422) for the corn with unspiked solution. The corn with unspiked solution had significantly ($p<0.0005$) more growth than the corn with spiked solution most likely due to the presence of atrazine which is an herbicide. The corn leaves with spiked solution showed signs of discoloration and leaf burn which did not occur with the unspiked corn. Transpiration volumes with plant growth for each corn plant are listed in Table A25. Pictures from the hydroponic experiment can be viewed in Figures A17-A21.

The average leaf, stem, and above ground concentrations are listed in ng/g and ng/g/L in Table 21 with fluoxetine having the most uptake (12,000 ng/g) and atrazine having the least (5.8 ng/g). The average exposure concentrations for each corn plant are listed in Table A26 and the deuterated recoveries are listed in Table A27. The TSCF values were calculated for the corn with spiked solution (Table A28) and the averages are listed in Table 22. TSCF values are lower than commonly reported values (Dettenmaier et al. 2008) which is possibly due to the potential toxic effects to plant cells. Wang et al. (2015) found that atrazine significantly decreased relative growth rates during a 15-day exposure but did not significantly impact relative growth rates for 30, 45, or 60-day exposures. There is also the potential for compounds to metabolize depending on their structure (Langebartels and Harms, 1985).

Table 21: Leaf, stem, and above ground average concentrations in ng/g (dry wt.) and ng/g/L (mass compound/dry wt./volume transpired) for hydroponic corn grown in spiked nutrient solution (approx. 200 ug/L).

Compound:	ATZ	CBZ	FLX	SMZ	TCS
	ng/g	ng/g	ng/g	ng/g	ng/g
Avg. Leaf Conc.	8.82	3995	16395	21.6	115.2
SD	4.26	1358	5227	8.2	24.6
Avg. Stem Conc.	0.76	552	4909	16.9	66.0
SD	0.53	172	3256	3.9	7.6
Avg. Above Ground	5.81	2696	12021	19.9	96.1
SD	2.79	834	3909	6.1	14.0
Compound:	ATZ	CBZ	FLX	SMZ	TCS
	ng/g/L	ng/g/L	ng/g/L	ng/g/L	ng/g/L
Avg. Leaf Conc.	14.62	6174	25757	32.9	184.3
SD	8.53	1817	8166	10.2	46.3
Avg. Stem Conc.	1.17	887	7642	26.4	105.1
SD	0.79	316	4803	4.5	19.2
Avg. Above Ground	9.58	4167	18813	30.6	153.6
SD	5.43	1059	5814	6.8	31.9

Table 22: Average TSCF values for each target compound calculated for the 5 corn plants with spiked solution in the hydroponic experiment.

Compound:	ATZ	CBZ	FLX	SMZ	TCS
Average TSCF	3.45E-05	0.0137	0.0831	1.01E-04	1.29E-03
Standard Dev.	2.03E-05	0.0030	0.027	2.10E-05	2.39E-04

The total above ground plant tissue concentrations were not determined for the Fall 2017 experiment so the hydroponic results were compared using just leaf concentrations (ng/L):

$$\frac{ng}{L}(estimated\ Fall\ 2017\ corn\ exposure\ concentration\ in\ growth\ media)$$

$$= \left(\frac{ng\ (compound\ in\ Fall\ 2017\ leaves)}{L\ (transpiration)}\right)$$

$$/(\frac{\left(\frac{ng\ (compound\ in\ hydroponic\ leaves)}{L\ (transpiration)}\right)}{\frac{ng\ (compound\ conc.\ in\ solution)}{L}})$$

The estimated exposure concentrations for the Fall 2017 corn experiment are listed in Table 23 along with the concentration of the irrigation solutions added onto the surface of the soil or sand listed in Table 24. The estimated root exposure values should be lower than the concentration of the irrigation solutions in all instances due to the sorption capacity of the growth media. The error in estimates suggests that it is difficult to compare leaf accumulation in short term growing studies using hydroponic corn versus corn grown in soil or sand. There were also differences in sunlight and temperature as the experiments took place in different seasons which could have affected transformation of compounds at different rates. Atrazine was the compound with the worst estimates for exposure suggesting toxicity to plant cells might be the factor causing discrepancy between the different growing experiments.

Table 23: Estimated root exposure concentrations (µg/L) for the Fall 2017 corn experiment using the hydroponic corn leaf and exposure concentrations.

µg/L	ATZ	CBZ	FLX	SMZ	TCS
Soil	11292	1431	2.2	590	715
Soil Perlite	13615	1215	4.4	554	729
Soil PJ	104	260	2.0	45	106
Soil LP	1620	328	0.5	71	126
Sand	794	3929	15.3	591	1334
Sand Perlite	421	6066	39.5	448	1549
Sand PJ	313	395	5.9	56	241
Sand LP	679	4314	16.8	401	506

Table 24: Irrigation solution concentrations (µg/L) for the Fall 2017 corn experiment which was applied onto the surface of the soil or sand.

µg/L	ATZ	CBZ	FLX	SMZ	TCS
SOIL	1063.0	1376.6	850.0	1136.0	911.2
Standard Dev.	9.3	12.0	7.4	9.9	8.0
SAND	1055.8	1367.2	844.2	1128.2	904.9
Standard Dev.	9.2	12.0	7.4	9.9	7.9

Column Sorption Experiment

The results for the column sorption experiment can be viewed in Table 25 with the recoveries listed in Table A29. The values were determined based on one test for each growth media (non-amended, LP-biochar amended, PJ-biochar amended, and activated carbon amended). Only one test was done due to time constraints as equilibrium took over two weeks to reach in some instances as well as the extraction with methanol to obtain target compound concentrations <MDL. Fluoxetine was not <MDL after two weeks of extraction due to slow release of the compound. It was believed the mass of fluoxetine not recovered during the extraction was sorbed to the growth media.

Fluoxetine was the only target compound in which the mass not recovered was included in the mass extracted in the numerator used to calculate the Kd value. All other target compounds had recoveries ±5% of the total mass added to the column except triclosan. The extract was tested for multiple samples and one of triclosan's primary photodegradation products (2,4-dichlorophenol) was detected in significant quantities (>500 µg/L) therefore it was believed that triclosan had partially photodegraded during the sorption experiment. Triclosan had shown a tendency to photodegrade in previous lab experiments even in low level exposure.

Table 25: Kd values (L/kg) determined in the column sorption experiment. There is ±10% error associated with each value based on analytical variability.

Growth Media	ATZ	CBZ	FLX	SMZ	TCS
	Kd (L/kg)	Kd (L/kg)	Kd (L/kg)	Kd (L/kg)	Kd (L/kg)
Soil	4.8	5.7	502	5.9	119
Soil-LP Biochar	7.0	9.3	650	7.6	291
Soil-PJ Biochar	30.3	48.6	522	12.8	237
Soil-Activated Carbon	302.7	251.2	1275	182.2	712
	Kd (L/kg)	Kd (L/kg)	Kd (L/kg)	Kd (L/kg)	Kd (L/kg)
Sand	0.1	0.2	22	0.1	1.5
Sand-LP Biochar	5.9	8.0	184	6.1	52.2
Sand-PJ Biochar	24.9	31.2	149	12.4	89.8
Sand-Activated Carbon	123.3	221.4	330	149.3	123.7

The trends for the sorption values were that soil > sand and activated carbon amended > PJ-biochar amended > LP-biochar amended > non-amended. This was not true in all instances as the LP-biochar amended had larger Kd values for FLX than PJ-biochar amended. The LP-biochar amended soil had a larger Kd value for TCS than the PJ-biochar amended soil however the PJ-biochar amended sand had a larger Kd value

than the LP-biochar amended sand. Also, the PJ-biochar amended sand had larger Kd values than the PJ-biochar amended soil for ATZ and SMZ though these were the only instances in which the Kd values were greater in sand than soil. These values were similar (difference in Kd<2) and could have been due experimental error. The Kd values for atrazine were compared to literature values. Francioso et al. (1992) determined Kd values for atrazine in 4 different non-amended soils ranging from 1.5-10.9 and that the Kd values were dependent on soil characteristics. Jin et al. (2016) determined Kd values for atrazine in non-amended soil (0.82) and soil amended with different biochars at 20% by mass ranging from 38.7-220.6. The reason the Kd values for atrazine in soil amended with biochar in the Jin study exceeded the values in this study (6.6-23.1) was most likely due to the greater percentage of biochar mass used (20%>5%).

The Kd values and leaf concentrations were plotted (Figures A22-A31) for the biochar amended and non-amended soil and sand. Carbamazepine is presented as an example (Figures 12-13). One possibility for the difference between the soil and sand plots is that the biochar amended soil columns did not reach equilibrium when watering in the Fall 2017 corn experiment. Fluoxetine had different trends from the other compounds and leaf concentrations did not correlate as closely to Kd values. This could possibly be due to the high water solubility of fluoxetine compared to the other target compounds. The perlite amended media only increased leaf concentrations for fluoxetine in sand compared to the non-amended sand and had the highest water holding capacity of any growth media used (Table A7). The LP-biochar amended media had significantly greater water holding capacity than PJ-biochar amended media which could explain the

higher leaf concentrations for the LP-biochar amended sand despite the higher Kd values compared to PJ-biochar.

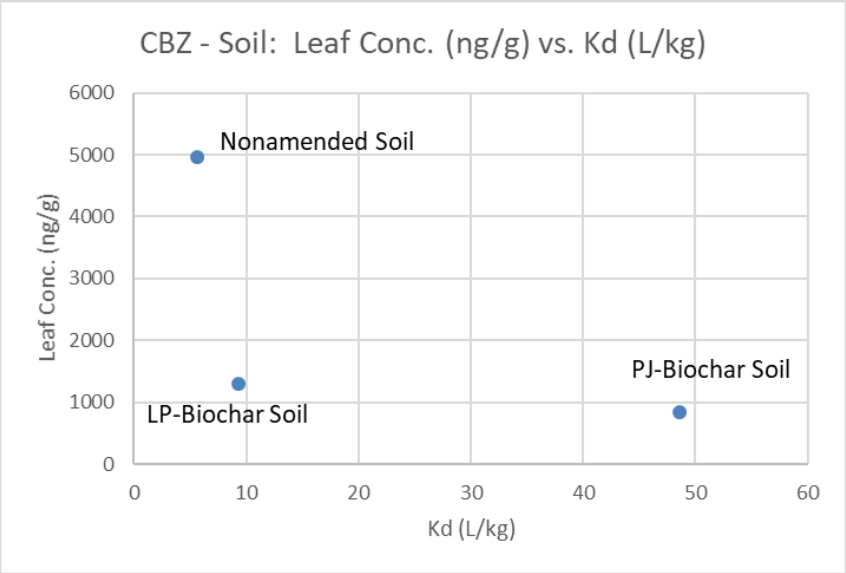


Figure 12: Scatterplot of leaf concentration vs. Kd value for carbamazepine in non-amended, PJ biochar amended, and LP biochar amended soil.

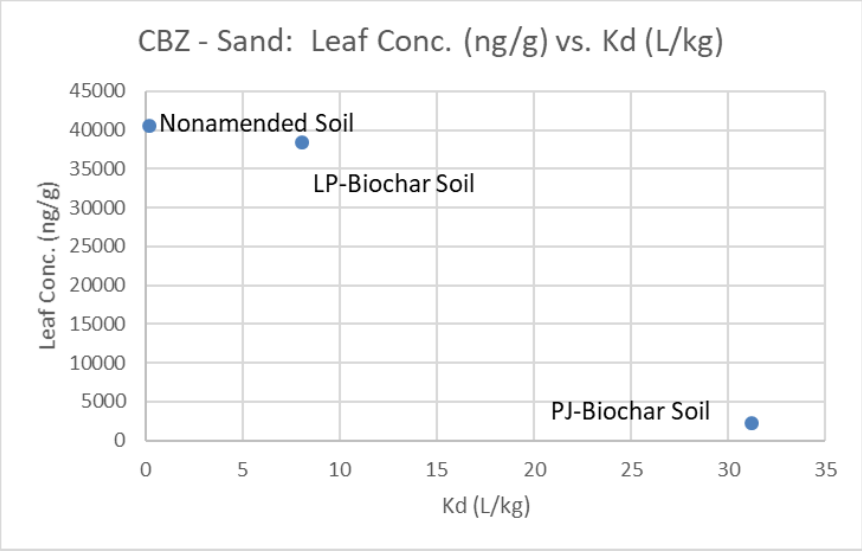


Figure 13: Scatterplot of leaf concentration vs. Kd value for carbamazepine in non-amended, PJ biochar amended, and LP biochar amended sand.

SUMMARY AND CONCLUSION

The March 2017 preliminary corn experiment indicated that the concentration of contaminants (10 µg/L) in the plant spiked solution was too low to be accurately detected in the leaves for a short term (30 days) corn experiment using soil. The corn growth/uptake experiment in Oct.-Nov. 2017 used a spike of 1 mg/L in order to detect all target compounds. The Oct.-Nov. 2017 experiment had low peak sunlight conditions (280 ±171 µmol/m^2s) resulting in slow growth compared to the follow up experiment in July-Aug. 2018 which had high peak sunlight conditions (1271 ±421.6 µmol/m^2s). The Oct.-Nov. 2017 corn experiment had higher leaf concentrations (ng/g) despite having less transpiration over the 28 days than the July-Aug. 2018 which lasted 15-20 days.

In the Oct.-Nov. 2017 corn experiment there were no statistical differences in corn growth between the growth media using soil. This could possibly be due to the high pH (9.2-9.4) of the biochars used in an alkaline soil (pH 7.7). Significant improvements in plant growth are common for biochar applied to acidic soils in the literature. In the sand media the PJ-biochar amended sand had significantly more growth than the non-amended sand and perlite amended sand. When comparing growth data in both the preliminary Mar. 2017 experiment and the Oct.-Nov. 2017 experiment the PJ-biochar had significantly more growth than the non-amended, perlite amended, and LP-biochar amended media. This suggests that the lack of significance in growth data for the Oct.-Nov. 2017 experiment could be due to the limited number of replicates. The LP-biochar corn leaves had significantly less chlorophyll than the unspiked corn leaves which could imply that the LP-biochar sequesters iron.

The PJ-biochar amended soil significantly ($p<0.006$) reduced compound concentrations and the LP-biochar amended soil significantly ($p< 0.015$) reduced compound concentrations compared to the non-amended soil. The PJ-biochar amended sand significantly ($p<0.000$) reduced compound concentrations but the LP-biochar amended sand did not reduce compound concentrations compared to the non-amended sand. Most of the leaf concentration variability was due to the non-amended leaf samples which had one out of the 3 samples <MDL for most compounds whereas the other 2 samples had relatively high leaf accumulation. There may have been growth deficiencies in the one sample which limited uptake of compounds. These possible outliers were included in the data analysis but if they had been discarded reduction of leaf concentrations using biochar and statistical significance would have been greater. For example, PJ biochar amended soil reduced atrazine leaf concentrations by 99% though this was not statistically significant due to the high variability in the non-amended soil.

Leaf concentrations in the corn grown in the perlite amended soil and sand were not different than corn grown in soil and sand except for fluoxetine where the leaf concentration in corn grown in perlite amended sand were significantly higher than in leaves from corn grown in sand. This could be due to the high water solubility of fluoxetine and the water holding capacity of the perlite amended growth media which was significantly greater than all other growth media.

Sorption coefficients for the target compounds were larger in soil than sand and activated carbon amended > PJ-biochar amended > LP-biochar amended > non-amended. This was not true for fluoxetine as the LP-biochar amended media had greater Kd values

than the PJ-biochar. Fluoxetine was the only positively charged compound suggesting that the biochars may have had different surface properties. Triclosan had mixed results as the LP-biochar had a larger Kd in the soil and the PJ-biochar had a larger Kd in the sand. This could be due to experimental or analytical error. It should be noted that the pKa for triclosan is 7.9 which was near the pH of the reclaimed water (7.7) used in the sorption experiment.

The scatterplots of leaf concentrations vs. Kd values displayed exponential trendlines in the soil media and linear trendlines in the sand media indicating that the soil columns in the corn experiment did not reach equilibrium. The linear data for the sand columns suggests that there was an inverse relationship between Kd values and leaf concentrations. Fluoxetine did not follow the linear sand trends of the other compounds possibly due to the high water solubility of fluoxetine and the significant differences in water holding capacity between PJ-biochar and LP-biochar growth media.

The results for the hydroponic experiments had significant differences in growth for the spiked vs. the unspiked corn suggesting that the 200 µg/L spike had a sub-lethal toxic effect on corn most likely due to the herbicide atrazine but possibly due to the target PPCPs. The results for above ground concentrations (dry wt.) were that fluoxetine had the highest uptake (12.0 µg/g ±3.9); then carbamazepine (2.70 µg/g ±0.83), triclosan (96.1 ng/g ±14.0), sulfamethoxazole (19.9 ng/g ±6.1), and atrazine had the least (5.81 ng/g ±2.79).

The hydroponic data was used to calculate the TSCF values. The TSCF values were lower than commonly reported values possibly due to the high exposure

concentration used (approx. 200 µg/L) and potential toxic effects to plant cells. There is also the possibility that some of the compounds may have metabolized. TSCF values were used to estimate exposure concentrations in the Oct.-Nov. 2017 corn experiment but results were tenuous due to differences in experimental conditions and analytical variability.

Results indicated that, in general, the pinyon-juniper (PJ) biochar was better than lodgepole pine (LP) biochar at improving corn growth, sorbing target contaminants, and reducing bioavailability for the particular soil and target compounds used in this study. This suggests that even when biochar is made from similar feedstock and pyrolyzed at similar temperatures there can still be great differences in the characteristics and effects of the biochars produced. Therefore, caution should be taken in generalizing characteristics of biochar and biochars should be tested or "fitted" to a soil before widespread application with considerations given for pretreatment to optimize desired results. The results from this study indicate that biochar has potential as a sorbent of PPCPs and can reduce PPCP bioavailability in the short term for some compounds and that biochar can improve plant growth even in slightly alkaline soil depending on the biochar used.

RECOMMENDATIONS FOR FUTURE WORK

In this study there was great variability in the corn uptake data. To reduce analytical variability, the plant samples should be cut into as many subsamples as possible while still maintaining target compounds above detection limit. This study used 3 corn plants for each experiment matrix but it is advisable to use at least 5 replicates when analyzing PPCPs in plant samples. If using many PPCPs consider doing multiple extractions with different solvents and combining the supernatants. This will require preliminary testing to compare optimal recovery for all the target compounds.

When measuring evaporation (in order to determine transpiration) in a growth/uptake experiment consider measuring the evaporation of leachate separately from the evaporation of the saturated growth media. This can reduce variability in the transpiration estimates. Transpiration values should be included in literature on uptake in order to compare plant tissue concentrations and TSCF values.

The largest loss of recovery during extraction and cleanup was due to concentrating the samples down to less than 1 mL using the Turbovap II. Plant residue was observed sorbed to the glass during this process. A better approach would be to concentrate the sample down to 5 mL and to transfer the sample to a vial. If the sample volume requires further concentration the vial could be air dried in the dark until the volume is reduced to an amount that achieves detection. The vial should then be sonicated to dissolve all particulate into the solvent.

It is also recommended that extraction recovery should be reported in the literature. In this study plant biomass concentrations were not adjusted for deuterated or

solvent recovery but up to 20% solvent loss was observed absorbed by the dry leaf material. Theoretically this solvent should be at equilibrium and if adjusted would change the uptake data.

Researchers should pursue efficient means to prepare biochar before application to optimize results such as soaking in compost or nutrients. This can reduce the need to apply additional fertilizer when using biochar. If applying to an alkaline soil consider ways to lower the pH of biochar or soil before application.

Another recommendation involves the terminology when discussing biochar. "Biochar" is a term used to describe a wide variety of different materials and pyrolysis conditions which could potentially lead to overgeneralizing characteristics. One way to minimize overgeneralizing is to always list the feedstock descriptor prior to the word "biochar" which can help narrow the range of properties. This is the reason the title for this paper used the phrase "wood biochar". Even when using similar feedstocks in this study the characteristics and effects of the wood biochars still differed greatly. It is easy to imagine that pig manure pyrolyzed at 350C for one hour would have different properties than hardwood pyrolyzed at 900C for ten hours, yet both are considered biochar.

Biochar has been described as a possible method for carbon sequestration which can reduce carbon emissions. The most well-established approach to carbon sequestration is reforestation - specifically in tropical regions. Tropical regions often have acidic soils and future studies should examine the potential to help reforestation efforts with biochar soil amendments in these regions. Biochar has been shown to be

effective at improving soil fertility and plant growth in acidic soils partly due to the high pH of biochar. There is historical precedence of *terra preta* (i.e. biochar) being successfully used in the Amazon. Both reforestation and biochar production/application could be combined to potentially achieve even greater carbon sequestration.

Concerns about possible desorption of contaminants by biochar after using it for contaminant sequestration should be addressed. A future study could soak biochar in PPCPs, apply it to soil, and observe the effects on plant uptake when irrigating with PPCP contaminated solution.

Biochar studies are limited in terms of estimating long term impact. Despite this being widely recognized in the literature there seems to be little response in conducting long term studies. This study examined the short-term impacts of biochar amendments on PPCP bioavailability but long-term sorption behavior could be estimated by doing a series of kinetic experiments. It is recommended that researchers begin trying to estimate long term impacts of biochar as there have been few attempts to bridge this gap in the literature.

ENGINEERING SIGNIFICANCE

This study helped to assess how wood biochar impacted PPCP uptake for corn crops in a short time period. Determining whether biochar has a positive impact on plant growth and contaminant uptake could lead to a cost-effective method for sequestering PPCP contaminants in the natural environment. The impact of having low-level near universal PPCP contamination in the natural environment is unknown but could have potentially negative effects on the ecosystem and human health. This study examined PPCP accumulation in corn leaves and stems which can be used to estimate accumulation in crops. It is common for livestock to consume the excess portions of crops such as leaves and stems which could accumulate in the livestock and eventually be a source of exposure to humans. Biochar usage could lead to lower levels of PPCP contaminants in food crops, soils, and surface waters, as well as improving crop yields while helping to mitigate climate change by sequestering carbon. Biochar production is a potential method of carbon sequestration which could reduce carbon emissions and mitigate some of the potential impacts of climate change. This study hopes to add to the existing literature examining the properties of biochar. While many uncertainties still exist with biochar usage, confidence in results builds when independent lines of investigation converge on consistent conclusions.

REFERENCES

Ahmadi, L., Dupont, R., McLean, J., (2018). "Investigation and analysis of a variety of pharmaceuticals and personal care products in reclaimed domestic wastewater used for urban agriculture in Northern Utah," USCID, 11th International Conference on Irrigation & drainage, Water Reuse and Non-Traditional Water Sources for Irrigated Agriculture, October 15-19, 2018, Phoenix, Arizona.

Amman, G., & Schmitz, R.F., (1988). "Mountain Pine Beetle: Lodgepole Pine Interactions and Strategies for Reducing Tree Losses". *Ambio*, 17(1), 62-68. Retrieved from: <http://www.jstor.org/stable/4313420>

Benotti, M. J., Trenholm, R. A., Vanderford, B. J., Holady, J. C., Stanford, B. D., & Snyder, S. A. (2008). Pharmaceuticals and endocrine disrupting compounds in US drinking water. *Environmental science & technology*, 43(3), 597-603.

Boreen, A. L., Arnold, W. A., & McNeill, K. (2004). "Photochemical fate of sulfa drugs in the aquatic environment: sulfa drugs containing five-membered heterocyclic groups," *Environmental Science & Technology*, 38(14), 3933-3940.

Brebu, M., and Vasile, C., (2010). "Thermal degradation of lignin—a review," *Cellulose Chemistry & Technology*, 44.9, 353.

Chen, B., Zhou, D., & Zhu, L. (2008). "Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures". *Environmental science & technology*, 42(14), 5137-5143.

Cornell University. (2006, March 1). "Amazonian Terra Preta Can Transform Poor Soil Into Fertile". *ScienceDaily*. Retrieved January 10, 2017 from: <http://www.sciencedaily.com/releases/2006/03/060301090431.htm>.

Dettenmaier, E. M., Doucette, W. J., & Bugbee, B. (2008). "Chemical hydrophobicity and uptake by plant roots," *Environmental Science & Technology*, 43(2), 324-329.

Doucette, W. J., Shunthirasingham, C., Dettenmaier, E. M., Zaleski, R. T., Fantke, P., and Arnot, J. A. (2018). "A review of measured bioaccumulation data on terrestrial plants for organic chemicals: Metrics, variability, and the need for standardized measurement protocols." *Environmental toxicology and chemistry*, 37(1), 21-33.

Downie, A., Crosky, A., & Munroe, P. (2009). "Physical properties of biochar," Biochar for environmental management. *Science and Technology*, 13-32.

DrugBank: “Fluoxetine”. Retrieved July 17, 2018 from: <https://www.drugbank.ca/drugs/DB00472>

Espinoza, L., & Ross, J. (2003). “Fertilization and liming.” *University of Arkansas Corn Production Handbook - MP437*, 23-27.

Ferrari, B., Paxeus, N., Giudice, R. L., Pollio, A., & Garric, J. (2003). “Ecotoxicological impact of pharmaceuticals found in treated wastewaters: study of carbamazepine, clofibric acid, and diclofenac,” *Ecotoxicology and environmental safety*, 55(3), 359-370.

Francioso, O., Bak, E., Rossi, N., & Sequi, P. (1992). “Sorption of atrazine and trifluralin in relation to the physio-chemical characteristics of selected soils,” *Science of the total environment*, 123, 503-512.

Gray, M., Johnson, M. G., Dragila, M. I., & Kleber, M. (2014). “Water uptake in biochars: the roles of porosity and hydrophobicity”, *Biomass and Bioenergy*, 61, 196-205.

Groot, H., Howe, J., Bowyer, J., Pepke, E., Levins, R. A., & Fernholz, K. (2017). Biochar as an Innovative Wood Product: A Look at Barriers to Realization of its Full Potential.

Hassanli, A.M., Ebrahimizadeh, M.A., Beecham, S., (2009). “The effects of irrigation methods with effluent and irrigation scheduling on water use efficiency and corn yields in an arid region”. *Agricultural Water Management*, 96(1), 93-99.

Jin, J., Kang, M., Sun, K., Pan, Z., Wu, F., & Xing, B. (2016). “Properties of biochar-amended soils and their sorption of imidacloprid, isoproturon, and atrazine,” *Science of the Total Environment*, 550, 504-513.

Jones, O. A. H., Voulvoulis, N., & Lester, J. N. (2002). “Aquatic environmental assessment of the top 25 English prescription pharmaceuticals,” *Water Research*, 36(20), 5013-5022.

Kaleniecka, A., & Zarzycki, P. K. (2015). “Pharmaceuticals in the aquatic environment: sources, effects, treatment methods”. *Archives of Physiotherapy & Global Researches.*

Karami, N., Clemente, R., Moreno-Jiménez, E., Lepp, N. W., & Beesley, L. (2011). “Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass”. *Journal of hazardous materials*, 191(1-3), 41-48.

Kupryianchyk, D., Hale, S., Zimmerman, A. R., Harvey, O., Rutherford, D., Abiven, S., ... & Cornelissen, G. (2016). "Sorption of hydrophobic organic compounds to a diverse suite of carbonaceous materials with emphasis on biochar". *Chemosphere*, 144, 879-887.

Laird, D., Fleming, P., Wang, B., Horton, R. & Karlen, D. (2010). "Biochar impact on nutrient leaching from a Midwestern agricultural soil". *Geoderma*, 158, 436–442.

Lal, R. (2016). "Beyond COP 21: potential and challenges of the '4 per Thousand' initiative". *Journal of Soil and Water Conservation*, 71(1), 20A-25A.

Lang A. (1990). "Xylem, phloem and transpiration flows in developing apple fruits". *J Exp Bot* 41, 645–651.

Langebartels, C., Harms, H.H., (1985). "Analysis for nonextractable (bound) residues of pentachlorophenol in plant cell using a cell wall fractionation procedure." *Ecotoxicol. Environ. Saf.* 10, 268–279.

Liu, Z., Dugan, B., Masiello, C. A., & Gonnermann, H. M. (2017). "Biochar particle size, shape, and porosity act together to influence soil water properties". *Plos one*, 12(6), e0179079.

Logan City, (2014). Water Quality Report. Available at: <https://www.loganutah.org/document_center/Public%20Works/Water%20Quality%20Report%202014.pdf>. (Nov. 14, 2018).

Marschner H. (1995). *Mineral Nutrition of Higher Plants*, *2nd ed*., Academic, Amsterdam, The Netherlands.

McAvoy, D., Kuhns, M., & Black, J. (2012). "Utah Forest Types: An Introduction to Utah Forests." Available at: <https://forestry.usu.edu/files/utah-forest-types-an-introduction-to-utah-forests.pdf>

Nguyen, T. H., Cho, H. H., Poster, D. L., & Ball, W. P. (2007). "Evidence for a pore-filling mechanism in the adsorption of aromatic hydrocarbons to a natural wood char". *Environmental science & technology*, 41(4), 1212-1217.

O'Neil, M.J. (ed). "The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals". Whitehouse Station, NJ: Merck and Co., Inc., (2006), 1659.

Ong, C. N. (2016). Water reuse, emerging contaminants and public health: state-of-the-art analysis. *International Journal of Water Resources Development*, 32(4), 514-525.

Paltiel, O., Fedorova, G., Tadmor, G., Kleinstern, G., Maor, Y., and Chefetz, B., (2016). "Human Exposure to Wastewater-Derived Pharmaceuticals in Fresh Produce: A Randomized Controlled Trial Focusing on Carbamazepine," *Environ. Sci. Technol.*, 50, 4476–4482.

PubChem Identifier: CID 2256. Available at: <https://pubchem.ncbi.nlm.nih.gov/compound/2256>. (July 12, 2018).

Pudasaini, K., Ashwath, N., Walsh, K., & Bhattarai, T. (2012). "Biochar improves plant growth and reduces nutrient leaching in red clay loam and sandy loam". *Hydro Nepal: Journal of Water, Energy and Environment*, 11(1), 86-90.

Ronsse, F., Van Hecke, S., Dickinson, D., & Prins, W. (2013). "Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions". *Gcb Bioenergy*, 5(2), 104-115.

Schulz, H., Dunst, G., Glaser, B., (2013). "Positive effects of composted biochar on plant growth and soil fertility," *Agronomy for Sustainable Development*, 33(4), 817-827.

Scotts, (2004). Scotts Testing Laboratory. Available at: <http://florawww.eeb.uconn.edu/msds/peters_5_11_26_hydrosol_label.pdf>. (Nov. 12, 2018).

Sima, L., Amador, J., da Silva, A. K., Miller, S. M., Morse, A. N., Pellegrin, M. L., Rock, C., and Wells, M. J. M. (2014). "Emerging Pollutants - Part I: Occurrence, Fate and Transport." *Water Environment Research*, 86(10), p. 1994-2035.

Singer, H., Muller, S., Tixier, C., Pillonel, L., (2002). "Triclosan: Occurrence and Fate of a Widely Used Biocide in the Aquatic Environment: Field Measurements in Wastewater Treatment Plants, Surface Waters, and Lake Sediments", *Environ. Sci. Technol.*, 2002, 36, p. 4998-5004.

Solanki, A., & Boyer, T. H. (2017). "Pharmaceutical removal in synthetic human urine using biochar". *Environmental Science: Water Research & Technology*, 3(3), 553-565.

Tang, J. X., Jin, Y. T., He, Z. L., Hou, Q. Y., & Zhao, C. T. (2018). A Review Of Researches On Biochar Adsorbing Organic Contaminants And Its Mechanism And Influence Factors. In IOP Conference Series: *Materials Science and Engineering* (Vol. 392, No. 5, p. 052030). IOP Publishing.

Terry, N., & Low, G. (1982). Leaf chlorophyll content and its relation to the intracellular localization of iron. *Journal of Plant Nutrition*, 5(4-7), 301-310.

US EPA. (2012). Estimation Programs Interface Suite for Microsoft Windows, v. 4.11, United States Environmental Protection Agency, Washington, DC, USA.

US EPA. (2016a). "Contaminants of Emerging Concern including Pharmaceuticals and Personal Care Products." <https://www.epa.gov/wqc/contaminants-emerging-concern-including-pharmaceuticals-and-personal-care-products>. (Sept. 27, 2016).

US EPA. (2016b). "Concentrations of prioritized pharmaceuticals in effluents from 50 large wastewater treatment plants in the US and implications for risk estimation." Mitchell S. Kostich, Angela L. Batt, James M. Lazorchak. <https://www.epa.gov/water-research/concentrations-prioritized-pharmaceuticals-effluents-50-large-wastewater-treatment>. (July 5, 2016).

Uzoma, K.C., Inoue, M., Andry, H., Fujimaki, H., Zahoor, A., Nishihara, E., (2011). "Effect of cow manure biochar on maize productivity under sandy soil condition", *Soil Use and Management*, Volume 27, Issue 2, 205–212.

Verheijen, F., Jeffery, S., Bastos, A. C., Van der Velde, M., & Diafas, I. (2010). Biochar application to soils. *A critical scientific review of effects on soil properties, processes, and functions. EUR*, 24099, 162.

Wannapeera, J., Fungtammasan, B., & Worasuwannarak, N. (2011). "Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass". *Journal of Analytical and Applied Pyrolysis*, 92(1), p. 99-105.

Wang, Q., Que, X., Zheng, R., Pang, Z., Li, C., & Xiao, B. (2015). "Phytotoxicity assessment of atrazine on growth and physiology of three emergent plants." *Environmental Science and Pollution Research*, 22(13), 9646-9657.

WinklerPrins, A.M., (2014). "Terra Preta: The Mysterious Soils of the Amazon." *The Soil Underfoot: Infinite Possibilities for a Finite Resource*, 235.

Wu, X., Conkle, J. L., & Gan, J. (2012). "Multi-residue determination of pharmaceutical and personal care products in vegetables". *Journal of chromatography A*, 1254, 78-86.

Wu, X., Dodgen, L., Conkle, J., Gan, J., (2015). "Plant uptake of pharmaceutical and personal care products from recycled water and biosolids: a review," *Science of The Total Environment*, 2015, Vol 536, p. 655-666.

Yamato, M., Okimori, Y., Wibowo, I.F., Anshori, S., Ogawa, M., (2006). “Effects of the application of charred bark of Acacia mangium on the yield of maize, cowpea and peanut, and soil chemical properties in South Sumatra, Indonesia,” *Soil Science and Plant Nutrition,* p. 489-495.

Yu, X.Y., Ying, G.G., Kookana, R.S., (2009). “Reduced plant uptake of pesticides with biochar additions to soil,” *Chemosphere,* 2009, 76(5), p. 665-671.

Zhao, L., Cao, X., Mašek, O., & Zimmerman, A. (2013). “Heterogeneity of biochar properties as a function of feedstock sources and production temperatures”. *Journal of hazardous materials*, 256, 1-9.

APPENDICES

Appendix A – Corn Growth/Uptake Experiments

Table A1: Initial growth media weight in the corn growth/uptake Fall 2017 experiment.

Column #	Growth Media/Matrix	Media Wt. (g)
1	Soil NO CORN	699.9
2	Soil NO CORN	700
3	Soil unspiked	699.4
4	Soil unspiked	700
5	Soil unspiked	700.1
6	Soil unspiked	701.3
7	Soil unspiked	700.8
8	Soil	699.6
9	Soil	700.3
10	Soil	700.4
11	Soil	700.1
12	Soil	699.7
13	Sand unspiked	950.8
14	Sand unspiked	949.6
15	Sand unspiked	950.4
16	Sand unspiked	950.1
17	Sand unspiked	950.4
18	Sand	949.8
19	Sand	950.4
20	Sand	950.4
21	Sand	949.8
22	Sand	950.6
23	Soil-Pinyon Juniper	660.3
24	Soil-Pinyon Juniper	659.6
25	Soil-Pinyon Juniper	659.8
26	Soil-Pinyon Juniper	660.5
27	Soil-Pinyon Juniper	659.4
28	Sand-Pinyon Juniper	833.7
29	Sand-Pinyon Juniper	833.7
30	Sand-Pinyon Juniper	833
31	Sand-Pinyon Juniper	833.6
32	Sand-Pinyon Juniper	833
33	Soil-Lodgepole Pine	660.6
34	Soil-Lodgepole Pine	659.3
35	Soil-Lodgepole Pine	659.7
36	Soil-Lodgepole Pine	659.8
37	Soil-Lodgepole Pine	659.3
38	Sand-Lodgepole Pine	833.4
39	Sand-Lodgepole Pine	833.3
40	Sand-Lodgepole Pine	833.7
41	Sand-Lodgepole Pine	833.7
42	Sand-Lodgepole Pine	833.4

43	Soil-Perlite	636.7
44	Soil-Perlite	635.6
45	Soil-Perlite	634.7
46	Soil-Perlite	634.8
47	Soil-Perlite	634.7
48	Sand-Perlite	857.9
49	Sand-Perlite	858.8
50	Sand-Perlite	858.2
51	Sand-Perlite	859.2
52	Sand-Perlite	859.3
53	Sand NO CORN	950.9
54	Sand NO CORN	950.1

Table A2: Method Detection Limit (MDL) values for the target compounds.

Compound	External Calibration	Isotope Dilution
	ng/L	ng/L
ATZ	0.38	0.53
CBZ	0.01	0.08
FLX	2.78	1.77
SMZ	0.69	0.87
TCS	3.45	3.96

Table A3: Chromatography gradient settings. Mobile phase A comprises 0.1 % formic acid and 0.1% methanol in water. Mobile phase B comprises 0.1 % formic acid (by volume) in LC/MS grade acetonitrile.

Time (min)	Mobile Phase A (%)	Mobile Phase B (%)
0.0	95.0	5.0
1.0	95.0	5.0
3.0	60.0	40.0
8.0	40.0	60.0
10.0	5.0	95.0

Table A4: Corn above ground fresh weight (g) for the preliminary experiment in March 2017.

Growth Media	Above Ground Fresh Wt. (g)	STDEV
	AVG.	
Nonamended Soil	4.16	1.40
LP Biochar-Soil	2.62	0.49
PJ Biochar-Soil	5.66	1.00
Perlite-Soil	3.33	1.44
Unspiked Nonamended Soil	2.29	0.99

Table A5: Tukey test results for above ground mass in the preliminary corn experiment (March 2017).

Tukey Test	diff. of means	lower bound	upper bound	p-value
Matrices				
Nonamended-LP Biochar	-1.50	-5.04	2.04	0.64535
Perlite-LP Biochar	-2.33	-6.11	1.46	0.32155
PJ Biochar-LP Biochar	-3.04	-6.83	0.74	0.13408
Unspiked-LP Biochar	-3.38	-7.61	0.85	0.13810
Perlite-Nonamended	-0.83	-4.37	2.71	0.93329
PJ Biochar-Nonamended	-1.55	-5.08	1.99	0.62035
Unspiked-Nonamended	-1.88	-5.89	2.13	0.56176
PJ Biochar-Perlite	-0.72	-4.50	3.07	0.96800
Unspiked-Perlite	-1.05	-5.28	3.18	0.91965
Unspiked-PJ Biochar	-0.33	-4.56	3.90	0.99882

Table A6: Total compounds added per column for each target compound based on total volume added over 28 days and sample concentrations from the spiked irrigation water.

Growth Media	ATZ (µg)	CBZ (µg)	FLX (µg)	SMZ (µg)	TCS (µg)
SOIL	773.5	1001.7	618.5	826.6	663.0
Standard Dev.	6.7	8.7	5.3	7.1	5.7
SAND	1035.0	1340.3	827.6	1106.1	887.1
Standard Dev.	9.1	11.7	7.2	9.7	7.8

Table A7: Amount of water remaining in each column (mL) and water per mass growth media (mL/g) after 28 days with averages and standard deviations.

Growth Media	Water (mL)	Average (mL)	stand. dev.	Water/Media Wt. (mL/g)	Average (mL/g)	stand. dev.
Soil Unspiked	195.7	199.6	2.8	0.280	0.285	0.004
	202.2			0.289		
	200.8			0.287		
Soil Spiked	203.9	209.4	4.0	0.291	0.299	0.006
	213			0.304		
	211.3			0.302		
Soil Perlite	239.6	237.1	2.3	0.377	0.373	0.004
	234.1			0.369		
	237.6			0.374		
Soil PJ	210.7	209.3	1.0	0.319	0.317	0.001
	208.5			0.316		
	208.8			0.316		
Soil LP	226	222.5	2.5	0.342	0.337	0.004
	221.2			0.335		
	220.3			0.334		
Total Soil AVG:		215.6	14.3		0.322	0.034
	Water (mL)	Average (mL)	stand. dev.			
Sand Unspiked	183.5	175.7	7.6	0.193	0.185	0.008
	165.5			0.174		
	178.2			0.188		
Sand Spiked	183.1	180.2	2.7	0.193	0.190	0.003
	176.5			0.186		
	180.9			0.190		
Sand Perlite	198.3	206.6	6.3	0.231	0.240	0.007
	213.5			0.249		
	207.9			0.242		
Sand PJ	180.1	184.7	3.3	0.216	0.222	0.004
	186.7			0.224		
	187.4			0.225		
Sand LP	188.6	194.6	4.4	0.226	0.234	0.005
	196.1			0.235		
	199.2			0.239		
Total Sand AVG:		188.4	12.2		0.214	0.023

Table A8: Tukey test results for water holding capacity between experiment matrices in the Fall 2017 corn experiment.

Tukey Test	diff. of means	lower bound	upper bound	p-value
Matrices				
Perlite-LP Biochar	0.0215	0.0110	0.0321	0.000048
PJ Biochar-LP Biochar	-0.0159	-0.0264	-0.0054	0.001693
Unamended-LP Biochar	-0.0410	-0.0515	-0.0305	0.000000
Unspiked-LP Biochar	-0.0502	-0.0607	-0.0397	0.000000
PJ Biochar-Perlite	-0.0375	-0.0480	-0.0270	0.000000
Unamended-Perlite	-0.0625	-0.0730	-0.0520	0.000000
Unspiked-Perlite	-0.0718	-0.0823	-0.0613	0.000000
Unamended-PJ Biochar	-0.0251	-0.0356	-0.0146	0.000006
Unspiked-PJ Biochar	-0.0343	-0.0448	-0.0238	0.000000
Unspiked-Unamended	-0.0092	-0.0197	0.0013	0.102655

Table A9: Corn growth based on stem and leaf fresh weight on days 8, 15, 22, 28.

Total Leaf and Stem Wt.				
Day:	Day 8	Day 15	Day 22	Day 28
Growth Media:	Fresh Wt. (g)	Fresh Wt. (g)	Fresh Wt. (g)	Fresh Wt. (g)
Soil no spike	0.525	3.07	3.77	6.51
Soil no spike	0.52			8.43
Soil no spike	0.215			9.29
Soil no spike	0.555			
Soil no spike	0.76			
Soil	0.51	2.28	4.45	7.34
Soil	0.495			8.33
Soil	0.23			7.81
Soil	0.36			
Soil	0.425			
Soil PJ	0.355	2.33	5.36	11.35
Soil PJ	0.515			7.46
Soil PJ	0.51			7.09
Soil PJ	0.42			
Soil PJ	n/a			
Soil LP	0.52	0.88	2.38	6.26
Soil LP	0.635			7.56
Soil LP	0.365			5.6
Soil LP	n/a			
Soil LP	n/a			
Soil Perlite	0.57	2.53	5.08	9.44
Soil Perlite	0.375			10.01
Soil Perlite	0.44			8.77
Soil Perlite	0.555			
Soil Perlite	0.26			
Sand no spike	0.215	2.3	6.27	6.05
Sand no spike	0.335			10.38
Sand no spike	0.48			13.45
Sand no spike	0.425			
Sand no spike	0.35			
Sand	0.295	1.75	5.38	6.28
Sand	0.39			5.49
Sand	0.16			6.39
Sand	0.445			
Sand	n/a			
Sand PJ	0.43	1.94	6.21	14.97
Sand PJ	0.21			13.87
Sand PJ	0.54			10.41
Sand PJ	0.33			
Sand PJ	0.36			
Sand LP	0.43	1.57	5.8	8.96

Sand LP	0.25			7.88
Sand LP	0.25			9.4
Sand LP	0.355			
Sand LP	n/a			
Sand Perlite	0.39	1.95	3.97	5.36
Sand Perlite	0.19			5.59
Sand Perlite	0.31			7.06
Sand Perlite	0.235			
Sand Perlite	0.55			

Table A10: Anova results for corn growth in soil.

ANOVA	degrees of freedom	sum of squares	mean squares	F Value	Pr(>F)
Corn soil growth					
dataset	4	14.13	3.534	1.916	0.184
residuals	10	18.44	1.844		

Table A11: Anova results for corn growth in sand.

ANOVA	degrees of freedom	sum of squares	mean squares	FValue	Pr(>F)
Corn sand growth					
dataset	4	105.2	26.3	6.2	0.0089
residuals	10	42.4	4.2		

Table A12: Tukey mean comparison results for corn growth in soil.

Tukey Test	difference in means	lower bound	upper bound	p-value
Matrix Comparison				
Soil LP-Soil	-1.35	-5.00	2.30	0.7407
Soil Perlite-Soil	1.58	-2.07	5.23	0.6270
Soil PJ-Soil	0.81	-2.84	4.46	0.9451
Soil Unspike-Soil	0.25	-3.40	3.90	0.9993
Soil Perlite-Soil LP	2.93	-0.72	6.58	0.1343
Soil PJ-Soil LP	2.16	-1.49	5.81	0.3542
Soil Unspike-Soil LP	1.60	-2.05	5.25	0.6151
Soil PJ-Soil Perlite	-0.77	-4.42	2.88	0.9525
Soil Unspike-Soil Perlite	-1.33	-4.98	2.32	0.7520
Soil Unspike-Soil PJ	-0.56	-4.21	3.09	0.9853

Table A13: Tukey mean comparison results for corn growth in sand. The squares shaded in yellow implies significance ($p<0.05$).

Tukey Test	difference in means	lower bound	upper bound	p-value
Matrix Comparison				
Sand Perlite-Sand LP	-2.74	-8.27	2.79	0.5113
Sand PJ-Sand LP	4.34	-1.19	9.87	0.1480
Sand-Sand LP	-2.69	-8.22	2.84	0.5276
Sand Unspike-Sand LP	1.21	-4.32	6.74	0.9465
Sand PJ-Sand Perlite	7.08	1.55	12.61	0.0121
Sand-Sand Perlite	0.05	-5.48	5.58	1.0000
Sand Unspike-Sand Perlite	3.96	-1.57	9.49	0.2053
Sand-Sand PJ	-7.03	-12.56	-1.50	0.0127
Sand Unspike-Sand PJ	-3.12	-8.65	2.41	0.3955
Sand Unspike-Sand	3.91	-1.62	9.44	0.2141

Table A14: MANOVA test comparing corn growth from the preliminary and main experiment. The squares shaded in yellow implies significance ($p<0.05$).

Tukey Test	difference in means	lower bound	upper bound	p-value
Matrix Comparison				
Perlite-LP Biochar	0.30	-1.94	2.54	0.9948
PJ Biochar-LP Biochar	3.18	0.94	5.42	0.0024
Spiked Corn-LP Biochar	-0.12	-2.30	2.07	0.9999
Unspiked Corn-LP Biochar	1.39	-0.92	3.70	0.4241
PJ Biochar-Perlite	2.88	0.64	5.12	0.0067
Spiked Corn-Perlite	-0.42	-2.60	1.77	0.9804
Unspiked Corn-Perlite	1.09	-1.22	3.40	0.6543
Spiked Corn-PJ Biochar	-3.30	-5.48	-1.11	0.0012
Unspiked Corn-PJ Biochar	-1.79	-4.10	0.52	0.1901
Unspiked Corn-Spiked Corn	1.51	-0.75	3.76	0.3212

Table A15: Total transpiration volume per column (mL) with dry leaf weight (g). Standard deviation for soil columns is 33.5 mL and for sand columns is 181.9 mL based on evaporation columns.

Growth Media	Col #	Dry Leaf Wt.	Transpired
		(g)	(mL)
Soil Unspiked	4	0.26	76.6
	5	0.32	109.3
	6	0.35	137.3
Soil Spiked	9	0.32	86.1
	10	0.28	76.2
	12	0.28	84.8
Sand Unspiked	14	0.29	207.6
	15	0.31	210.0
	16	0.45	267.3
Sand Spiked	18	0.22	192.1
	20	0.20	171.4
	22	0.26	194.4
Soil PJ	24	0.28	73.6
	25	0.30	68.6
	26	0.39	120.3
Sand PJ	28	0.52	260.3
	29	0.44	173.0
	30	0.35	149.8
Soil LP	33	0.23	73.3
	34	0.29	82.2
	37	0.20	66.2
Sand LP	38	0.27	164.1
	41	0.24	187.5
	42	0.26	200.9
Soil Perlite	44	0.29	89.5
	46	0.32	81.4
	47	0.30	75.1
Sand Perlite	48	0.17	108.8
	49	0.17	154.7
	52	0.24	178.6

Table A16: Anova results for chlorophyll (µmol/m2) of corn leaves grown in soil media.

ANOVA	degrees of freedom	sum of squares	mean squares	F Value	Pr(>F)
Chlorophyll					
dataset	4	25053	6263	2.111	0.154
residuals	10	29674	2967		

Table A17: Tukey t-test results for chlorophyll (µmol/m2) of corn leaves grown in soil media.

Tukey Test	difference in means	lower bound	upper bound	p-value
Matrix Comparison				
Soil LP-Soil	-95.9	-242.3	50.4	0.2698
Soil Perlite-Soil	-11.6	-158.0	134.7	0.9988
Soil PJ-Soil	-1.7	-148.0	144.7	1.0000
Soil Unspiked-Soil	22.6	-123.8	169.0	0.9846
Soil Perlite-Soil LP	84.3	-62.1	230.7	0.3781
Soil PJ-Soil LP	94.3	-52.1	240.6	0.2837
Soil Unspiked-Soil LP	118.5	-27.8	264.9	0.1304
Soil Perlite-Soil PJ	-10.0	-156.3	136.4	0.9993
Soil Unspiked-Soil Perlite	34.2	-112.1	180.6	0.9337
Soil Unspiked-Soil PJ	24.3	-122.1	170.6	0.9801

Table A18: Anova results for chlorophyll (µmol/m2) of corn leaves grown in sand media.

ANOVA	degrees of freedom	sum of squares	mean squares	F Value	Pr(>F)
Chlorophyll					
dataset	4	4773	1193	0.681	0.621
residuals	10	17521	1752		

Table A19: Tukey t-test results for chlorophyll (µmol/m2) of corn leaves grown in sand media.

Tukey Test	difference in means	lower bound	upper bound	p-value
Matrix Comparison				
Sand LP-Sand	-33.4	-145.8	79.1	0.860
Sand PJ-Sand	-12.2	-124.7	100.2	0.996
Sand Perlite-Sand	1.8	-110.7	114.2	1.000
Sand Unspiked-Sand	20.8	-91.7	133.2	0.971
Sand PJ-Sand LP	21.1	-91.3	133.6	0.969
Sand Perlite-Sand LP	35.1	-77.3	147.6	0.837
Sand Unspiked-Sand LP	54.1	-58.3	166.6	0.538
Sand Perlite-Sand PJ	14.0	-98.5	126.5	0.993
Sand Unspiked-Sand PJ	33.0	-79.5	145.5	0.864
Sand Unspiked-Sand Perlite	19.0	-93.5	131.5	0.979

Table A20: Tukey t-test results for chlorophyll (µmol/m2) of corn leaves grown in soil and sand media. The squares shaded in yellow implies significance ($p<0.05$).

Tukey Test	diff. of means	lower bound	upper bound	p-value
Matrices				
Perlite-LP Biochar	59.72	-24.21	143.64	0.246793
PJ Biochar-LP Biochar	57.70	-26.22	141.62	0.276358
Unamended-LP Biochar	64.65	-19.27	148.57	0.184297
Unspiked-LP Biochar	86.33	2.41	170.26	0.041889
PJ Biochar-Perlite	-2.02	-85.94	81.91	0.999993
Unamended-Perlite	4.93	-78.99	88.86	0.999766
Unspiked-Perlite	26.62	-57.31	110.54	0.874156
Unamended-PJ Biochar	6.95	-76.97	90.87	0.999092
Unspiked-PJ Biochar	28.63	-55.29	112.56	0.842762
Unspiked-Unamended	21.68	-62.24	105.61	0.935412

Table A21: Corn leaf concentration data (ng/g dry leaf wt.) of target analytes for 30 leaf samples grown 28 days for the Fall 2017 corn experiment.

Uptake (ng/g)	ATZ	CBZ	FLX	SMZ	TCS
Soil No PPCPs	<MDL	<MDL	<MDL	<MDL	<MDL
	<MDL	<MDL	<MDL	<MDL	<MDL
	<MDL	<MDL	<MDL	<MDL	<MDL
Soil	<MDL	3360.0	<MDL	<MDL	98.5
	157.7	8030.7	101.1	13.9	228.0
	108.3	3478.0	25.8	19.5	193.1
Soil Perlite	184.8	6298.7	235.5	18.4	241.4
	136.6	3929.5	24.3	8.7	269.9
	<MDL	2450.1	17.7	4.6	11.0
Soil PJ	<MDL	487.9	31.8	<MDL	10.4
	<MDL	1186.9	52.7	<MDL	27.4
	<MDL	836.0	23.7	<MDL	35.4
Soil LP	1.1	1037.2	2.6	1.9	10.7
	<MDL	739.7	<MDL	1.3	5.1
	42.8	2130.2	30.3	<MDL	90.6
Sand No PPCPs	<MDL	<MDL	<MDL	<MDL	<MDL
	<MDL	<MDL	<MDL	<MDL	<MDL
	<MDL	<MDL	<MDL	<MDL	<MDL
Sand	5.0	46052.3	867.8	30.8	857.8
	45.0	38204.5	1303.8	43.7	927.0
	6.1	37571.8	555.3	25.1	1042.2
Sand Perlite	4.2	57675.9	2086.2	17.6	798.4
	9.5	71854.6	2662.3	29.6	1229.9
	13.3	42716.5	1611.7	22.3	1032.8
Sand PJ	<MDL	2873.0	54.6	<MDL	27.9
	9.4	2635.6	161.1	3.5	116.7
	<MDL	1010.3	314.7	<MDL	116.3
Sand LP	20.4	37353.5	699.3	15.1	157.7
	13.3	41778.4	1135.2	21.8	653.0
	4.7	35960.7	745.2	21.8	164.6

Table A22: Recovery of deuterated compounds in corn leaf samples for the Fall 2017 corn experiment. Standard deviation is abbreviated as Sd.

Deuterated Compounds	FLX	Sd.	GFB	Sd.	TCS	Sd.	SMZ	Sd.	ATZ	Sd.	CBZ	Sd.
RECOVERY %	73.0 %	11.4 %	8.8 %	8.7 %	72.8 %	14.0 %	42.7 %	5.9 %	70.8 %	9.5 %	86.8 %	13.4 %

Table A23: Corn leaf concentration (ng/g) significant difference tests with ANOVA for the Fall 2017 corn experiment. Shaded squares are significant ($p<0.05$).

Anova Sig. Difference	ATZ	CBZ	FLX	SMZ	TCS
Mean Comparison	Pr(>F)	Pr(>F)	Pr(>F)	Pr(>F)	Pr(>F)
Soil to Perlite	0.8100	0.7210	0.5550	0.9100	0.9930
Soil to PJ Biochar	0.1438	0.0459	0.9688	0.1247	0.0212
Soil to LP Biochar	0.2261	0.0712	0.5118	0.1525	0.0294
Soil to both biochars	0.0391	0.0081	0.4384	0.0258	0.0027
	Pr(>F)	Pr(>F)	Pr(>F)	Pr(>F)	Pr(>F)
Sand to Perlite	0.5100	0.1300	0.0316	0.1980	0.5960
Sand to PJ Biochar	0.4394	0.0000	0.0358	0.0016	0.0024
Sand to LP Biochar	0.8691	0.6971	0.9728	0.0713	0.0118
Sand to both biochars	0.3158	0.1350	0.2118	0.0152	0.0011

Table A24: Total compounds added per column for each target compound based on total volume added during the July 2018 corn experiment.

Compound:	ATZ	CBZ	FLX	SMZ	TCS
	Soil (µg)	Soil (µg)	Soil (µg)	Soil (µg)	Soil (µg)
TOTALS	629.8	646.1	1044.6	767.6	1040.8
St. Dev.	5.4	5.6	9.0	6.6	9.0
	ATZ	CBZ	FLX	SMZ	TCS
	Sand (µg)	Sand (µg)	Sand (µg)	Sand (µg)	Sand (µg)
TOTALS	1651.3	1578.4	2805.9	2174.9	2589.3
St. Dev.	14.3	13.7	24.3	18.8	22.4

Table A25: Transpiration volume (mL) and above ground biomass (dry wt.) for each corn plant in the hydroponic experiment.

Round 1	transpiration (mL)	stem/leaf dry wt. (g)
Spiked Solution	763	0.784
Spiked Solution	520	0.708
Spiked Solution	682	0.760
Nonspiked Solution	1127	2.404
Nonspiked Solution	824	1.725
Nonspiked Solution	1066	1.901
Round 2		
Spiked Solution	672	0.550
Spiked Solution	591	0.675
Nonspiked Solution	874	2.014
Nonspiked Solution	753	1.170

Table A26: Exposure concentrations (µg/L) for each corn plant which received the spiked hydroponic nutrient solution.

Compound:	ATZ	CBZ	FLX	SMZ	TCS
	µg/L	µg/L	µg/L	µg/L	µg/L
Round 1	199.7	227.8	176.5	209.7	85.7
Round 1	199.6	220.4	179.7	221.7	88.8
Round 1	194.6	216.9	164.7	230.9	82.9
Round 2	194.2	192.5	133.1	195.4	80.8
Round 2	190.0	186.2	139.9	191.0	72.0

Table A27: Recovery of deuterated compounds in corn leaf samples for the hydroponic experiment with standard deviations.

Compound:	ATZ	CBZ	FLX	SMZ	TCS
RECOVERY %	72.0%	69.1%	56.5%	60.5%	65.6%
SD	8.5%	14.7%	5.5%	8.0%	4.9%

Table A28: TSCF dimensionless ratio values for the 5 hydroponic spiked corn plants using ng/L (mass compound extracted from above ground biomass/transpiration volume) over the exposure concentration for the hydroponic solution (ng/L).

Compound:	ATZ	CBZ	FLX	SMZ	TCS
Round 1	1.6E-05	0.012	0.055	1.2E-04	9.4E-04
Round 1	6.6E-05	0.009	0.049	6.9E-05	1.6E-03
Round 1	5.1E-05	0.017	0.088	1.3E-04	1.5E-03
Round 2	1.5E-05	0.017	0.111	1.1E-04	1.1E-03
Round 2	2.3E-05	0.014	0.113	8.5E-05	1.3E-03

Table A29: Recovery of target compounds for the column sorption experiment.

	ATZ	CBZ	FLX	SMZ	TCS
Growth Media	Recovery	Recovery	Recovery	Recovery	Recovery
Soil	101.6%	102.4%	98.8%	96.5%	93.9%
Soil-LP Biochar	97.7%	96.0%	88.4%	96.6%	87.0%
Soil-PJ Biochar	103.5%	103.6%	104.3%	101.1%	97.1%
Soil-Activated Carbon	98.3%	96.5%	81.9%	95.3%	76.6%
Sand	100.1%	100.5%	92.6%	101.0%	91.0%
Sand-LP Biochar	101.1%	98.3%	93.7%	98.5%	89.8%
Sand-PJ Biochar	101.0%	102.4%	85.9%	100.4%	82.8%
Sand-Activated Carbon	100.9%	103.8%	84.5%	97.9%	77.9%

Figure A1: Setup for main corn growth/uptake experiment (Oct.-Nov. 2017).

Figure A2: Preliminary corn experiment (March 2017) with LED panels at the waterlab (UWRL).

Figure A3: Preliminary corn experiment (March 2017) with LED panels at the waterlab (UWRL).

Figure A4: 28 day corn in LP biochar amended sand (closest row) and LP biochar amended soil (row to right).

Figure A5: 28 day corn in LP biochar amended soil (closest row, 34A, 33A, 37A) and LP biochar amended sand (center row, 38A, 41A, 42A).

Figure A6: 28 day corn in LP biochar amended soil (closest row, 34A, 33A, 37A) and PJ biochar amended sand (left row, 28A, 29A, 30A).

Figure A7: 28 day corn in PJ biochar amended sand (closest row, 28A, 29A, 30A) and PJ biochar amended soil (right row, 24A, 25A, 26A)

Figure A8: 28 day corn in PJ biochar amended soil (left row, 24A, 25A, 26A) and PJ biochar amended sand (closest row, 28A, 29A, 30A).

Figure A9: 28 day corn in PJ biochar amended soil (left row, 24A, 25A, 26A) and PJ biochar amended sand (closest row, 28A, 29A, 30A).

Figure A10: 28 day corn in PJ biochar amended soil (left row, 24A, 25A, 26A) and non-amended sand (closest row, 18A, 20A, 22A).

Figure A11: 28 day corn in non-amended soil (left row, 9A, 10A, 12A) and non-amended unspiked sand (closest row, 14A, 15A, 16A).

Figure A12: 28 day corn in non-amended soil (center row, 9A, 10A, 12A) and non-amended unspiked sand (left row, 14A, 15A, 16A).

Figure A13: 28 day corn in non-amended unspiked soil (left row, 4A, 5A, 6A) and non-amended unspiked sand (right row, 14A, 15A, 16A).

Figure A14: 28 day corn in perlite amended sand (closest row, 48A, 49A, 52A) and perlite amended soil (further row on left, 44A, 46A, 47A).

Figure A15: 28 day corn in perlite amended sand (center row, 48A, 49A, 52A) and perlite amended soil (row on left, 44A, 46A, 47A).

Figure A16: Follow-up corn experiment (July-Aug. 2018) of soil (261, 262, 263) and sand (254, 255, 256).

Figure A17: Hydroponic unspiked corn (Sep. 2018).

Figure A18: Hydroponic corn experiment (Aug. 2018) of spiked corn (2 plants, front left and back left) and unspiked corn (3 plants, front right, back center, and back right).

Figure A19: Hydroponic corn experiment (Aug. 2018) of spiked corn (1 plant, right) and unspiked corn (2 plants, front left and back left).

Figure A20: Hydroponic spiked corn (Sep. 2018).

Figure A21: Hydroponic unspiked corn (Sep. 2018) and spiked corn (back).

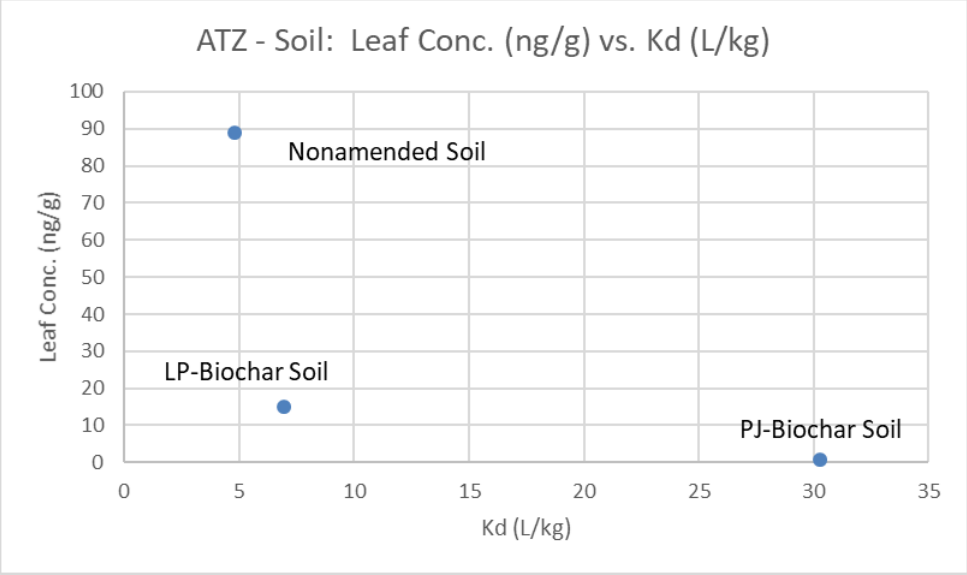


Figure A22: Scatterplot of leaf concentration vs. Kd value for atrazine in non-amended, PJ biochar amended, and LP biochar amended soil.

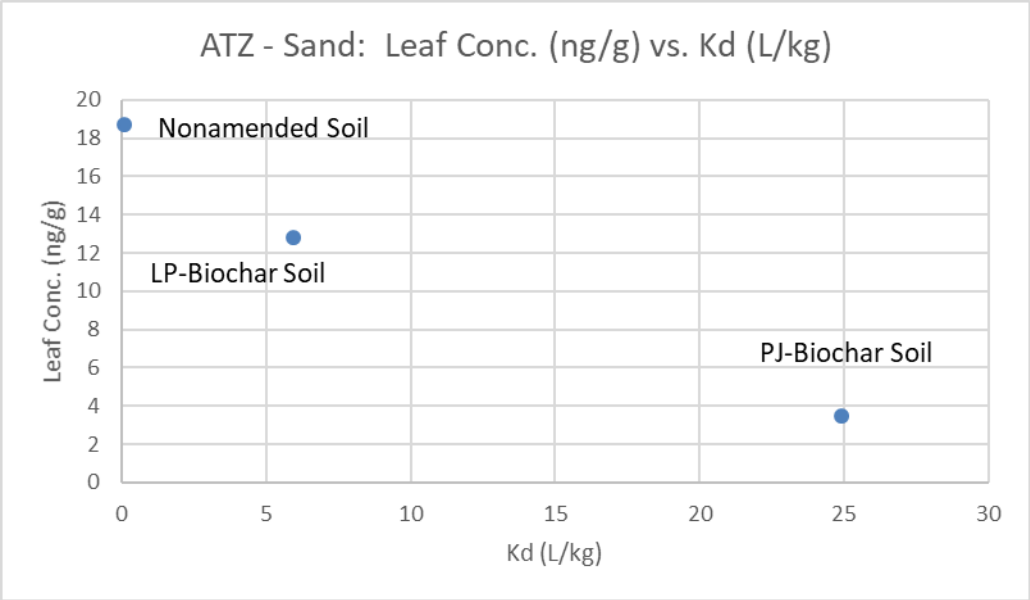


Figure A23: Scatterplot of leaf concentration vs. Kd value for atrazine in non-amended, PJ biochar amended, and LP biochar amended sand.

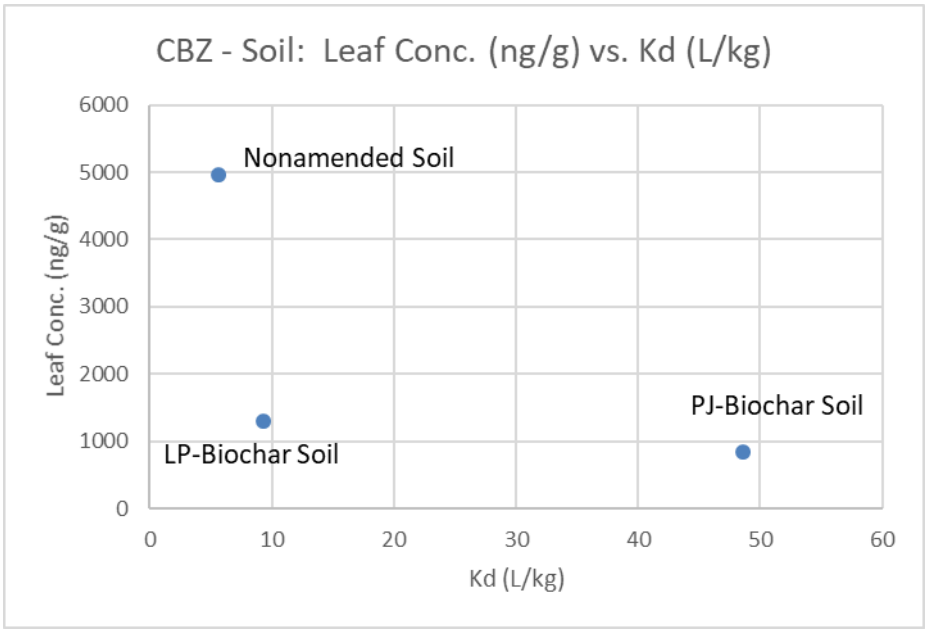


Figure A24: Scatterplot of leaf concentration vs. Kd value for carbamazepine in non-amended, PJ biochar amended, and LP biochar amended soil.

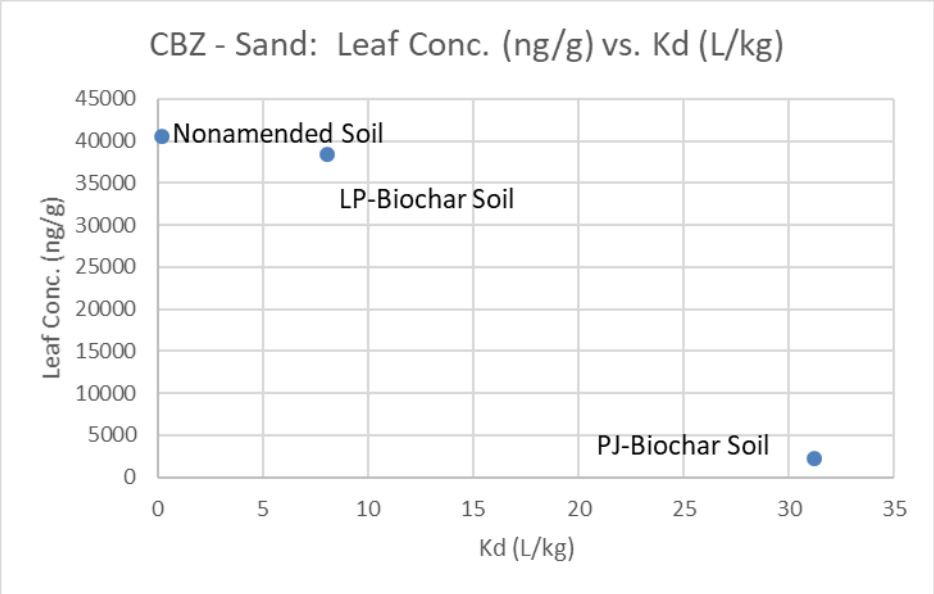


Figure A25: Scatterplot of leaf concentration vs. Kd value for carbamazepine in non-amended, PJ biochar amended, and LP biochar amended sand.

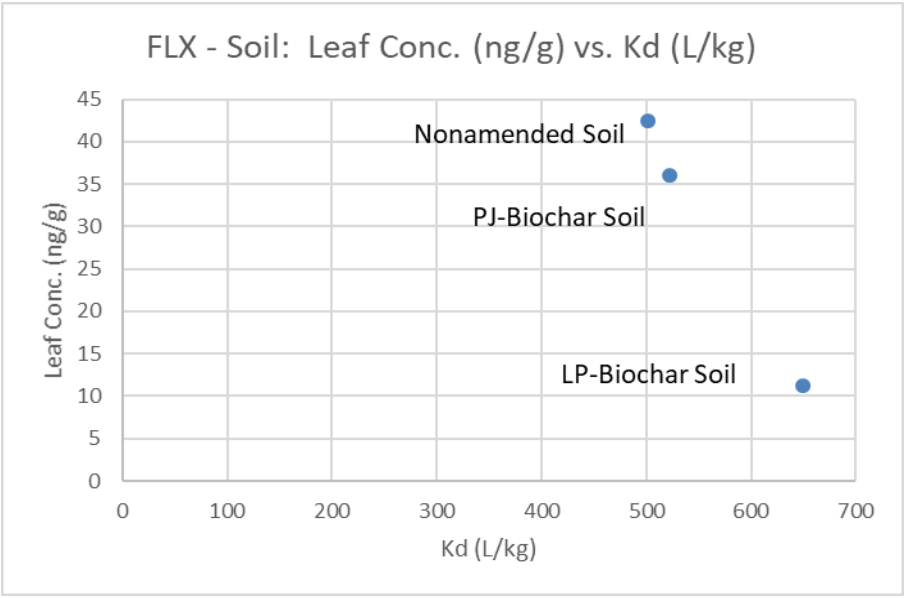


Figure A26: Scatterplot of leaf concentration vs. Kd value for fluoxetine in non-amended, PJ biochar amended, and LP biochar amended soil.

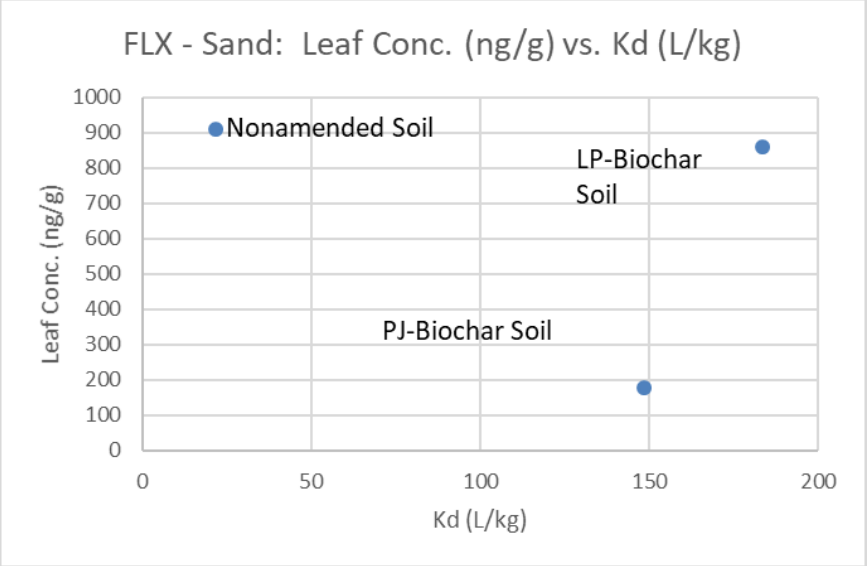


Figure A27: Scatterplot of leaf concentration vs. Kd value for fluoxetine in non-amended, PJ biochar amended, and LP biochar amended sand.

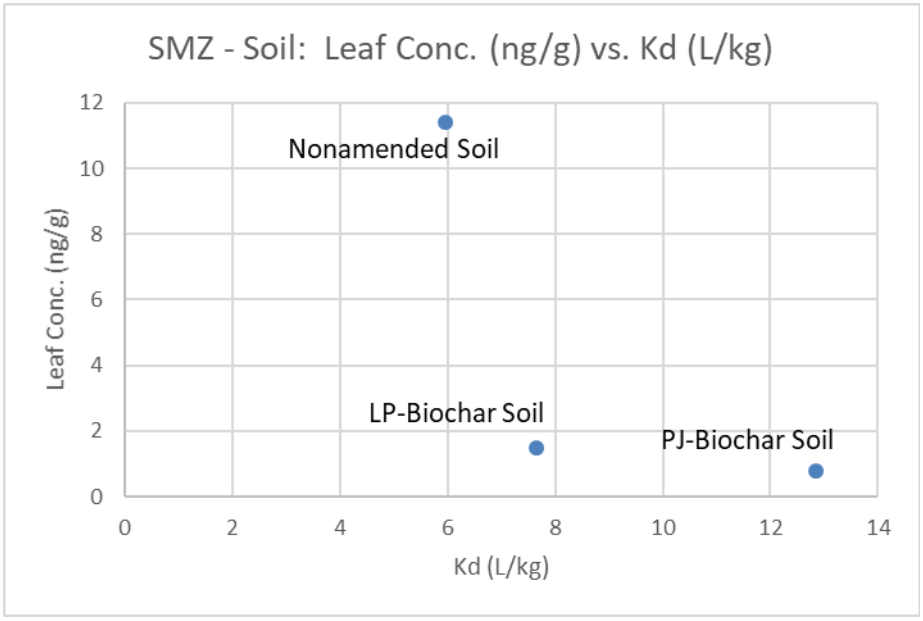


Figure A28: Scatterplot of leaf concentration vs. Kd value for sulfamethoxazole in non-amended, PJ biochar amended, and LP biochar amended soil.

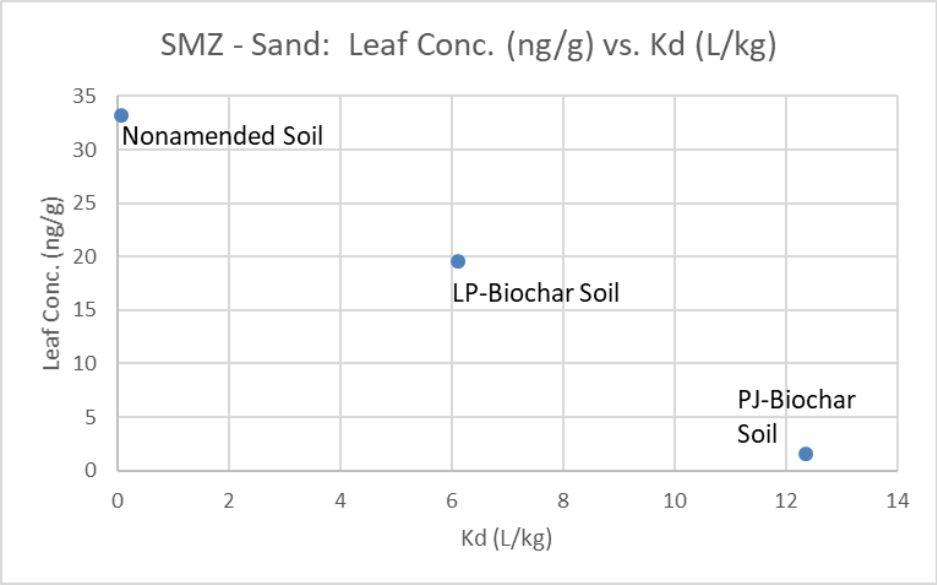


Figure A29: Scatterplot of leaf concentration vs. Kd value for sulfamethoxazole in non-amended, PJ biochar amended, and LP biochar amended sand.

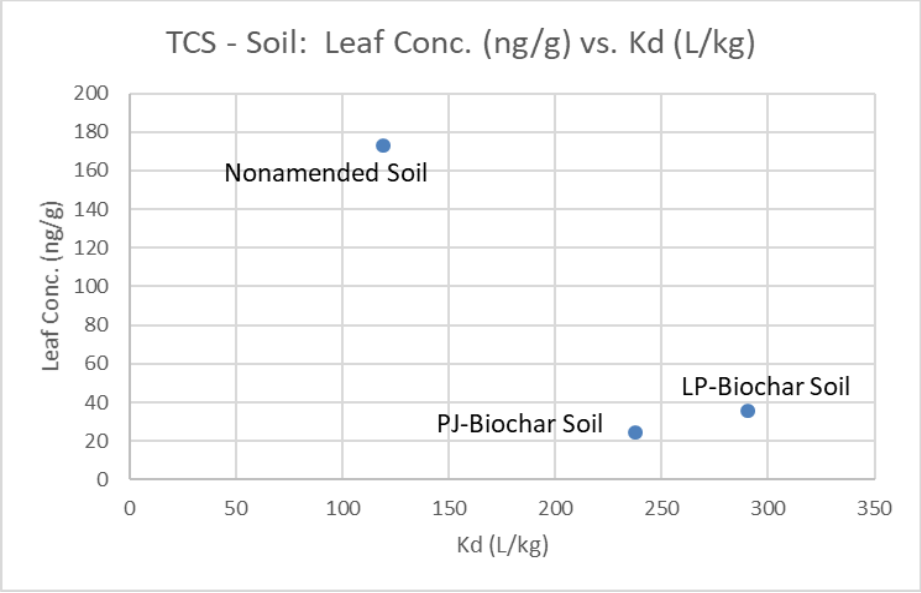


Figure A30: Scatterplot of leaf concentration vs. Kd value for triclosan in non-amended, PJ biochar amended, and LP biochar amended soil.

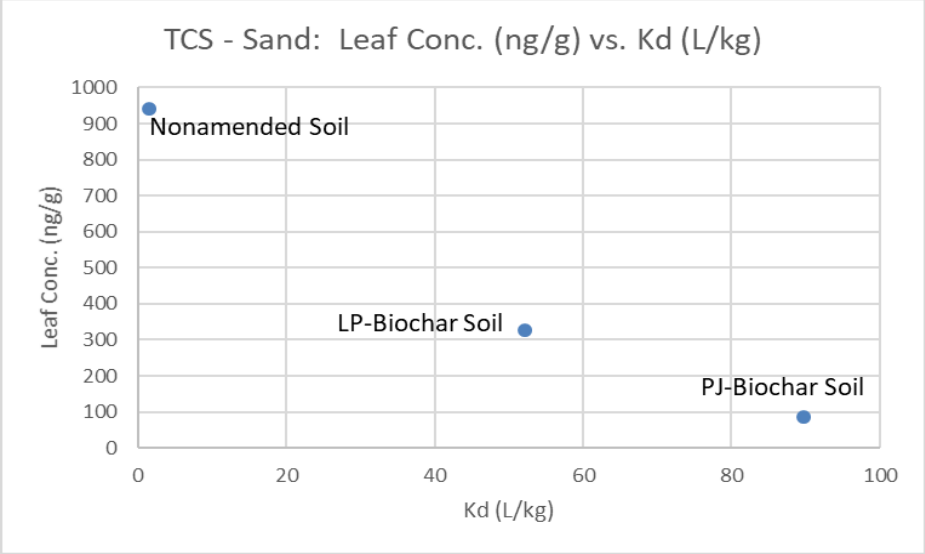


Figure A31: Scatterplot of leaf concentration vs. Kd value for triclosan in non-amended, PJ biochar amended, and LP biochar amended sand.