ATRAZINE LEACHING FROM BIOCHAR-AMENDED SOILS

A Thesis

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Master of Science

by

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ABSTRACT

The herbicide atrazine is used extensively throughout the United States for weed control, and is a widespread ground water and surface water contaminant. Biochar has been shown to strongly sorb organic compounds, and could provide a way to reduce atrazine leaching. Using lab and field experiments, we studied how biochar impacts atrazine leaching under increasingly heterogeneous soil conditions. Lab-scale soil columns dosed with biochar, atrazine, and simulated rain demonstrated that biochar application does reduce atrazine leaching. Both homogenized and undisturbed soil cores demonstrated lower atrazine leaching with biochar addition, though the increased variability in results for the undisturbed cores masked the statistical significance of this finding. We attribute increased variability to the increased complexity of the soil pore structure. Field plot treatments included biochar, acidified biochar, peat plus biochar mixture, and peat moss. Mean groundwater atrazine concentrations were 34% and 53% lower for biochar and acidified biochar plots, respectively, relative to the control plots; the acidified biochar plots were significantly lower ($p=0.0056$). Plots receiving peat plus biochar showed no reduction, indicating that organic matter may compete for biochar sorption sites. Peat moss alone had no effect on atrazine leaching. We conclude that biochar application has the potential to decrease atrazine leaching, but heterogeneous soil conditions may reduce this impact.

BIOGRAPHICAL SKETCH

Kyle Delwiche grew up in the Central Valley of California. Her interest in science and the environment started early in her life and led her to pursue a bachelor's degree in Civil and Environmental Engineering from the University of California, Berkeley. During her undergraduate years Kyle spent a summer at Cornell as part of the Research Experience for Undergraduates Program. After graduating in May 2007, Kyle went to work for Engeo Incorporated, an engineering consulting firm specializing in geotechnical and environmental engineering. At Engeo Kyle worked as a water resources engineer. She designed stormwater detention facilities for hydromodification and water quality treatment, monitored wetlands, and wrote engineering reports. In April of 2010 Kyle earned her Professional Engineers license in the state of California. Deciding her heart lay in academia, Kyle started her Master's degree at Cornell University in Biological and Environmental Engineering in the fall of 2010. After submitting this thesis she will graduate, get married, and move to Boston to start her PhD in Civil and Environmental Engineering at Massachusetts Institute of Technology.

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Table of Contents

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Pesticides are used extensively for pest and weed control in agricultural settings. While pesticides can improve crop productivity and resistance to disease, widespread use of these chemicals can lead to environmental contamination. Extensive studies conducted between 1992 and 2001 by the United States Geologic Survey detected pesticides or pesticide residues in over 90% of sampled streams and 60% of shallow groundwater taken from beneath agricultural and urban areas (Gilliom et al., 2006). Such widespread contamination raises potential concerns for human and environmental health.

Atrazine is the most commonly used herbicide in the United States and is also the most frequently detected herbicide in drinking water aquifers and shallow groundwater beneath agricultural areas (Barbash et al., 2001). Atrazine is a neutral, moderately polar organic compound based on a triazinin ring structure (Welhouse and Bleam, 1992). Using sediment samples, Sun et al., 2010, found that atrazine has a log Koc value between 1.79 and 1.95, indicating the potential for a relatively high mobility within the environment. This mobility, combined with a long half-life (3-4 months in soil), contributes to widespread atrazine contamination of water resources. Atrazine has been shown to act as an endocrine disruptor in humans (Lasserre et al., 2009). Understanding how atrazine leaches into groundwater, and identifying ways to reduce leaching rates, would represent an important gain for environmental health.

Increasing atrazine retention within the soil profile through enhanced sorption could be one way to reduce atrazine leaching to groundwater. Recent work studying potential pesticide sorbents has found that black carbon has a high affinity for sorbing organic contaminants (Accardi-Dey and Gschwend, 2003; Lohmann et al., 2005; Yang et al., 2006; Smernik, 2009). In particular, the black carbon form known as biochar readily sorbs atrazine (Cao et al., 2009; Loganathan et al., 2009; Zheng et al., 2010). The term biochar refers to the carbon rich product formed from the pyrolysis of organic matter such as wood chips, animal wastes, and crop residues (Lehmann and Joseph, 2009; Kookana et al., 2011). Biochar incorporation into soil has been shown to improve soil fertility and to sequester atmospheric carbon in relatively recalcitrant soil deposits (Glaser et al., 2002; Lehmann et al., 2006; Chan et al., 2007; Lehmann, 2007; Lal, 2008; Sohi et al., 2010). Recent studies have examined biochar's enhanced ability to sorb pesticides and have concluded that this increased sorption could potentially decrease pesticide leaching to groundwater (Spokas et al., 2009; Zheng et al., 2010).

Despite the wealth of evidence demonstrating that biochar will readily sorb pesticides, complicating factors make it difficult to predict if this sorption will translate to less atrazine entering the groundwater. One process that could influence atrazine leaching is colloid-facilitated transport, the process by which otherwise immobilized pollutants are moved through the soil profile via adsorption to mobile colloids (Gao, 1997; Flury and Qui, 2008). Biochar has been shown to contain colloidal-sized particles, which could mobilize through soil pore water flows (Zhang et al., 2010; Abiven et al., 2011,). Multiple studies have shown that aromatic black carbon (biochar-like material produced by natural wildfires) migrates downwards through the soil profile (Skjemsted et al., 1999; Dai et al., 2005; Rodionov et al., 2006). In regards to atrazine transport, one study found that 4.9% – 30% of total atrazine collected from field

lysimeters was associated with colloids (Sprague et al., 2000). Cabrera et al., 2011, found that some biochar can actually increase herbicide transport, potentially through increased mobility via dissolved organic carbon. Since atrazine can associate with colloids and biochar colloids have been shown to mobilize through soil pores, there is a possibility that biochar additions to soil could increase colloid-facilitated transport of atrazine.

Considering native soil pore structure adds additional complexity to the question of how biochar will impact pesticide leaching. Previous studies have demonstrated that preferential flow through macro-pores increases contaminant movement through the soil profile (Camobreco et al., 1996; Akhtar et al., 2003). Studies have also shown that colloid-facilitated transport is enhanced by preferential flow through soil macropores (Seta and Karathanasis, 1997; Jacobsen et al., 1997; Villholth et al., 2000). If biochar particles influence atrazine leaching via colloid-facilitated transport, we would expect this effect to be enhanced by the presence of soil macropores. The above discussion of atrazine leaching and potential contributing factors leads us to the research questions we will address in this study: 1) Can increased sorption to biochar reduce atrazine leaching?, 2) Do increasingly complex soil structures impact atrazine leaching?, and 3) Does increased facilitated transport offset any potential reduction in atrazine leaching due to biochar addition?

In order to address these questions and increase our understanding of whether or not biochar use could help mitigate atrazine leaching, we designed a series of three experiments with increasing complex soil conditions. The progression of experiments began with homogeneous, packed soil columns to study atrazine leaching in a simplified soil structure. We then used undisturbed soil cores to see if the presence of macro-pores changed biochar's impact on atrazine

leaching. Finally, we used field-scale plot treatments to determine if biochar could impact atrazine leaching in the most heterogeneous, real-world conditions. In addition to the biochar and control treatments used in the laboratory experiments, we added three additional soil treatments to the field study. These three additional treatments included an acidified biochar treatment, peat plus biochar, and peat alone. The acidified biochar treatment was chosen to determine if the biochar surface pH influenced results. The peat and peat plus biochar treatments were included to see if the organic matter content of the soil would alter any impact of biochar on atrazine leaching. Previous research suggests that soil organic matter may also sorb to biochar and could compete with atrazine for adsorption sites (Xing et al., 1996; Qiu, 2009). The peat treatment will act as a control for the peat plus biochar treatment.

CHAPTER 2

MATERIALS AND METHODS

Chemicals

The atrazine product AAtrex© Nine-O© produced by Syngenta was acquired from Cornell Farm Services. The product comes in the form of water-dispersible granules and is 88.2% atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine). The atrazine product has a pH of 8.5, a solubility in water of 33 mg/L at 20 ºC, and a specific gravity of 0.48 g/cm^3.

Biochar and Soils

We used two different batches of biochar for these experiments, both purchased from Biochar Solutions Inc. (then Biochar Engineering Corporation). We purchased a smaller batch for the homogenized soil column trials, and then a larger batch for the field experiment and undisturbed soil columns. Both batches were produced from similar feedstock of wood chips, primarily from pine trees. Biochar Solutions produces biochar for commercial sale using a proprietary, two-stage process. During the first stage, wood chip feedstock is carbonized in an oxygen-limited environment at 700-750 ºC for less than one minute. The material is then passed to the second stage where it is held in a sweep gas environment between 400-550 ºC for approximately 10-14 minutes. No oxygen is available during the second stage. We determined that the biochar used in the field experiment had a surface pH of 8.5, a nitrogen content of 0.04% and a carbon content of 88.09%.

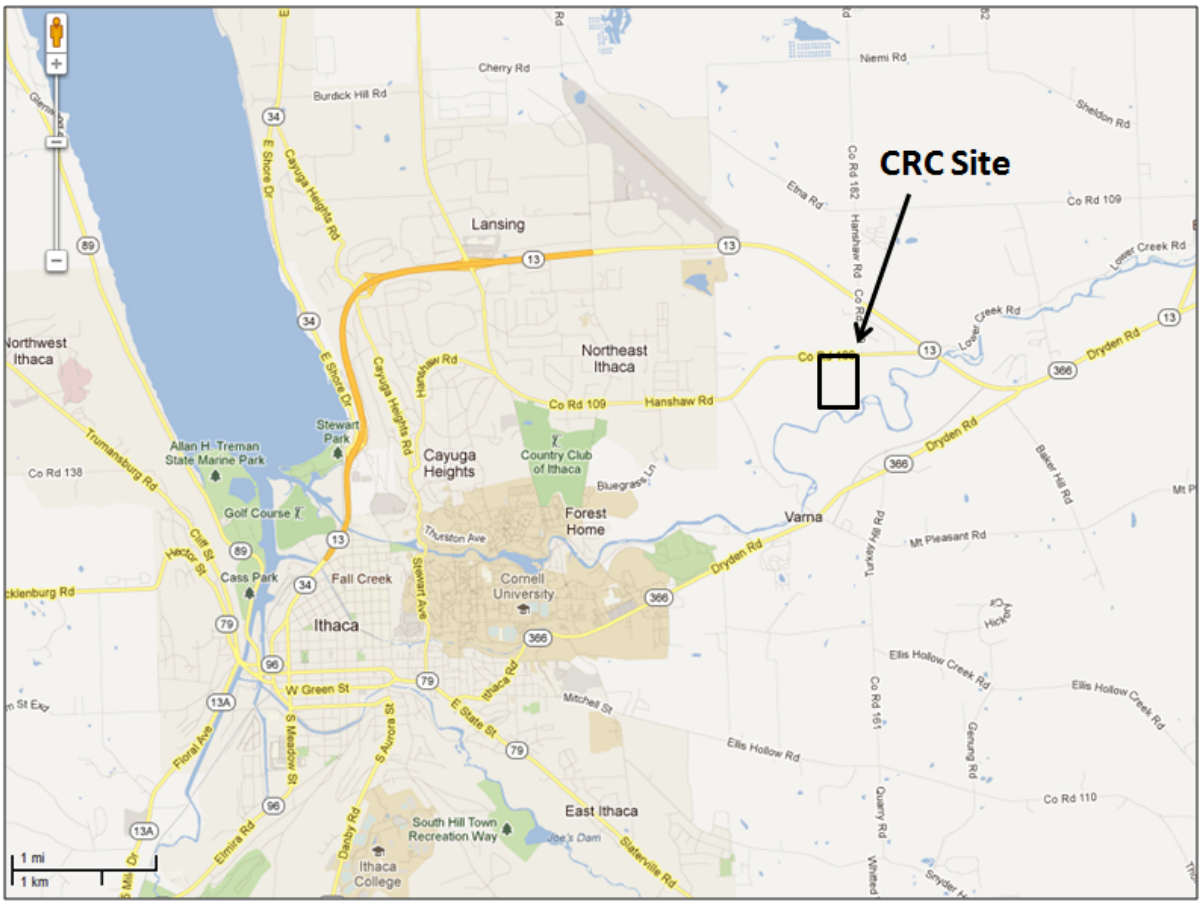

Figure 1 - Location of Cornell Recreation Center (CRC) site, the location of the biochar field plots.

The soil used for the soil column experiments came from the Cornell Recreation Center (CRC) site (Figure 1), which is also where we installed the biochar test plots. The CRC site encompasses 6.5 ha that, due to poor drainage conditions and modest soil fertility, has been historically underutilized. As part of a broader study looking at perennial grass bioenergy production, we incorporated our biochar treatment plots into a portion of the field being planted with switchgrass seeds (Figure 2). According to a detailed soil survey published by Cornell in

1966, the soils present in our treatment plots are classified as Canaseraga channery silt loam (Cline, 1966). These soils are characterized by an upper silty mantle typically between 0.45 m and 1.0 m deep. Underlying the silt mantle is a fragipan layer that extends downwards to approximately 1.5 meters, past which is a firm glacial till. The slope is generally flat, with localized depressions. Laboratory tests show that the soil pH is 5.6.

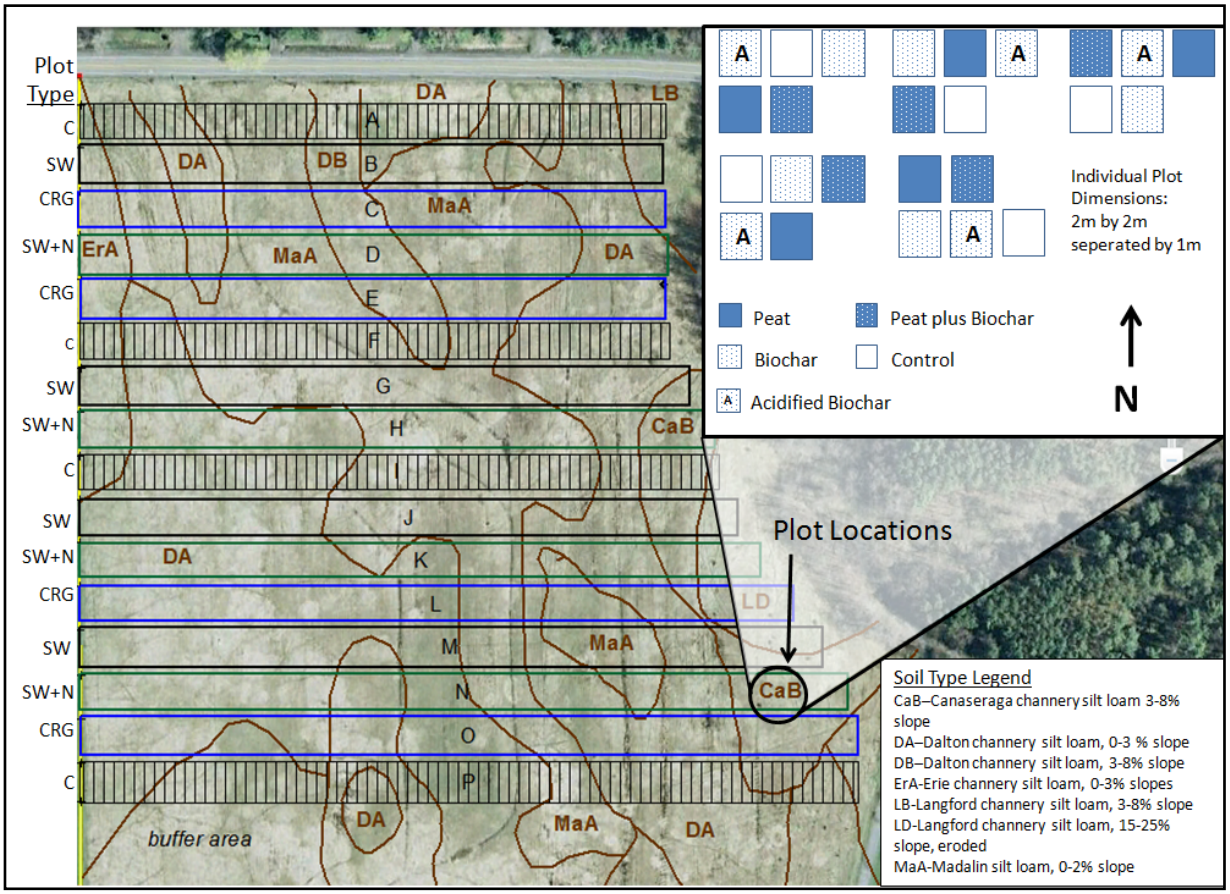

Figure 2 - Biochar plot treatment design and broader field-experiment plot layout. Column on left explains the planting design for the broader field; C = control, SW = switchgrass, SW+N = switchgrass plus nitrogen (fertilization beginning in 2012), CRG = Canary Reed Grass.

Laboratory Leaching Experiments

Homogenized Soil Columns

Soil for homogenized soil columns was extracted from the CRC field site and allowed to air dry inside the laboratory. Large soil aggregates were broken up mechanically, and soil was passed through a 2.8 mm sieve. To improve infiltration capacity, soil was mixed 50/50 by weight with industrial quartz sand. The soil/sand mixture was then loaded into 32 cm tall and 10 cm diameter PVC pipes. The soil column was capped on the bottom and perforated to allow leachate to pass through, and a 200 g quartz sand bottom layer prevented soil migration into the leachate.

Biochar surface application and control treatments were run simultaneously and in triplicate. Biochar columns were each amended with 8 g dry biochar, consistent with a field application rate of 10 T/ha. The biochar was mixed in to approximately the top 4 cm of soil. The top 4 cm of control column soil were similarly mixed for consistency. We then applied 0.85 mg atrazine dissolved in 40 mL deionized water to each column, consistent with a field application rate of 1.1 kg/hectare. Next we applied tap water at an average rate of 0.75 L/hr per column for 9 hours and periodically collected water samples from column leachate. All samples were filtered to 0.45 μm and frozen until analysis.

Undisturbed Soil Cores

We next studied the impact of soil pore structure on atrazine leaching by using undisturbed soil cores extracted from the CRC field site. These soil cores were approximately 18 cm in diameter and 30 cm long, with small variations caused by heterogeneous, rocky soil conditions. Cores were extracted from the top soil layer as described in previous research by

Camobreco et al., 2006 and Akhtar et al., 2003. Cores were stored in a temperature controlled laboratory and periodically watered prior to experimental use.

In preparation for experimental run, we drip-irrigated the soil cores until observing the onset of water seepage. Three cores were then dosed with 24.8 grams of biochar mixed into the top 7 cm of soil surface, equivalent to 10 T/ha. We also mixed the top soil in control columns for consistency. All six cores received 6.29 mg of atrazine in 50 mL of deionized water applied via spray bottle, equivalent to the 2.2 kg/hectare. We used a rainfall simulator with 23 gauge blunt nosed needles to produce artificial raindrops. Each column received artificial rain at a rate of 0.96 mL/hr and we periodically collected water samples from the leachate. Due to space constraints, we ran 2 columns at a time on three separate days (one biochar treatment and one control per day). All samples were filtered to 0.45 μm and frozen until analysis.

Field Leaching Experiments

Experimental Design

As described above, our field plots were incorporated into a broader five year study on perennial grass biofuels production in marginal farmland. For plot treatments we chose the control and biochar conditions studied in the lab. We also included three additional soil treatments to maximize the information we could glean from the field plots. These three additional soil treatments were acidified biochar, peat moss, and peat moss plus biochar. The peat moss treatments were included to study how higher organic matter in soils could affect biochar impacts on atrazine leaching. The acidified biochar treatment was included to determine if the surface pH of the biochar was a significant factor in atrazine leaching. The 5 treatments were each repeated in 5 blocks, using a randomized Latin square design to ensure the treatments

were never in the same position within each block (Figure 2). All treatments plots were 2 meters by 2 meters, separated from each other by 1 meter. Preliminary chloride tracer experiments had demonstrated minimal lateral groundwater flow between wells 1 meter apart over a 24 hour period.

Biochar Preparation

We prepared the acidified biochar by soaking biochar in a pH 1.4 solution of hydrochloric acid. After 24 hours, the acidic solution was drained and the biochar was rinsed once with tap water. The pH measurements on the rinse water indicated that the biochar surface pH had dropped from approximately 8.5 to 6.8. For consistency, the non-acidified biochar was soaked in tap water and drained after 24 hours.

Experimental Installation

Prior to the experimental installation, the field was mechanically mowed, plowed, and disced. To apply the biochar and peat moss, we hand-spread the materials across the 4 m^2 plots. Each plot received the equivalent of 4 kg of dry biochar, consistent with a loading rate of 10 T/ha. Peat moss was applied at a rate of 3.75 kg per square meter. After hand application, biochar and peat moss were raked into the top 5-10 cm of soil.

Immediately after biochar and peat moss installation, the switchgrass seeds were mechanically broadcasted across the plots. We then installed 4 shallow groundwater wells per plot for a total of 100 wells. Wells consisted of 3.8 cm diameter PVC pipe, drilled with numerous holes for the bottom ~60 cm, and wrapped in screen. We used a tractor mounted drill rig to drill 1.2 m deep holes for well installation (1.2 m being approximately sufficient to intersect the fragipan layer). Gaps in between the well and soil were packed with pea gravel and

surface-capped with bentonite clay to reduce water flow into the gravel pack. On August 4, 2011 we applied atrazine at a rate of 2.2 kg/ha using a backpack sprayer.

Sampling Methods

We collected groundwater samples at the first occasion when there was sufficient water in the majority of wells. This occurred on August 30, 2011, 48 hours after 3.8 cm of rain fell courtesy of Hurricane Irene (rainfall amounts acquired from Accuweather website). The 48 hour interval between rainfall and sampling was close enough to the 24 hour interval used in the tracer experiment that we did not expect significant lateral groundwater flow to have occurred. Samples were collected by lowering a 50 mL Teflon centrifuge tube into each well. Samples were filtered to 0.45 μm and frozen until analysis.

Soil Extractions

In addition to groundwater samples we extracted soil samples to test for residual atrazine content. The soil samples were taken in December, 2011. Samples were taken from the top 15 cm using a 2cm diameter hand-coring device. We gathered 4 samples per plot and air dried the samples in the laboratory. Samples were ground and sieved to 2 mm, and 5 grams of each were weighed into a 50 mL Teflon centrifuge tube. We then added 15 mL of 75:25 MeOH:H_2O solution and placed the tubes horizontally on a shake table. Samples were shaken for 24 hours, allowed to settle for several hours, and then filtered with 0.2 μm nylon syringe filters. A small subset of soil samples was extracted in duplicate and spiked with 5 μg of atrazine to assess extraction efficiency and precision. Duplicate tests for extractions were within 8% of each other, and spiked samples were within 4% of the expected value. Samples were stored in the refrigerator prior to analysis.

Isotherm Analysis

We conducted isotherm tests to determine the atrazine sorption affinity of the biochar. We conducted 4 types of isotherms with biochar: biochar, acidified biochar, biochar plus peat, and acidified biochar plus peat. For all isotherms, we used 25 mL of 0.1, 1, 2, 5, 10, and 20 µg/L atrazine in 0.01 M $CaCl_2$. All biochar was oven dried, ground, and sieved to 250 µm. For the biochar and acidified biochar isotherm tests we used 0.050 grams of biochar per 25 mL solution. For the peat plus biochar isotherms we used 0.050 grams biochar and 0.050 grams peat (peat ground and sieved to 250 µm). All isotherm samples were shaken horizontally for 24 hours, centrifuged, and filtered to 0.45 µm. Samples were then analyzed using the HPLC method.

We fitted the isotherms to the Freundlich model:

$$q = K_f c_{eq}^{\ N}$$

and Langmuir model:

$$q = \frac{bK_L c_{eq}}{1 + K_L c_{eq}}$$

where q is the amount sorbed, c_{eq} is the equilibrium concentration and K_F, K_L, b and N are positive adjustable parameters (N constrained to lie between 0 and 1) (Essington, 2004).

Concerned about apparent bentonite migration downwards and into water samples collected from field plots, we also conducted an isotherm analysis for atrazine and bentonite. Results are included in Appendix A.

ELISA and HPLC Measurements

Samples were analyzed using the RaPID Assay® Atrazine Test Kit available from Strategic Diagnostics (recently acquired by Modern Water). The test kit uses the principles of the enzyme linked immunosorbent assay (ELISA) method. Samples were mixed first with an enzyme conjugate and then with paramagnetic particles affixed with atrazine specific antibodies. The atrazine within the sample and the enzyme conjugate compete for binding sites on the paramagnetic particles. The paramagnetic particles are then separated from the solution using a magnetic field, and the presence of atrazine is detected by adding the enzyme substrate (hydrogen peroxide) followed by the chromogen (3,3', 5,5' tetramethylbenzinide). The resulting mixture becomes colored in response to the presence of the enzyme conjugate. Due to the initial competition for binding between the atrazine in the sample and the enzyme conjugate, a darker mixture color indicates less atrazine was present in the original sample. Samples are analyzed using a spectrophotometer at a wavelength of 450 nm and quantified by comparison to a standard curve. The ELISA lower detection limit is 0.05 µg/L and the upper limit is 5.0 µg/L. All samples above 5.0 µg/L were diluted prior to analysis with deionized water, and all samples measurements were performed in duplicate. Duplicate samples with a coefficient of variation above 10% were considered errant and re-analyzed.

Samples from the soil extraction procedure, the biochar isotherms, and a subset from the groundwater sampling were analyzed using a high performance liquid chromotograph (HPLC). We used a Shimadzu SIL-10advp injector connected to a Shimadzu SPD-10avp UV-VIS detector and a Chromolith Performance RP-18e 100-4.6mm column. Using an isocratic mobile phase of 50:50 methanol and deionized water, we were able to detect atrazine concentrations from 10 µg/L to 20,000 µg/L using a detection wavelength of 222 nm. We also conducted a comparison

between the ELISA results and HPLC results, and found that the HPLC results were within 8 ± 6 % of the ELISA results.

Statistical Analysis

Statistical analysis was conducted using the proprietary statistical software JMP® (produced by SAS Institute Inc.). If data sets failed to conform to normality assumptions, we used the nonparametric Kruskal-Wallis and Steel-Dwass methods to detect significant results within the data. For data conforming to normality assumptions, we used the standard one-way analysis of variance (ANOVA) methods. We also used JMP for linear regression and checking that model residuals met the appropriate normality assumptions. We used the free-ware program R to calculate the R^2 coefficients for the Freundlich and Langmuir models used in the isotherm analysis.

CHAPTER 3

RESULTS AND DISCUSSION

Laboratory Leaching Experiments

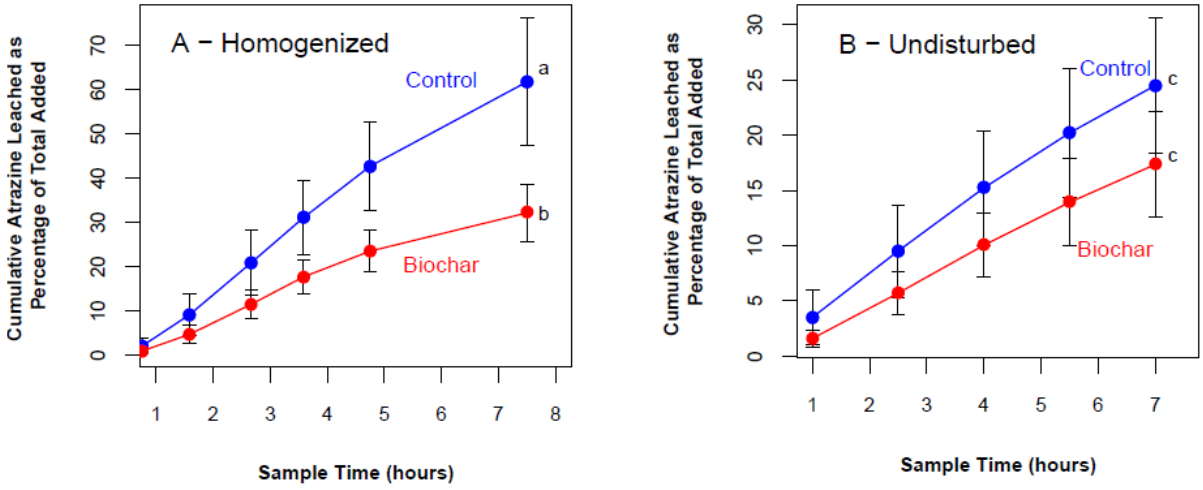

Figure 3. Average cumulative atrazine leached over time, expressed as a percentage of total atrazine added, for control and biochar-treated homogenized soil columns (A) and undisturbed soil cores (B). Error bars represent standard deviation from 3 replicates. [a,b] Statistically different, [c] Not statistically different.

Biochar amendments to homogenized soil columns resulted in significantly lower total atrazine leaching ($p=0.0298$) (Figure 3a). For all but the first two sampling events, the average atrazine concentration in the control column leachate was higher than in the biochar column leachate ($p<0.05$). The biochar columns also had a statistically lower peak atrazine concentration (Table 1, $p=0.0193$). After the peak, concentration values declined until the final sample was taken 7.5 hours after leaching began (approximately 6 L of total water leached per

column). These results indicate that in a simple, packed soil condition, biochar can reduce atrazine leaching.

Table 1 – Average peak atrazine concentration measured in leachate and cumulative leached water volume for homogenized control and biochar columns.

Column	Peak Atrazine Concentration – Homogenized Columns (μg/L)	Peak Atrazine Concentration – Undisturbed Soil Cores (μg/L)[1]
Control	140.7 ± 20.3[a]	317.5 ± 123.2
Biochar Treatment	78.3 ± 8.4[b]	204.0 ± 68.8

[1]Undisturbed soil cores were sprayed with the equivalent of 2.2 kg/ha atrazine compared to 1.1 kg/ha atrazine used in homogenized columns. [a,b] Statistically different means.

We see similar trends when comparing the undisturbed soil core results to the homogenized columns. As before, the control cores have a higher average leached atrazine amount than the biochar cores (Figure 3b). The biochar-amended cores also had a lower peak atrazine concentration in leachate (Table 1). For all cores, the atrazine concentration in the leachate dropped between all consecutive samples after the peak. The main difference between the undisturbed and homogenized data is that the difference in cumulative atrazine leached is not significant for the undisturbed cores. The addition of soil macro-pores both increases the variability in atrazine leaching and decreases the difference in average leached atrazine between treatments.

The differences between the homogenized and undisturbed columns indicate that soil macro-pore structure plays a significant role in controlling atrazine leaching. For example, one of the control cores experienced the peak atrazine concentration in leachate in the first sample

(447.6 µg/L), which was much higher than the average first value for the other two control columns (83 µg/L). This rapid leaching event could have been caused by local macro-pore structure. Previous studies have found that preferential flow through macro-pores is an important factor controlling pesticide leaching (Flury, 1996; Jarvis, 2007). In addition to the increased variability, we also see that the effect of biochar on atrazine leaching is diminished in the presence of macropores. While this could be because increased leaching via preferential flow offsets decreased leaching due to biochar, we would expect that macro-pores would increase the leaching potential in both un-amended and biochar amended columns.

Since leaching increased in biochar-amended cores compared to un-amended cores there may be an interaction effect between the biochar amendments and macropores. This could be evidence that biochar increased colloid-facilitated transport of atrazine via macropores. A study by Seta and Karathanasis, 1997, found that soil colloids increased atrazine transport 2 to 18%, and transport was greatest in soils with well-developed macro-pore systems. Authors de Jonge et al., 2000, found that in undisturbed columns, colloid-facilitated transport accounted for 1-52% of glyphosate transport. These studies demonstrate the potential for preferential flow to enhance colloid-facilitated transport. This phenomenon may explain the atrazine leaching patterns we observed between biochar-amended columns either with or without macro-pores.

Field Experiments

Groundwater Concentration and Soil Extraction Results

Table 2 – Atrazine leachate concentration for the field experiment.

Treatment	Sample Size	Mean Concentration (µg/L)
Acidified Biochar	14	36.8 ± 19.5
Biochar [a]	15	75.1 ± 64.8
Peat	18	79.4 ± 40.2
Peat plus Biochar	13	92.5 ± 36.3
Control	13	79.5 ± 37.1

[a] When omitting the two outlying data points, the sample size becomes 13 and the mean concentration is 52.0 ± 23.6µg/L.

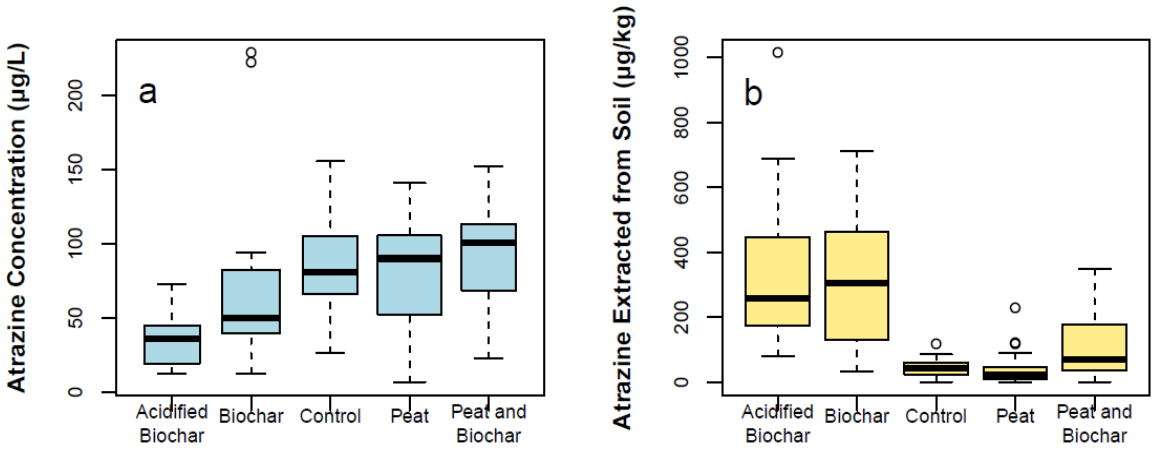

Figure 4. Atrazine concentrations in µg/L measured in groundwater samples, (a); Amount of atrazine in µg extracted per kg of soil sample, broken out by plot treatment type (b). Boxes represent the interquartile range (IQR) and whiskers extend to 1.5 times the IQR. Data marked with hollow circles fall outside 1.5 times the IQR.

During the August 30th, 2011 sampling event, 73 of the 100 wells had sufficient water for sampling (Table 2). Our analysis results indicate that the control, peat, and peat plus biochar treatments have similar atrazine concentrations in leachate (Table 2). The acidified biochar

leachate and biochar leachate both had lower atrazine concentrations. We also note the observation of two atrazine concentration outliers in the biochar treatment samples (Figure 4a). These data points are far above the third highest data point found in a control sample. These two outlying points reflect the large variation in atrazine leaching observed in undisturbed soil cores used in the laboratory experiments. As with the laboratory columns, this large variation could be attributed to local macro-pore structure that influences chemical transport processes within the soil. We will present statistical analysis with and without these outliers to maximize our ability to draw conclusions from the data.

Table 3 – P-value results for nonparametric Steel-Dwass multiple comparisons of leachate atrazine concentration between treatment pairs.

Comparison Pair	Steel-Dwass Comparisons	Steel-Dwass Comparisons Omitting Biochar Outliers[a]
Peat plus Biochar/Acidified Biochar	0.0033[b]	0.0033[b]
Control / Acidified Biochar	0.0056[b]	0.0056[b]
Peat / Acidified Biochar	0.0336[b]	0.0336[b]
Biochar/Acidified Biochar	0.1949	0.4199
Peat plus Biochar / Biochar	0.2988	0.0386[b]
Control / Biochar	0.5794	0.1423
Peat / Biochar	0.7657	0.2555
Peat plus Biochar / Peat	0.9470	0.9470
Peat plus Biochar / Control	0.9861	0.9861
Peat / Control	0.9990	0.9990

[a] Comparisons conducted omitting the 2 outlying data points in the biochar sample set (circles in Figure 4a).

[b] The means of these two treatment are significantly different ($p<0.05$).

Using the nonparametric Kruskal-Wallis method (data did not meet the normality requirements necessary to conduct an ANOVA), we found that the treatment effect was significant with or without the outliers included ($p=0.0011$ and $p=0.0002$, respectively). We then conducted multiple comparisons using the nonparametric Steel Dwass method (equivalent to the parametric Tukey HSD method) to determine which treatment pairs were different. The acidified biochar treatment is statistically different from all other treatments except the biochar treatment (Table 3). The biochar treatment itself is statistically the same as all other treatments, except peat plus biochar, when excluding the outliers.

The standard deviations around the mean concentrations (Table 2) show that there is large overall variability between samples in the same treatment group. This variability indicates that local heterogeneities within the soil structure can greatly impact the concentration of atrazine leached. We believe these heterogeneities are also responsible for the anomalously large leaching values found in the laboratory undisturbed cores and the 2 outlying samples from the biochar plots. Prior research has demonstrated the importance of micro/macro pore structure on chemical transport within the soil (Camobreco et al., 1996; Akhtar et al., 2003). The variability we observed would support the idea that atrazine transport is influenced by the local soil pore structure. This conclusion is further supported by the fact that variability increased between the homogenized and undisturbed column laboratory experiments.

Figure 4b shows that the soil extraction results are inversely related to the atrazine concentrations measured in leachate. Soil atrazine concentrations are highest for the biochar and acidified plots, the same plots that experienced the lowest average atrazine leaching. The Steel-Dwass multiple comparisons demonstrate that both the biochar and the acidified biochar plots

have significantly more atrazine in the surface soil than the control, peat, and peat plus biochar plots (Table 4). The peat plus biochar average atrazine extracted is higher than for peat and control, but this effect is not statistically significant (Table 4) and requires further investigation. These results signify that the reduction in atrazine leaching observed for the acidified biochar occurred because more of the atrazine was held within the soil profile. Recent work with C^{14} labeled simazine found that biochar-induced reduction in simazine leaching corresponded with simazine accumulation around biochar particles (Jones et al., 2011). Other studies have also found that adding biochar to soils increases pesticide concentrations near soil surface (Yu et al., 2009). Based on our results and previous studies, we attribute the observed reductions in atrazine leachate concentrations to an increased accumulation of atrazine within the soil profile.

Table 4 - P-value results from nonparametric Steel-Dwass multiple comparison results for comparisons of extracted atrazine between treatments.

Comparison Pair	Steel-Dwass Comparisons
Peat plus Biochar/Acidified Biochar	0.0008 [b]
Control / Acidified Biochar	<0.0001 [b]
Peat / Acidified Biochar	<0.0001 [b]
Biochar/Acidified Biochar	0.9999
Peat plus Biochar / Biochar	0.0108 [b]
Control / Biochar	<0.0001 [b]
Peat / Biochar	<0.0001 [b]
Peat plus Biochar / Peat	0.0611
Peat plus Biochar / Control	0.3583
Peat / Control	0.6567

[b] statistically significant difference between treatment means

Atrazine/Biochar/Peat Isotherms

The results for atrazine concentration in leachate show that acidified biochar produces a statistically significant reduction in atrazine leaching compared to control, peat, and peat plus biochar treatments (Table 3). Regular biochar does not have this statistical effect, although it does appear to have systematically reduced atrazine leaching. This leads to the question of whether the acidified biochar actually behaves differently from the regular biochar, and what might contribute to this difference. In order to gain more insight into the sorption capabilities of acidified biochar versus biochar we conducted sorption isotherms with biochar, peat, and atrazine. This isotherm study included untreated and acidified biochar, as well as untreated and acidified biochar plus peat. Results presented in Figure 5 show that the acidified biochar appears to be slightly better at sorbing atrazine than the regular biochar both with and without peat.

Table 5– Fitted Langmuir and Freundlich parameters for the biochar, acidified biochar, biochar plus peat, and acidified biochar plus peat isotherms.

		Biochar		Acidified Biochar		Biochar Plus Peat		Acidified Biochar Plus Peat	
Model	Parameter	Value	R^2	Value	R^2	Value	R^2	Value	R^2
Freundlich	K_f (μg/mg)(L/mg)^N	0.777	0.966	1.402	0.956	0.958	0.983	1.131	0.983
	N	0.749		0.553		0.538		0.500	
Langmuir	K_L (L/mg)	0.016	0.964	0.069	0.940	0.130	0.944	0.176	0.928
	b (μg/mg)	30.78		12.59		6.26		6.00	

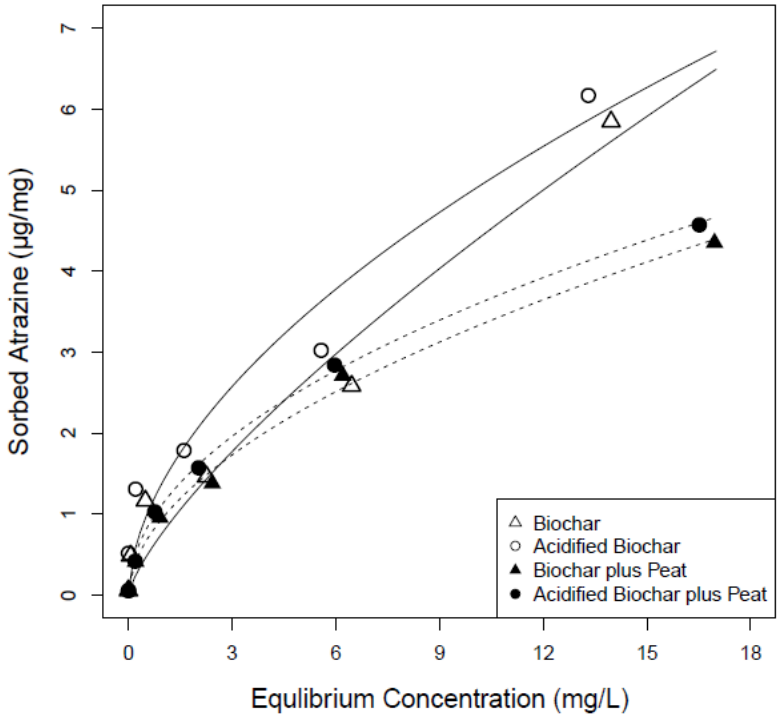

Figure 5. Sorption isotherms for biochar (hollow triangle), acidified biochar (hollow circle), biochar plus peat (triangle), and acidified biochar plus peat (circle) showing sorbed atrazine in µg/mg versus equilibrium concentration (mg/L). Plotted lines are derived from the Freundlich model with dashed lines for isotherms with peat and solid lines for isotherms without peat (model values in Table 5).

We note that while the data have a high degree of correlation with the model predictions (see R^2 values in Table 5), close examination of Figure 5 shows that there may be evidence for dual-mode sorption behavior in the isotherms without peat. Specifically, data appears to follow a non-linear trend at low concentrations, transitioning to an apparently linear trend at higher concentrations. Previous studies have shown similar sorption patterns for organic compounds and have attributed this phenomenon to adsorption-dominated sorption at low equilibrium concentrations and partitioning-dominated sorption at high equilibrium concentrations (Xing et al., 1996; Chiou et al., 1998; Chen et al., 2008). More work would be needed to determine if this

dual-sorption phenomenon is occurring. The increases in sorption capacity for the acidified biochar relative to the untreated biochar are consistent with our field results; i.e., the lower atrazine concentrations in the acidified biochar plot samples relative to the untreated biochar plot samples.

Both the atrazine concentration in field samples and the isotherm analysis indicate that the acidified biochar treatment may sorb atrazine more effectively than the regular biochar. The exact mechanism for this enhanced adsorption is still unknown, but one possibility is that biochar surface impurities that could reduce microporosity were removed during the acidification step. Jia et al., 2008, used a scanning electron micrograph to show that some char surfaces were covered in tar-like deposits. Another study by Lozano-Castello et al., 2001, found that washing pyrolyzed anthracite in HCl reduces ash content from 7% wt to < 1% wt and increases micropore volume. It is possible that the biochar acidification step removed surface impurities and therefore exposed more micropores to atrazine sorption. Further work is needed to determine the exact sorption mechanisms.

Peat Moss Effect

The field data show that average leachate concentration for the peat plus biochar treatments is similar to the control treatments, and apparently higher than the biochar treatments. Peat moss alone is not statistically different than the control group, indicating that it's affinity for sorbing atrazine is not significantly higher than the native soil. The soil extraction results show that adding peat to biochar-amended soil will significantly reduce the amount of atrazine retained in the soil profile. The leachate and extraction results show that the peat plus biochar plots had both lower atrazine retention in the soil surface and higher atrazine concentration in leachate

compared to control. Additionally, the isotherm results (Figure 5) show that adding peat to biochar increases the amount of atrazine in solution.

These results are consistent with the hypothesis that the peat moss is impeding biochar's ability to sorb atrazine. This hypothesis is supported by previous studies showing that the presence of organic matter in soils can decrease biochar sorption of organic compounds (Pignatello et al., 2006; Qiu et al., 2009). Pignatello et al. found evidence that humic substances reduce organic compound sorption to char by either blocking access to char micropores or competing for char surface adsorption sites. Qiu et al. also found evidence that dissolved organic matter blocks biochar micropores and decreases pesticide sorption. Our results are consistent with either organic-matter induced pore-blocking or sorption competition between organic matter and atrazine. We therefore assume that the effects of biochar on atrazine leaching will be less pronounced in soils with naturally high organic matter contents.

CHAPTER 4

CONCLUSIONS

We conclude that biochar use as a soil amendment may reduce atrazine leaching. This effect appears to depend significantly on heterogeneous soil pore structure. In homogenized soil we see a reduction in atrazine leaching with biochar use. Adding complexity in the soil pore structure increases variation and reduces the difference in atrazine leaching between biochar and control experiments. Anomalously large leaching events appear to occur irrespective of soil treatment, indicating that localized soil structure heterogeneities could play a dominant role in causing rare, large leaching events. Even with soil heterogeneities, it appears that biochar acidified prior to soil application can significantly reduce atrazine concentrations in leachate. More work is needed to quantify the amount of atrazine leached from biochar-amended fields to determine if the reduced leaching is significant enough to reduce groundwater contamination levels. Continuing to gather water samples in future years from these plots will provide important information on how biochar aging affects atrazine leaching, and whether trends observed in the first year will be maintained in subsequent years.

APPENDIX A – Bentonite Clay Isotherms

Upon collecting and filtering the samples, we noted that many of the samples contained a clay-like substance that we assumed to be the bentonite clay used to cap the wells. Upon closer inspection of the wells, we determined that some of the bentonite from the surface cap had migrated downwards through the gravel surrounding the wells, and had potentially entered the water samples. Concerned about bentonite's potential ability to sorb atrazine and interfere with our samples, we conducted a 24 hour bentonite/atrazine sorption isotherm test. Bentonite isotherms were conducted in duplicate using 0.5 grams of dry bentonite powder mixed with 25 mL of varying concentrations of atrazine (10, 50, 100, 300, and 1,000 µg/L atrazine in 0.01 M CaCl2). Samples were shaken horizontally for 24 hours, centrifuged, and filtered to 0.45 µm.

The results of this test show an essentially linear isotherm over relevant atrazine concentrations (Figure 6). Based on these data we assume that the presence of bentonite has some ability to sorb atrazine, potentially changing the atrazine concentrations in our samples. We approximated the quantity of clay in each sample, and grouped our samples into low to high categories. Water samples with very low clay amounts had lower atrazine concentrations than samples with either a medium or high amount of clay ($p < 0.0001$ and $p=0.0027$, respectively). This result indicates that even though bentonite is capable of sorbing some atrazine, samples with increased bentonite still had more atrazine than those with low concentration. The presence of bentonite might therefore be indicative of soil conditions that increase transport of material from the soil surface to the subsurface. Specifically, this transport could occur through soil macropores, or potentially through the gravel casing around the well. We used linear regression

to model atrazine concentration as a function of clay content category and soil treatment. When accounting for clay in the samples and removing the outliers, the soil treatment still had a significant effect on leachate atrazine concentrations (p=0.0138). We therefore assume that while the presence of clay may be indicative of local transport processes, our results regarding treatment effect on atrazine leaching are still valid. Prior to the onset of the winter season, the remaining bentonite caps were removed and replaced with native soil to limit future bentonite migration into samples.

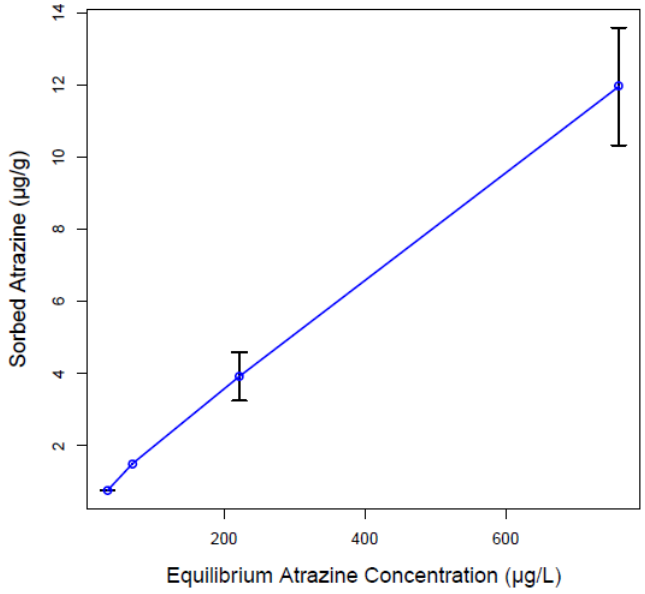

Figure 6. Bentonite and atrazine sorption isotherm. Horizontal axis represents equilibrium atrazine concentration in µg/L and vertical axis represents amount of atrazine sorbed to bentonite in µg/g. Error bars are standard deviation from two samples.

APPENDIX B – Data

Table 6 - Data from Homogenized Soil Column Experiment

Column	Treatment	Sample Time (hours)	Atrazine Concentration (µg/L)	Cumulative Leached Water Volume (L)
1	Control	0.75	79.13	0.8
1	Control	1.58	127.86	1.5
1	Control	2.67	125.27	2.4
1	Control	3.58	93.38	3.2
1	Control	4.75	81.27	4.2
1	Control	7.50	33.93	6.4
2	Control	0.75	7.66	0.6
2	Control	1.58	92.91	1.1
2	Control	2.67	133.04	1.8
2	Control	3.58	127.35	2.4
2	Control	4.75	99.09	3.2
2	Control	7.50	63.24	5.0
3	Biochar	0.75	44.47	0.9
3	Biochar	1.58	102.58	1.6
3	Biochar	2.67	75.39	2.4
3	Biochar	3.58	64.13	3.1
3	Biochar	4.75	61.68	4.1
3	Biochar	7.50	19.96	6.3
4	Control	0.75	106.20	1.0
4	Control	1.58	144.46	1.6
4	Control	2.67	163.71	2.4
4	Control	3.58	101.17	3.1
4	Control	4.75	156.19	4.0
4	Control	7.50	29.56	6.3
5	Biochar	0.75	32.73	1.0
5	Biochar	1.58	59.81	1.5
5	Biochar	2.67	71.70	2.3
5	Biochar	3.58	46.46	3.1
5	Biochar	4.75	34.26	4.1
5	Biochar	7.50	18.80	6.3
6	Biochar	0.75	19.73	0.7
6	Biochar	1.58	52.35	1.3
6	Biochar	2.67	87.68	2.0

6	Biochar	3.58	52.21	2.8
6	Biochar	4.75	46.44	3.7
6	Biochar	7.50	23.52	5.8

Table 7 – Data from Undisturbed Soil Column Experiment

Column	Treatment	Sample Time (hours)	Atrazine Concentration (µg/L)	Cumulative Leached Water Volume (L)
1	Control	0	447.62	0.00
1	Control	1	371.34	0.96
1	Control	2.5	310.02	2.40
1	Control	4	231.28	3.84
1	Control	5.5	179.51	5.28
1	Control	7	126.65	6.72
2	Biochar	0	39.78	0.00
2	Biochar	1	157.46	0.96
2	Biochar	2.5	142.55	2.40
2	Biochar	4	141.98	3.84
2	Biochar	5.5	121.69	5.28
2	Biochar	7	95.99	6.72
3	Control	0	106.73	0.00
3	Control	1	276.39	0.96
3	Control	2.5	302.30	2.40
3	Control	4	253.80	3.84
3	Control	5.5	246.49	5.28
3	Control	7	199.74	6.72
4	Biochar	0	71.84	0.00
4	Biochar	1	243.66	0.96
4	Biochar	2.5	283.01	2.40
4	Biochar	4	234.56	3.84
4	Biochar	5.5	189.54	5.28
4	Biochar	7	176.40	6.72
5	Control	0	60.52	0.00
5	Control	1	115.15	0.96
5	Control	2.5	198.22	2.40
5	Control	4	202.52	3.84
5	Control	5.5	192.28	5.28
5	Control	7	183.08	6.72
6	Biochar	0	25.10	0.00
6	Biochar	1	87.25	0.96
6	Biochar	2.5	162.89	2.40

6	Biochar	4	171.53	3.84
6	Biochar	5.5	159.54	5.28
6	Biochar	7	155.49	6.72

Table 8 - Atrazine Concentrations in Groundwater Samples Collected From Field Plots

Block	Treatment	Well ID	Atrazine Concentration (µg/L)	Water Height Within Well (cm)	Approximate Clay Concentration Within Water Sample (mg/mL)
1	Acidified Biochar	A1	25.26	2.1	0
1	Acidified Biochar	A2	15.09	0.8	0
1	Acidified Biochar	A3	44.97	0.7	0
1	Acidified Biochar	A4	12.58	0.1	0
1	Control	B1	66.05	0.3	0
1	Control	B2	35.45	1.6	0
1	Control	B3	56.17	0.4	0
1	Control	B4	26.37	0.5	0
1	Biochar	C1	90.08	1.4	3.36
1	Biochar	C2	12.26	0.9	0
1	Biochar	C3	50.11	0.6	0
1	Biochar	C4	35.07	0.2	0
1	Peat	D1	105.51	1.1	6.45
1	Peat	D2	140.77	-	13.85
1	Peat	D3	99.12	1.4	2
1	Peat	D4	85.10	1.1	0
1	Peat/Biochar	E1	108.46	0.5	0
1	Peat/Biochar	E2	48.39	0.0	0
1	Peat/Biochar	E3	-	0.3	0
1	Peat/Biochar	E4	-	-	-
2	Biochar	F1	37.91	0.4	0
2	Biochar	F2	44.34	0.3	0
2	Biochar	F3	74.40	0.6	0
2	Biochar	F4	31.04	0.8	0
2	Peat	G1	29.55	0.5	0
2	Peat	G2	103.59	2.3	0
2	Peat	G3	13.23	1.8	0
2	Peat	G4	65.59	0.4	12.15
2	Acidified Biochar	H1	17.37	0.7	0
2	Acidified Biochar	H2	73.07	0.9	3.9
2	Acidified Biochar	H3	34.94	0.0	0

Table 8 - Continued

2	Acidified Biochar	H4	39.66	0.4	0
2	Peat/Biochar	I1	68.51	1.5	5.85
2	Peat/Biochar	I2	84.58	1.0	0
2	Peat/Biochar	I3	63.58	1.0	2.95
2	Peat/Biochar	I4	113.37	0.6	5.15
2	Control	J1	105.42	0.1	0
2	Control	J2	133.33	0.1	26.5
2	Control	J3	155.55	1.8	5.45
2	Control	J4	73.46	0.7	10.05
3	Peat/Biochar	K1	-	-	-
3	Peat/Biochar	K2	-	-	-
3	Peat/Biochar	K3	22.76	1.5	1.95
3	Peat/Biochar	K4	113.79	0.9	8
3	Acidified Biochar	L1	19.35	0.0	0
3	Acidified Biochar	L2	-	-	-
3	Acidified Biochar	L3	25.29	0.9	0
3	Acidified Biochar	L4	-	-	-
3	Peat	M1	27.86	0.3	0
3	Peat	M2	114.55	0.8	3.95
3	Peat	M3	-	-	-
3	Peat	M4	-	-	-
3	Control	N1	101.55	0.1	13.35
3	Control	N2	-	-	-
3	Control	N3	-	-	-
3	Control	N4	119.90	0.4	19.55
3	Biochar	O1	228.39	0.1	18.9
3	Biochar	O2	67.40	0.3	15.1
3	Biochar	O3	222.33	0.5	15.25
3	Biochar	O4	-	-	-
4	Control	P1	80.65	0.8	3.35
4	Control	P2	81.04	1.3	5.3
4	Control	P3	77.70	0.6	1.1
4	Control	P4	-	0.6	8.55
4	Biochar	Q1	45.10	0.8	0
4	Biochar	Q2	52.67	0.7	0
4	Biochar	Q3	41.07	0.3	31.2
4	Biochar	Q4	-	-	-
4	Peat/Biochar	R1	139.92	0.5	21.3
4	Peat/Biochar	R2	-	-	-
4	Peat/Biochar	R3	-	-	-
4	Peat/Biochar	R4	-	-	-
4	Acidified Biochar	S1	42.58	0.9	4.5
4	Acidified Biochar	S2	37.00	0.3	0

Table 8 - Continued

4	Acidified Biochar	S3	58.52	0.2	0
4	Acidified Biochar	S4	68.92	0.9	7.5
4	Peat	T1	74.83	1.0	3.45
4	Peat	T2	52.31	0.8	7.8
4	Peat	T3	114.93	1.3	5.55
4	Peat	T4	6.69	0.0	0
5	Peat	U1	100.91	0.4	15
5	Peat	U2	133.42	0.5	9.15
5	Peat	U3	66.03	0.3	9
5	Peat	U4	94.97	1.3	5
5	Peat/Biochar	V1	100.51	0.1	38.2
5	Peat/Biochar	V2	108.92	0.1	0
5	Peat/Biochar	V3	78.11	0.2	21.25
5	Peat/Biochar	V4	152.20	0.2	18
5	Biochar	W1	-	-	-
5	Biochar	W2	-	-	-
5	Biochar	W3	94.24	0.3	20
5	Biochar	W4	-	0.2	19.58
5	Acidified Biochar	X1	-	-	-
5	Acidified Biochar	X2	-	0.3	18.9
5	Acidified Biochar	X3	-	0.2	4.75
5	Acidified Biochar	X4	-	-	-
5	Control	Y1	-	0.1	21.6
5	Control	Y2	-	-	-
5	Control	Y3	-	-	-
5	Control	Y4	-	0.0	9.55

Table 9 - Atrazine Extracted from Field Soil Samples

Block	Plot Treatment	Sample Location ID	Measured Atrazine Concentration in Extract (µg/L)	Atrazine Extracted from Soil Sample (µg atrazine/g soil)
1	Acidified Biochar	A1	29.83	0.09
1	Acidified Biochar	A2	128.83	0.39
1	Acidified Biochar	A3	26.36	0.08
1	Acidified Biochar	A4	60.37	0.18
1	Control	B1	11.85	0.04
1	Control	B2	21.91	0.07
1	Control	B3	14.28	0.04

Table 9 - Continued

1	Control	B4	19.31	0.06
1	Biochar	C1	146.03	0.44
1	Biochar	C2	71.94	0.22
1	Biochar	C3	13.34	0.04
1	Biochar	C4	96.06	0.29
1	Peat	D1	0.00	0.00
1	Peat	D2	29.65	0.09
1	Peat	D3	15.49	0.05
1	Peat	D4	10.16	0.03
1	Peat/Biochar	E1	60.21	0.18
1	Peat/Biochar	E2	113.94	0.34
1	Peat/Biochar	E3	25.13	0.08
1	Peat/Biochar	E4	52.21	0.16
2	Biochar	F1	104.08	0.31
2	Biochar	F2	112.65	0.34
2	Biochar	F3	203.98	0.61
2	Biochar	F4	162.33	0.49
2	Peat	G1	14.93	0.04
2	Peat	G2	8.46	0.03
2	Peat	G3	14.32	0.04
2	Peat	G4	5.64	0.02
2	Acidified Biochar	H1	87.76	0.26
2	Acidified Biochar	H2	145.65	0.44
2	Acidified Biochar	H3	66.56	0.20
2	Acidified Biochar	H4	168.70	0.51
2	Peat/Biochar	I1	16.69	0.05
2	Peat/Biochar	I2	5.08	0.02
2	Peat/Biochar	I3	116.52	0.35
2	Peat/Biochar	I4	18.03	0.05
2	Control	J1	12.70	0.04
2	Control	J2	38.67	0.12
2	Control	J3	27.32	0.08
2	Control	J4	18.18	0.05
3	Peat/Biochar	K1	0.07	0.00
3	Peat/Biochar	K2	8.40	0.03
3	Peat/Biochar	K3	24.94	0.07
3	Peat/Biochar	K4	20.75	0.06
3	Acidified Biochar	L1	337.77	1.01
3	Acidified Biochar	L2	55.49	0.17
3	Acidified Biochar	L3	229.25	0.69
3	Acidified Biochar	L4	56.42	0.17
3	Peat	M1	39.60	0.12
3	Peat	M2	75.48	0.23

Table 9 - Continued

3	Peat	M3	7.13	0.02
3	Peat	M4	0.07	0.00
3	Control	N1	11.93	0.04
3	Control	N2	19.32	0.06
3	Control	N3	28.55	0.09
3	Control	N4	13.73	0.04
3	Biochar	O1	39.02	0.12
3	Biochar	O2	48.71	0.15
3	Biochar	O3	180.72	0.54
3	Biochar	O4	141.80	0.43
4	Control	P1	19.67	0.06
4	Control	P2	6.66	0.02
4	Control	P3	20.44	0.06
4	Control	P4	6.70	0.02
4	Biochar	Q1	237.60	0.71
4	Biochar	Q2	100.08	0.30
4	Biochar	Q3	11.22	0.03
4	Biochar	Q4	129.33	0.39
4	Peat/Biochar	R1	44.71	0.13
4	Peat/Biochar	R2	11.18	0.03
4	Peat/Biochar	R3	59.06	0.18
4	Peat/Biochar	R4	18.19	0.05
4	Acidified Biochar	S1	55.00	0.16
4	Acidified Biochar	S2	67.69	0.20
4	Acidified Biochar	S3	152.30	0.46
4	Acidified Biochar	S4	134.86	0.40
4	Peat	T1	0.00	0.00
4	Peat	T2	39.70	0.12
4	Peat	T3	0.00	0.00
4	Peat	T4	0.00	0.00
5	Peat	U1	6.68	0.02
5	Peat	U2	5.85	0.02
5	Peat	U3	6.47	0.02
5	Peat	U4	8.52	0.03
5	Peat/Biochar	V1	0.00	0.00
5	Peat/Biochar	V2	60.82	0.18
5	Peat/Biochar	V3	77.64	0.23
5	Peat/Biochar	V4	12.42	0.04
5	Biochar	W1	31.55	0.09
5	Biochar	W2	58.53	0.18
5	Biochar	W3	193.26	0.58
5	Biochar	W4	20.18	0.06
5	Acidified Biochar	X1	192.91	0.58

Table 9 - Continued

5	Acidified Biochar	X2	84.82	0.25
5	Acidified Biochar	X3	122.97	0.37
5	Acidified Biochar	X4	58.77	0.18
5	Control	Y1	9.14	0.03
5	Control	Y2	0.00	0.00
5	Control	Y3	6.47	0.02
5	Control	Y4	0.00	0.00

Table 10 - Data from atrazine/biochar isotherm study.

	Equilibrium Atrazine Concentration (µg/L) for:			
Initial Atrazine Concentration (µg/L)	Regular Biochar	Acidified Biochar	Regular Biochar + Peat	Acidified Biochar + Peat
100	0.00	0.00	11.09	7.36
100	0.00	0.00	8.98	6.69
100	0.00	0.00	13.52	10.37
1,000	62.58	16.00	193.07	141.59
1,000	57.22	5.62	230.51	210.59
1,000	78.56	12.51	211.32	225.81
2,000	410.84	185.90	1167.32	773.41
2,000	588.12	218.30	676.35	694.31
2,000	475.23	217.58	893.96	822.32
5,000	2410.27	1652.56	2488.92	2109.16
5,000	2181.50	1686.93	2441.82	1893.79
5,000	2190.34	1503.01	2344.29	2092.17
10,000	6506.53	5422.63	5713.40	6027.02
10,000	6472.77	5591.32	6088.17	5819.79
10,000	6399.09	5734.90	6790.77	6023.52
20,000	13709.18	13559.41	18537.76	15834.05
20,000	14298.56	13592.66	16718.17	17258.34
20,000	13876.72	12752.85	15605.01	16451.97

Table 11 - Results from atrazine/bentonite isotherm study

Initial Atrazine Concentration (µg/L)	Equilibrium Atrazine Concentration (µg/L)
0	0.83
0	0.48
50	34.47
50	34.88
100	69.99
100	69.87
300	212.10
300	231.06
1,000	737.67
1,000	783.76

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