SORPTION-DESORPTION, LEACHING, AND BIOVAILABILITY OF
AMINOCYCLOPYRACHLOR AND INDAZIFLAM IN MINNESOTA SOILS

A Thesis
SUBMITTED TO THE FACULTY OF
UNIVERSITY OF MINNESOTA
BY

Jennifer L. Rittenhouse

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
MASTER OF SCIENCE

Pamela Rice

February 2015

Acknowledgements

I would like to acknowledge my committee members Drs. Pamela Rice, Kurt Spokas, and Jeffrey Gunsolus for their patience and guidance with this research. Special thanks to Dr. William Koskinen for sharing his time, laboratory, and wealth of knowledge on chemical analysis of pesticides. The good fortune of having these four scientists and their varying research expertise on my team has helped me strengthen my approach to problem-solving. This skill will last me a lifetime.

The master of all problem-solving is Brian Barber who graciously gave of his time to troubleshoot and maintain laboratory equipment used in this research, for which I am very grateful. Additional laboratory assistance and morale boosting was provided by Kate Hall. The steadfast attitudes and diligence demonstrated by these individuals are remarkable and I cannot thank them enough for their help.

Lastly I want to thank Kevin Hamlin, my soon-to-be husband. Kevin endured reading and re-reading nearly every draft of my thesis and was always willing to make a late night food run. His patience and understanding throughout this process have been inspiring.

Dedication

I dedicate this thesis in loving memory of my grandmother, Ethel Johnson.

Abstract

Knowledge of the environmental fate of pesticides is important for practical application and regulatory purposes, to enhance product efficacy and maintain environmental quality. Sorption-desorption of pesticides on soil influence their bioavailability and mobility and are important input parameters for environmental fate and transport models. Limited information on the sorption-desorption of aminocyclopyrachlor and indaziflam is available in the scientific literature. Sorption coefficients (K_d and K_{oc}) of these herbicides in surface and subsurface soils were determined for three locations in Minnesota, USA, and predictions for their off-site transport were established using Groundwater Ubiquity Scores. I observed that indaziflam moderately sorbed to these soils with greater sorption in the surface soil, hysteretic desorption and moderate leaching potential. Aminocyclopyrachlor sorption was low for all soils, desorption was hysteretic and the leaching potential was classified as high to very high, which prompted follow up research in attempt to reduce aminocyclopyrachlor bioavailability.

Sorption studies with activated charcoal, biochar, soil, and biochar-soil systems (<10% biochar by weight) were performed on the same soils as the initial sorption experiments. Biochar produced from olive mill waste feedstock was the most effective biochar that we assessed for reducing the aqueous herbicide concentration. Then we also evaluated an activated charcoal in soil since this is the current recommendation for limiting non-target impacts and remediation efforts. Incorporating activated charcoal into the soil removed >99% of the aminocyclopyrachlor in solution and would potentially

limit the bioavailability of aminocyclopyrachlor to non-target flora. We concluded that these biochars reduced the liquid-phase aminocyclopyrachlor concentrations, implementing biochar for remediation would require extraordinarily high application rates in order to reduce the concentration by 50%; at least 0.92×10^5 kg ha^{-1}. The application rates are not currently economically viable. This research emphasizes the need for additional work to identify dominant sorption-desorption mechanisms of aminocyclopyrachlor and indaziflam in a wide variety of soils to improve model predictions of their environmental fate.

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction

Minnesota, located in the Midwestern United States is rich in water resources including 12,000 lakes, 104,000 miles of streams, and 9.3 million acres of wetlands (MPCA, 2014). In addition, Minnesota is the home of the headwaters of the Mississippi River which transects the country for 2,350 miles then drains into the Gulf of Mexico (NPS, 2015). The discharge area of the Gulf includes a hypoxic zone that is severely impaired by a lack of oxygen caused by excess nutrients and sediments delivered by the river (Rabalais, et al 2002). Discharge water quality and quantity are linked to land use and climate events for the entire watershed, including Minnesota. For example, the 2012 Midwestern drought caused the hypoxic zone to shrink because there was reduced runoff; therefore, less pollutants made their way into the river and to the Gulf (NOAA, 2012). This link between Minnesota water quality and the Gulf of Mexico water quality demonstrates the importance of research on the fate and transport of chemicals in the state's soils.

Chemical fate and transport depends on several site-specific factors such as climate, soil type, or land use. It is important to evaluate new pesticide chemistries in a variety of soils to determine if the pesticides are likely to bind to soil particles or remain in the water phase where they can be transported by overland flow and leach into surface waters and groundwater. This research specifically addressed the sorption-desorption of aminocyclopyrachlor and indaziflam, two relatively new herbicides, in Minnesota soils. The second chapter describes how using the batch-equilibrium method, we determined the dissociation constant (K_d) for each chemical in the surface and subsurface soils for the

three soil types. The K_d values are important because they are necessary data inputs for chemical transport models.

We further investigated the transport of aminocyclopyrachlor and indaziflam by evaluating how sorption-desorption behaviors fit the Freundlich model and whether they were likely to leach (Chapter 3) utilizing the Freundlich equation provided information about whether the herbicide sorption to soil was dependent on the herbicide concentration or not. Furthermore, the Freundlich model was used to assess the likelihood of the sorbed herbicide to desorb into the soil-water, which would make it bioavailable (OECD, 2000). Finally, we classified leaching potential of the herbicides according to Groundwater Ubiquity Scores (GUS) (Gustafson, 1989).

Aminocyclopyrachlor was suspected to be highly mobile in various soils because of previous evidence that it had damaged non-target vegetation. For example, sensitive tree species, such as spruce, pine, and honey locust, were damaged following aminocyclopyrachlor application to nearby turf (Patton et al., 2013). Using the batch-equilibrium method, we evaluated the efficacy of an activated biochar, and activated charcoal and various biochar amendments to reduce the bioavailability of aminocyclopyrachlor. Practical application of biochar as a remediation tool was also determined by calculating the quantity of biochar required to reduce the concentration of aminocyclopyrachlor in the soil-water by half.

The following chapters describe in detail experiments conducted to evaluate the mobility of aminocyclopyrachlor and indaziflam in a variety Minnesota soils and to assess the impact of the addition of biochar on bioavailability of aminocyclopyrachlor.

3

The results show that the implications of herbicide mobility need to be studied further to determine the effects on water resources. Furthermore, it highlights the importance of in-depth research on newly approved pesticides: their efficacy and their environmental implications. This is especially important in Minnesota where there is an abundance of water resources, which as stated, impacts major watersheds such as the Mississippi Watershed as far away as the Gulf of Mexico.

Chapter 2

Mobility of Aminocyclopyrachlor and Indaziflam in Minnesota Soils as Predicted by

Sorption-Desorption

2.1. Introduction

Aminocyclopyrachlor (6-amino-5-chloro-2-cyclopropyl-4-pyrimidinecarboxylic

acid) (Figure 1a) and indaziflam (N-[(1R,2S)-2,6-dimethyl-2,3-dihydro-1H-inden-1-yl]-

6-(1-fluoroethyl)-1,3,5-triazine-2,4-diamine) (Figure 1b) were registered with the U.S.

Environmental Protection Agency (USEPA) in 2010 (Ryman, 2010; USEPA, 2010). Both

herbicides are used at low application rates and have lower toxicity profiles than other

herbicides, such as glyphosate or 2,4-D (USEPA, 2009).

a   b
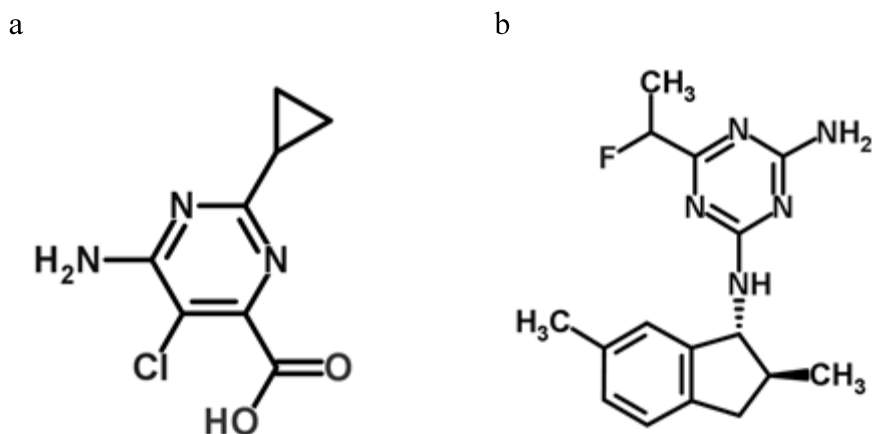
Figure 2.1.a & 2.1.b. Chemical structure of aminocyclopyrachlor and indaziflam.

Aminocyclopyrachlor, a pyrimidine carboxylic acid, is the active ingredient in

commercially available products Imprelis™, Perspective™, Streamline™, and

Viewpoint™ (DuPont, Wilmington, DE USA). This synthetic auxin is used to control

broad leaf weeds and grasses (Claus et al, 2008). In Minnesota in 2011, the majority of

aminocyclopyrachlor was sold for use as an industrial, rights-of-way, and forestry

6

chemical, additionally it was used as a turf and ornamental pesticide (MDA, 2014). National sales and use data of aminocyclopyrachlor was not available.

Indaziflam is an alkylazine herbicide found in the formulated products Alion™, Durazone™, Esplanade™, and Specticle™ (Bayer CropScience, Research Triangle Park, NC, USA), which acts as a cellulose biosynthesis inhibitor to control pre-emergence grasses and broadleaf weeds (USEPA, 2010). Indaziflam was sold as a garden and lawn pesticide in Minnesota in 2011, however it was not widely used (MDA, 2014). Despite not being used currently in Minnesota, the USGS estimates that in the United States in 2011, over 6 thousand pounds of indaziflam was applied to orchards and grapes in California, Florida, Georgia, Alabama, Washington, and Oregon (USGS, 2014).

The fate and transport of herbicides in the environment affect their efficacy and potential for environmental contamination. Sorption-desorption characteristics, which influence bioavailability and off-site mobility, are complex because the mixed-media soil system includes soil, water, gases, and plant matter. A frequently cited technique to quantify sorption-desorption is the batch-equilibrium method (OECD, 2000). Although this analysis does not offer detailed mechanistic information, it indicates the sorption potential of an herbicide to soil particles, the extent to which the sorbed herbicide will readily desorb, and investigate concentration dependence of soil. Sorption coefficients can be further used to assess environmental risk such as the Groundwater Ubiquity Score (GUS) that allows the ranking of herbicide leachability (Gustafson, 1989).

7

In order to provide information on aminocyclopyrachlor and indaziflam sorption-desorption to soil and their influence on mobility, we determined the sorption coefficients and hysteresis factors for both surface and subsurface soil from three locations across Minnesota. Furthermore, GUS values were estimated to determine each chemical's likelihood for off-site transport and groundwater contamination risk. This data will contribute to a broader understanding of these herbicides in the environment.

2.2. Materials and Methods

2.2.1. Soils

Soil collected from three locations in Minnesota, USA, were classified as follows: Hubbard loamy sand (sandy, mixed, frigid Entic Hapludoll) from the Sand Plain Research Farm (Becker, MN); Webster clay loam (fine, loamy, mixed, mesic Typic Haplaquoll) from the Southwest Research and Outreach Center (Lamberton, MN); and a Waukegon silt loam (fine-silty, mixed, mesic Typic Hapludoll) from the Rosemount Research and Outreach Center at UMore Park (Rosemount, MN).

All surface soils (0-15 cm depth) and subsurface soils (30-45 cm) were air dried, sieved to 2 mm, and stored at ambient temperature in air-tight containers. Air-dried soil moisture content ranged from 1-4%. Cation exchange capacity was analyzed using the summation of cations method. Organic matter was determined by loss of weight on ignition methodology. We multiplied the organic matter results by a conversion factor, 0.58, to estimate the organic carbon content of the soils. The hydrometer method was used to determine the texture (percentage sand, silt, and clay) of the soil. The soil pH was

evaluated using an electrode in a 1:1 soil-to-water mixture. All of the aforementioned soil analysis was performed by Midwest Laboratories (Omaha, NE, USA). The results of these soil analyses are summarized in Table 2.1.

Table 2.1. Summary of Minnesota, USA soil properties

| Soil type | C.E.C. (meq/100g) | % OC | Texture | | pH H$_2$O |
			% clay	% sand	
Becker, MN					
Surface (0-15 cm)	7.5	0.93	10	78	6.1
Subsurface (30-45 cm)	7.5	0.70	8	82	5.8
Lamberton, MN					
Surface (0-15 cm)	21.6	1.57	36	32	6.9
Subsurface (30-45 cm)	21.4	1.22	30	34	7.6
Rosemount, MN					
Surface (0-15 cm)	16.5	1.86	18	28	7.4
Subsurface (30-45 cm)	16.6	1.62	10	22	7.1

2.2.2. Herbicides

Analytical and ^{14}C-labeled compounds used in the study (DuPont, Wilmington, DE, USA; BayerCrop Science, Wuppertal Germany). A summary of the physicochemical properties of aminocyclopyrachlor and indaziflam are provided in Table 2.2. Aminocyclopyrachlor (Figure 2.1.a) is weakly acidic, lacks lipophilicity, and has a low vapor pressure. Indaziflam (Figure 2.1.b) is also a weak acid, slightly lipophilic, and has a low vapor pressure. Standards were prepared at 0.01, 0.03, 0.10, and 0.30 mg L^{-1} concentrations for each compound. The mean and standard deviation of the radioactivity

9

of the aminocyclopyrachlor standards was 117 ± 1.5 Bq mL^{-1} and the radioactivity of the

indaziflam standards was 71 ± 2.7 Bq mL^{-1}.

Table 2.2. Physicochemical properties of aminocyclopyrachlor and indaziflam

Properties	Aminocyclopyrachlor[A]	Indaziflam[B]
Chemical class	pyrimidine carboxylic acid	alkylazine
Formula	$C_8H_8ClN_3O_2$	$C_{16}H_{20}FN_5$
Molecular weight (g/mol)	213.62	301.36
Acid dissociation constant (pK$_a$)	4.65	3.5
Water solubility (g/L)	3.13-4.20	2.80×10^{-3}
Vapor pressure (Pa at 20°C)	6.92×10^{-6}	2.5×10^{-8}
Henry's law constant (Pa x m³/mol at 20 °C)	3.52×10^{-7}	2.69×10^{-6}
Liquid density (g mL^{-1})	1.6	1.3
Octanol-water partition coefficient (Log K$_{OW}$)	-2.48	2.8
Half-life (days)	22-128	> 150

[A] Aminocyclopyrachlor properties from Finkelstein et al, 2009 except for pKa and Henry's law constant which are reported by USEPA/OPPTS, 2010.
[B] Indaziflam properties from USEPA 2010.

2.2.3. Sorption

Sorption and desorption experiments were carried out according to the batch equilibrium method (Goetz et al, 1986). Isotopic-labeled herbicide solution was added to each soil in a glass 50-mL centrifuge tube with a Teflon-lined cap then shaken end-to-end overnight. After centrifuging, the solid and liquid phases were separated and a 1 mL aliquot of the liquid phase was sampled. Samples were analyzed using a liquid scintillation counter (LSC) (Packard 1500; Packard Tri-Carb, Downers Grover, IL).

A 1:1 soil-to-aminocyclopyrachlor solution ratio (10 g soil; 10 mL herbicide solution) was used, which followed that of Oliveira et al. (2011). Each mixture was vortexed for 30 s, inverted, vortexed for 30 s, and then placed on the shaker. After shaking overnight, each sample was centrifuged for 20 min at 1280 $\times$ g. A 1-mL aliquot of the supernatant was pipetted into a scintillation vial to which 5 mL of scintillation cocktail (EcoLyte, cocktail, ICN Biomedicals, Costa Mesa, CA) was added. The vials were capped then inverted several times to mix. Each vial was wiped with methanol then placed on the LSC to determine radioactivity. The ^{14}C-indaziflam sorption experiment followed this same method, however the soil-to-indaziflam solution ratio (4 g soil; 10 mL herbicide solution) was adjusted according to Alonso et al. (2011). Preliminary sorption-desorption experiments

2.2.4. Desorption

Desorption experiments were performed in four sequential steps by removing and replacing the supernatant from the batch equilibrium method. Following the same protocols as the sorption experiments, 10 g of soil and 10 mL of 0.10 mg L^{-1} [14]C-

11

aminocyclopyrachlor were mixed in a centrifuge tube, placed on the shaker then centrifuged. Three milliliters of supernatant was removed and a 1-mL aliquot was analyzed by LSC. The removed supernatant was replaced with 3 mL of 0.01 N CaCl$_2$. This procedure was completed three more times to create a 4-point desorption curve.

The indaziflam desorption experiments were carried out the same way using 4 g of soil and 10 mL 0.30 mg L^{-1} ^{14}C-indaziflam for the Rosemount and Lamberton soils and 0.01 mg L^{-1} for the Becker soils. We removed 5 mL supernatant, analyzed 1 mL, and replaced it with 0.01 N CaCl$_2$. Four-point desorption curves were generated for each soil and depth using the Freundlich equation.

2.2.4. Calculations

Sorption coefficients were calculated using the equation,

[Equation 2.1] $$K_d = C_s/C_e,$$

where C_s is the concentration of herbicide sorbed to the soil (ng g^{-1}) and C_e is the concentration of herbicide in the liquid phase at equilibrium (ng mL^{-1}). To normalize the sorption data to soil OC, the K_{oc} was calculated by dividing the sorption coefficient by the following

[Equation 2.2] $$K_{oc} = K_d \div [\%OC \div 100\%],$$

where %OC is the percentage of organic carbon in the soil. The units of K_d and K_{oc} were mL g^{-1}.

In order to estimate the parameters for sorption-desorption, the logarithms of C_s (x-axis) and C_e (y-axis) were plotted using Sigma Plot, version 11.0, which mathematically fit the log-transformed Freundlich equation:

[Equation 2.3] $\log [C_s] = \log [K_f] + 1/n \log [C_e]$,

where $\log [K_f]$ was the y-intercept of the line and $1/n$ was the slope. The resulting units of K_f were $ng^{(1-1/n)} mL^{1/n} g^{-1}$. The hysteresis coefficient, H, was calculated by dividing the Freundlich desorption slope ($1/n_{desorption}$) by the Freundlich sorption slope ($1/n_{sorption}$), or mathematically:

[Equation 2.4] $H = [1/n_{desorption}]/ [1/n_{sorption}]$.

However, this was only calculated for soils which exhibited hysteresis, which is defined where $1/n_{desorption}$ is less than $1/n_{sorption}$.

The GUS was calculated using the equation:

[Equation 2.5] $GUS = \log [t_{1/2}] \times [4 - \log (K_{oc})]$,

in order to calculate the GUS index. Herbicide $t_{1/2}$ were found in literature. According to Gustafson (1989), GUS values can be classified by the following categories:

Table 2.3. Groundwater Ubiquity Score classifications

GUS value	Leaching potential
< 0.1	Extremely low
0.10 – 1.0	Very low
1.0 – 2.0	Low

2.0 – 3.0	Moderate
3.0 – 4.0	High
> 4.0	Very high

2.2.5. Statistics

Statistical differences in sorption to each soil was determined by an unpaired t-test using GraphPad Software (www.graphpad.com/quickcalcs/ttest1). Significant relationships between soil properties and sorption coefficients or hysteresis factors were established with ANOVA tests and linear regression analysis using statistical software R (www.r-project.org).

2.3. Results

2.3.1. Aminocyclopyrachlor

Aminocyclopyrachlor sorption for all soils was low (Table 2.4.). Sorption coefficients, K_d, narrowly ranged from 0.21 to 0.62 mL g^{-1} for the surface soils and was positively correlated to soil-sand content (p=0.03; R^2=0.998). The K_d values in the subsurface soil were lower (K_d=0.08-0.24 mL g^{-1}). There was no statistical difference observed between the Becker and Rosemount subsurface sorption coefficients. We found no statistical relationships between aminocyclopyrachlor sorption and soil properties. Sorption to all soils fit the Freundlich equation (R^2>0.93) with a slope of ≈ 1 (Table 2.5.).

Table 2.4. Aminocyclopyrachlor sorption coefficients and hysteresis factors.

Soil type	$K_d{}^A$ (mL g^{-1})	$K_{OC}{}^A$ (mL g^{-1})	H
Becker surface 0-15 cm depth	0.62 ± 0.04	67.14 ± 4.64	0.53
Becker subsurface 30-45 cm depth	0.24 ± 0.03	33.63 ± 3.61	0.61
Lamberton surface 0-15 cm depth	0.26 ± 0.02	16.42 ± 1.18	0.64
Lamberton subsurface 30-45 cm	0.08 ±0.03	6.83 ± 2.06	0.54
Rosemount surface 0-15 cm	0.21 ± 0.01	11.13 ± 0.59	0.39
Rosemount subsurface 30-45 cm depth	0.24 ± 0.02	14.63 ± 1.18	0.84

^{A}Mean ± standard deviation.

Table 2.5. Freundlich coefficients for aminocyclopyrachlor in Minnesota, USA, soils.

Soil type	$K_f{}^A$ (ng$^{(1-1/n)}$ mL$^{1/n}$ g^{-1})	1/n sorption	R^2	1/n desorption	R^2
Becker surface 0-15 cm depth	1.06 (-0.35-1.77)	0.96±0.01	0.9981	0.51±0.06	0.9625
Becker subsurface 30-45 cm depth	1.09 (-0.78-1.39)	0.93±0.02	0.9963	0.57±0.15	0.8137
Lamberton surface 0-15 cm depth	1.07 (-0.78-1.36)	0.97±0.02	0.9975	0.62±0.10	0.9279
Lamberton subsurface 30-45 cm	1.21 (-1.09-1.33)	0.93±0.05	0.9831	0.50±0.10	0.8971
Rosemount surface 0-15 cm	1.06 (-1.09-1.33)	0.98±0.01	0.9984	0.38±0.07	0.9149
Rosemount subsurface 30-45 cm depth	1.06 (-0.78-1.35)	0.95±0.02	0.9979	0.80±0.10	0.9509

^{A}Freundlich sorption coefficient mean ± one standard deviation.

Desorption of aminocyclopyrachlor was hysteretic in all soils (Table 2.4.). No significant

statistical relationship between the hysteresis coefficient and the soil properties was

oberved. The lowest (H=0.39) and highest (H=0.84) hysteresis coefficient was observed

in the soil from Rosemount. The published half-life of aminocyclopyrachlor ranges from

22-128 d, therefore we calculated two GUS values using the shortest and longest half-life

durations. The leaching potential for aminocyclopyrachlor in Minnesota soils was high to

very high with most GUS values exceeding 4 (Table 2.6.).

Table 2.6. Aminocyclopyrachlor GUS classifications.

Soil type	GUS[A]	Leaching potential	GUS[B]	Leaching potential
Becker surface 0-15 cm depth	2.92	moderate	7.45	very high
Becker subsurface 30-45 cm depth	3.32	high	7.33	very high
Lamberton surface 0-15 cm depth	3.74	high	7.22	very high
Lamberton subsurface 30-45 cm	4.25	very high	7.10	very high
Rosemount surface 0-15 cm	3.96	high	7.17	very high
Rosemount subsurface 30-45 cm depth	3.81	high	7.21	very high

[A] Groundwater ubiquity score calculated from 22 d half-life.
[B] Groundwater ubiquity score calculated from 128 d half-life.

2.3.2. Indaziflam

Indaziflam sorption was low to moderate, varying by soil type (Table 2.7.).

Sorption to the surface soil (K_d=17.51-22.70 mL g^{-1}) was greater than sorption to the

subsurface soils (K_d=6.17-13.31 mL g^{-1}). After normalizing the sorption coefficients to the organic carbon content (Equation 2.2.), we found there was no statistical difference in sorption to the subsurface soils. Sorption fit the Freundlich equation (R^2>0.90) and the slope was 1 (Table 2.8.).

Table 2.7. Indaziflam sorption coefficients and hysteresis factors.

Soil type	K_d[A] (mL g^{-1})	K_{OC}[A] (mL g^{-1})	H
Becker surface 0-15 cm depth	17.51 ± 1.47	1775 ± 158.6	0.23
Becker subsurface 30-45 cm depth	6.17 ± 0.59	881.1 ± 83.83	0.72
Lamberton surface 0-15 cm depth	19.63 ± 3.41	1250 ± 217.3	0.63
Lamberton subsurface 30-45 cm	9.97 ± 1.20	817.4 ± 98.61	[C]
Rosemount surface 0-15 cm	22.70 ± 1.1[B]	901[B]	0.17
Rosemount subsurface 30-45 cm depth	13.31 ± 1.96	821.6 ± 120.7	0.66

[A]Mean ± standard deviation.
[B]Data published in Alonso et al 2011.
[C]No hysteresis observed.

Table 2.8. Freundlich coefficients for indaziflam in six Minnesota, USA, soils

Soil type	K_f^A (ng$^{(1-1/n)}$ mL$^{1/n}$ g^{-1})	1/n sorption	R^2	1/n desorption	R^2
Becker surface 0-15 cm depth	17.84 (16.98-18.74)	0.96±0.02	0.9967	0.22±0.04	0.8905
Becker subsurface 30-45 cm depth	7.23 (7.08-7.40)	0.94±0.02	0.9996	0.68±0.13	0.8997
Lamberton surface 0-15 cm depth	15.76 (15.02-16.54)	0.91±0.02	0.9973	0.57±0.08	0.9427
Lamberton subsurface 30-45 cm	12.10 (11.70-12.51)	0.92±0.01	0.9988	1.04±0.17	0.9240
Rosemount surface 0-15 cm	14.26[B] (13.88-14.66)	0.92±0.01[B]	0.9999[B]	0.16[B]	0.9585[B]
Rosemount subsurface 30-45 cm depth	23.62 (22.67-24.60)	0.90±0.02	0.9975	0.59±0.12	0.8812

[A]Freundlich sorption coefficient mean ± one standard deviation.
[B]Value taken from literature (Alonso et al, 2011).

No hysteresis was observed in the subsurface soil from Lamberton. Indaziflam leaching

potential was classified as low to moderate by the GUS index (Table 2.9.).

18

Table 2.9. Indaziflam GUS classifications.

Soil type	GUS sorption	Leaching potential
Becker surface 0-15 cm depth	1.63	low
Becker subsurface 30-45 cm depth	2.30	moderate
Lamberton surface 0-15 cm depth	1.97	low
Lamberton subsurface 30-45 cm	2.37	moderate
Rosemount surface 0-15 cm	2.27	moderate
Rosemount subsurface 30-45 cm depth	2.36	moderate

2.4. Discussion

2.3.1. Aminocyclopyrachlor Sorption

Low K_d values for aminocyclopyrachlor indicate that there was more herbicide in solution than was sorbed to the soil particles. This suggests that this weakly sorbed chemical is mobile in the soil water phase and will readily leach. Often sorption is driven by soil pH, OC, CEC, or clay content, but that was not the case here.

The sorption-desorption of aminocyclopyrachlor to Minnesota soils conformed with the Freundlich equation. The $1/n_{sorption}$ was approximately 1 which allowed us to compare the K_f values and provided evidence that sorption was independent of herbicide concentration. There was little variation in K_f so we concluded that the mechanistic processes of aminocyclopyrachlor sorption were similar in each soil. Desorption was

19

hysteretic for all soils and indicated that although very little of the applied pesticide was bound to the soil, the portion of bound pesticide would not readily desorb. The lowest desorption was seen in the Rosemount surface soil as shown by the low hysteresis factor, H=0.39. Conversely, the greatest hysteresis factor was observed in the Rosemount subsurface soil (H=0.84), meaning the slope of the Freundlich desorption isotherm was nearly that of the slope of the Freundlich sorption isotherm. The higher H-factor indicates higher aminocyclopyrachlor bioavailability because the herbicide is weakly sorbed then easily desorbed. Hysteresis factors for the Becker and Lamberton soils were similar.

2.4.2. Aminocyclopyrachlor Predicted Mobility

The GUS indicies provide further evidence of leaching potential and offsite transport of aminocyclopyrachlor in soil as the leaching potential classification was moderate to very high. The soil from Becker had the lowest GUS values because it had the highest K_{oc}; the two parameters are inversely related. The GUS values calculated from the longer aminocyclopyrachlor half-life were higher, which indicates increased leaching potential with increasing half-life. The high potential for offsite transport of aminocyclopyrachlor in soil is in agreement with previously published research. Aminocyclopyrachlor sorption to Brazilian soils, Hawaiian soils, and other Minnesota soils was very low and attributed to soil clay content and OC, but not soil pH (Oliveira Jr. et al, 2011; Oliveira Jr. et al, 2013). A soil property or group of properties that consistently determine the sorption-desorption of aminocyclopyrachlor is yet to be determined but would be useful to limit or control it's mobility in the soil-water.

20

Despite the low application rate of aminocyclopyrachlor for control of weeds and grasses, its high mobility may result in unintended exposure and harm to non-target sensitive organisms such as conifers, deciduous trees, and ornamental shrubs due to uptake by plant roots (E.I. DuPont, 2012). Patton, et al. (2013) reported damage to trees and ornamental plant species near aminocyclopyrachlor-treated turf. Other research indicates aminocyclopyrachlor taken up in plants can be released into soil as plant residues degrade, becoming bioavailable and remaining biologically active for further uptake into non-target plants (Lewis et al, 2014).

2.4.3. Indaziflam Sorption

Sorption of indaziflam to Minnesota soils ranged from K_d=6.17-22.70 mL g^{-1} and was at least an order of magnitude higher than that of aminocyclopyrachlor perhaps due to its lower water solubility. Overall indaziflam sorption to surface soils was moderate and the K_d values were double the subsurface soil K_d values, where sorption was low. We did not find a relationship between sorption and soil pH, CEC, or texture that was more likely than chance. These findings did not agree with previously published studies of indaziflam sorption to other soils which was influenced by pH (Alonso et al, 2011; Trigo et al, 2014). Indaziflam sorption to subsurface soils increased with increased concentration of soil OC. In addition, sorption decreased with increased concentration of soil potassium. We speculate potassium outcompeted indaziflam for exchange sites on clay particles, where pesticides often bind.

Indaziflam sorption-desorption fit the Freundlich equation with the $1/n_{sorption}$ approaching 1. The K_f values were compared and fount to vary soil-to-soil therefore no inferences were made regarding mechanistic sorption-desorption processes. The hysteresis factor was low in Becker and Rosemount surface soils which implied that indaziflam is more irreversibly bound to these soil types. Hysteresis was also observed in subsurface Becker and Rosemount soils, but not in Lamberton subsurface soil where the slope of the desorption isotherm exceeded the slope of the sorption isotherm. This indicated that indaziflam is more bioavailable in the Lamberton subsurface soil because the sorbed fraction easily desorbs from the soil into the soil-water where it could move offsite. From Becker and Rosemount surface soils, 20% of the sorbed indaziflam would readily desorb into the soil-water and nearly 70% would desorb from the subsurface soils.

Other studies of indaziflam sorption-desorption established significant relationships between soil properties and indaziflam sorption. An analysis of Brazilian oxisol soils and Minnesota mollisol soils demonstrated that indaziflam sorption was driven by OC and soil-clay content (Alonso et al, 2011). Sorption was influenced by soil pH of the Minnesota soils, but not of Brazilian soils. The authors concluded that indaziflam would likely leach in both soils (Alonso et al, 2011). An evaluation of Arizona sandy soils, determined that low indaziflam sorption was attributed to pH (Trigo et al, 2014). When these data were applied to the GUS model, indaziflam leaching potential in Arizona soils was moderate to high. In Florida soils under heavy rainfall conditions indaziflam did not leach beyond 30 cm depth which determined that leaching was a function of soil depth (Jhala and Singh, 2012).

2.4.4. Indaziflam Predicted Mobility

Indaziflam had a low to moderate leaching potential for all soils in this study, as classified by the GUS calculations. This agreed with the moderate sorption determined by the K_d and moderate hysteresis factors. It is possible that the batch-equilibrium method over-estimated the K_d values because it only accounted for short term sorption. According to Wauchope et al. (2002), field observations can be up to 2X different than observed in the lab. If this was the case then the GUS values would indicate higher leaching potential (GUS>3.0).

It was surprising that neither aminocyclopyrachlor nor indaziflam sorption was found to correlate with soil pH. Both are weakly acidic herbicides with pK_a values lower than the soil pH, therefore, both herbicides would be present as anions in these soils and less likely to sorb to the negatively charged soil particles. As the soil pH increased, herbicide sorption should decrease. However, no such relationship was determined. It is presumed that there was not a strong interaction between the sorbent and sorbate because sorption-desorption of both aminocyclopyrachlor and indaziflam did not vary with herbicide concentration (Singh and Singh, 2012). Additional research on each herbicide is needed to understand the dominant sorption-desorption mechanisms to better predict or model sorption to a wider variety of soils.

Environmental fate and transport models, such as SCI-GROW, GENEEC, FIRST, and

PRZM used by the USEPA (USEPA, 2009), require K_d or K_{oc} data. Here we have presented site-specific information about aminocyclopyrachlor and indaziflam sorption to a variety of Minnesota soils intended for use in such models. Our research was the first to describe aminocyclopyrachlor and indaziflam in the evaluated soil types. Sorption-desorption trends and factors that influence these processes were found to differ from those reported in other soils. This highlights the importance and need for additional research to determine the dominant sorption-desorption mechanisms of these herbicides in order to accurately predict or model their sorption, bioavailability, and mobility in a wider variety of soils. Accurate prediction of the environmental fate of pesticides is important for practical application and regulatory purposes to enhance product efficacy and maintain environmental quality.

2.5. References

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99, 19-33.

Alonso, D.G., Koskinen, W.C., Oliveira Jr, R.S., Constantin, J., Mislankar, S., 2011. Sorption-desorption of indaziflam in selected agricultural soils. J. Agric. Food Chem. 59, 13096-13101.

Anonymous. Fall 2011 guidelines for planting trees on properties that have been treated with Imprelis herbicide. DuPont Professional Products, Wilmington, DE. 2011.

Bayer Environmental Science. 2014. Bayer Spect(i)cle FLO™ [product label]. Research Triangle Park, North Carolina, USA.

Beesley L., Moreno-Jiménez, E., Gomez-Eyles, J.L., Harris, E., Robinson, B., Sizmur, T., 2011. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. Environ. Pollut. 159, 3269-3282.

Bovey, R., Miller, F., 1969. Effect of activated carbon on phytotoxicity of herbicides in tropical soil. Weed Sci. 17, 189-192.

Bukun, B., Lindenmayer, B., Nissen, S.J., Westra, P., Shaner, D.L., Brunk, G., 2010. Absorption and translocation of aminocyclopyrachlor and aminocyclopyrachlor-methyl ester in Canada thistle (*Cirsium arvense*). Weed Sci. 58, 96-102.

Cabrera-Mesa, A., Spokas, K., 2011. Impacts of biochar (black carbon) additions on the sorption and efficacy of herbicides, in: Andreas Kortekamp ed., Herbicides and Environment, In Tech. pp. 315-340.

Cabrera, A., Trigo, C., Cox, L., Celis, R., Hermosin, M.C., Cornejo, J., Koskinen, W.C., 2012. Sorption of the herbicide aminocyclopyrachlor by cation-modified clay minerals. Eur. J. Soil Sci. doi: 1111/j.1365-2389.2012.01466.x

Chen, B., Zhou, D., Zhu, L., 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needs with different pyrolytic

temperatures. Environ. Sci. Technol. 42, 5137-5143.

Chen B., Yuan, M., 2011. Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar. J. Soils Sed. 11, 62-71.

Claus, J., Turner, R., Armel, G., Holliday, M., 2008. DuPont aminocyclopyrachlor (proposed common name) (DPX-MAT/KJM44) herbicide for use in turf, IWC, bareground,and brush markets. In: Proceedings of the 5th International Weed Science Congress, vol. 1. InternationalWeed Science Society, Fayetteville, AR, p. 654.

Clay, S.A., Malo, D.D. 2012. The influence of biochar production on herbicide sorption characteristics, Herbicides – Properties, Synthesis and Control of Weeds, Dr. Mohammed Nagib Hasaneen (Ed.), ISBN: 978-953-307-803-8, InTech, DOI: 10.5772/31492. Available from: http://www.intechopen.com/books/herbicides-properties-synthesis-and-control-of-weeds/the-influence-of-biochar-production-on-herbicide-sorption-characteristics. Accessed February 9, 2015.

Coffey, D.L., Warren, G.F., 1969. Inactivation of herbicides by activated carbon and other adsorbents. Weed Sci. 17, 16-19.

E.I. DuPont de Nemours and Company. 2011. DuPont™ Streamline® herbicide [product label]. Wilmington, Delaware, USA.

E.I. DuPont de Nemours and Company. 2012. DuPont land management: Use of DuPont™ Perspective®, Streamline®, and Viewpoint® herbicides near trees and shrubs. Wilmington, Delaware, USA.

Finkelstein, B.L., Armel, R.G., Bolgunas S.A., Clark, D.A., Claus, J.S., Crosswicks, R.J., Hirata, C.M., Hollinghaus, G.J., Koeppe, M.K., Rardon, P.L., Wittenbach, V.A., Woodward, M.D., 2009. DuPont DPX-MAT28 herbicide. Technical Bulletin. Reorder No.: K15023. E.I. du Pont de Nemours and Company 8 p.

Flessner, M.L., Dute, R.R., McElroy, J.S., 2011. Anatomical response of St. Augustinegrass to aminocyclopyrachlor treatment. Weed Sci. 59, 263-269.

Foo, K.Y., Hameed, B.H., 2010. Detoxification of pesticide waste via activated carbon adsorption process. J Hazard Mater. 175, 1-11.

Graber, E.R., Tsechansky, L., Gerstl, Z., Lew, B., 2012. High surface area biochar negatively impacts herbicide efficacy. Plant Soil 353, 95-106.

Goetz, A.J., Wehtje, G., Walker, R.H., Hajek, B. 1986. Soil solution and mobility characterization of imazaquin. Weed Sci. 34, 788-793.

Gustafson, D.I., 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. Environ. Toxicol. Chem. 8, 339-357.

Finkelstein, B.L., Armel, R.G., Bolgunas, S.A., Clark, D.A., Claus, J.S., Crosswicks, R.J., Hirata, C.M., Hollinghaus, G.J., Koeppe, M.K., Rardon, P.L., Wittenbach, V.A., Woodward, M.D., 2009. DuPont DPX-MAT28 Herbicide. Technical Bulletin. Reorder No.: K15023. E.I. du Pont de Nemours and Company, p. 8.

Jhala, A.J. and Singh, M. 2012. Leaching of indaziflam compared with residual herbicides commonly used in Florida citrus. Weed Technol. 26, 602-607.

Johnson, B.J. 1976. Effect of activated charcoal on herbicide injury during establishment of centipedegrass. Agron. J *68,* 802-805.

Jones D.L., Edwards-Jones, G., Murphy, D.V., 2011. Biochar mediated alterations in herbicide breakdown and leaching in soil. Soil Biol. Biochem. 43, 804-813.

Kniss, A.R., Lyon, D.J., 2011. Winter wheat response to preplant applications of aminocyclopyrachlor. Weed Technol. 25, 51-57.

Koepke-Hill, R.M., Armel, G.R., Brosnan, J.T., Breeden, G.K., Vargas, J.J., Mueller, T.C., 2012. Control of silk tree (*albizia julibrissin*) with aminocyclopyrachlor and other herbicides. Weed Sci. 60, 345-349.

Kookana, R.S., 2010. The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review. Soil Res. 48, 627-637.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems – a review. Mitig Adapt Strategy Global Change. 11, 403-427.

Lewis, D. F., 2012 Environmental fate and biological impact of aminocyclopyrachlor 343 in turfgrass and neighboring systems. North Carolina State, PhD Dissertation. 344 pp.152.

Lewis, D.F., Jeffries, M.D., Gannon, T.W., Richardson, R.J., Yelverton, F.H. 2014. Persistence and Bioavailability of Aminocyclopyrachlor and Clopyralid in Turfgrass Clippings: Recycling Clippings for Additional Weed Control. Weed Science: July-September 2014, Vol. 62, No. 3, pp. 493-500.

Lima, I. M., McAloon, A., Boateng, A. A., 2008. Activated carbon from broiler litter: Process description and cost of production. Biomass Bioenerg. 32, 568-572.

Lindenmayer, L., Westra, P., Brunk, G., 2009. Soil interactions with DOX-KJ44 and DPX-MAT28. Proc. Weed Sci. Soc. Am. 62, 515.

Minnesota Department of Agriculture, 2014. Pesticide sales information. http://www2.mda.state.mn.us/webapp/lis/chemsold_results.jsp. Accessed: December 29, 2014.

Minnesota Pollution Control Agency. 2014. Water types and programs: surface water. http://www.pca.state.mn.us/index.php/water/water-types-and-programs/surface-water/index.html. Accessed: February 9, 2015.

Mozammel, H., Masahiro, O., Bhattacharya, S., 2002. Activated charcoal from coconut shell using $ZnCl_2$ activation. Biomass Bioenerg. 22, 397-400.

Nanita, S.C., Pentz, A.M., Grant, J., Vogl, E., Devine, T.J., Henze, R.M. 2009. Mass spectrometric assessment and analytical methods for quantitation of the new herbicide aminocyclopyrachlor and its methyl analogue in soil and water. Anal. Chem. 81, 797-808.

National Park Service. 2015. Mississippi River facts. http://www.nps.gov/miss/riverfacts.htm. Accessed: February 9, 2015.

National Ocianic and Atmospheric Administration. 2012. NOAA scientists: Midwest drouth brings fourth smallest Gulf of Mexico 'dead zone' since 1985. July 27, 2012. http://www.noaanews.noaa.gov/stories2012/20120727_midwestdrought.html. Accessed: February 9, 2015.

OECD, 2000. OECD guidelines for the testing of chemicals, adsorption/desorption using a batch equilibrium method OECD Test Guideline, vol. 106. OECD Publications, Paris.

Ogbonnaya, U., Semple, K., 2013. Impact of biochar on organic contaminants in soil: A tool for mitigating risk? Agron J. 3, 349-375.

Oliveira Jr, R.S., Alonso, D.G., Koskinen, W.C., 2011. Sorption-desorption of aminocyclopyrachlor in selected Brazilian soils. J. Agric. Food Chem. 59, 4045-4050.

Oliveira Jr, R.S., Alonso, D.G., Koskinen, W.C., Papiernik, S.K. 2013. Comparative sorption, desorption and leaching potential of aminocyclopyrachlor and picloram. J. Environ. Sci. Heal. B 48, 1049-1057.

Patton, A.J., Ruhl, G.E., Creswell, T.C., Wan, P., Scott, D.E., Becovitz, J.D., Weisenberger, D.V. 2013. Potential damage to sensitive landscape plants from wood chips of aminocyclopyrachlor damaged trees. Weed Technol. 27, 803-809.

Rabalais, N.N., Turner, R.E., Wiseman, Jr., W.J. 2002. Gulf of Mexico hypoxia, A.K.A. "The dead zone". Annu. Rev. Ecol. Syst. 33, 235-263.

Rick, S. K., Turner, R.G., Meredith, J.H., 2008. Biology review of aminocyclopyrachlor. North Central Weed Sci. Soc. Proc. 63, 202.

Rupp, R.N., Edwards, M., Harbour, J., Meredith, J.H., Rick, S.K., 2011. Weed control with aminocyclopyrachlor in pastures and rangeland. Proc. Weed Sci. Soc. Am. Abstr. 49, Abstract 244.

Ryman, J., Miller, J.S., Morton, T., 2010. Aminocyclopyrachlor: Human health risk assessment for proposed uses as an herbicide. USEPA Office of Prevention, Pesticides and Toxic Substances. March 17, 2010.

Sarmah A.K., Srinivasan, P., Smernik, R.J., Manley-Harris, M., Antal, M.J., Downie, A., van Zwieten, L., 2010. Retention capacity of biochar-amended New Zealand dairy farm soil for an estrogenic steroid hormone and its primary metabolite. Aust. J. Soil Res. 48, 648-658.

Singh, N., Singh, S.B. 2012. Sorption-desorption behavior of metsulfuron-methyl and sulfosulfuron in soils. J. Environ. Sci. Heal. B 47, 168-174.

Spadotto, C.A. 2002. Screening method for assessing pesticide leaching potential. Pesticidas: R.Ecotoxicol. e Meio Ambiente, Curitiba.12, 69-78

Spokas, K.A., Koskinen, W.C., Baker, J.M., Reicosky, D.C., 2009. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. Chemosphere 77, 574-581.

Spokas, K.A., 2010. Review of the stability of biochar in soils; predictability of O:C molar ratios. Carbon Manage. 1, 289-303.

Spokas, K. A., Cantrell, K. B., Novak, J. M., Archer, D. W., Ippolito, J. A., Collins, H. P., Boateng, A. A., Lima, I. M., Lamb, M. C., McAloon, A. J., Lentz, R. D., Nichols, K. A., 2012. Biochar: A synthesis of its agronomic impact beyond carbon sequestration. J. Envioron Qual. 41, 973-989.

Strachan, S.D., Nanita, S.C., Ruggiero, M., Casini, M.S., Heldreth, K.M., Hageman, L.H., Flanigan, H.A., Ferry, N.M., Pentz, A.M., 2011. Correlation of chemical analysis of residual levels of aminocyclopyrachlor in soil to biological responses in alfalfa, cotton, soybean, and sunflower. Weed Technol. 25, 239-244.

Strek, H.J., Weber, J.B., Shea, P.J., Mrozek Jr., E., Overcash, M.R., 1981. Reduction of polychlorinated biphenyl toxicity and uptake of carbon-14 activity by plants through the use of activated carbon. J. Agric. Food. Chem. 29, 288-293.

Trigo, C., Koskinen, W.C., Kookana, R.S. 2014. Sorption-desorption of indaziflam and its three metabolite in sandy soils. J. Environ. Sci. Heal. B 49, 836-843.

Uchimiya M., Lima, I.M., Klasson, K.T., Chang, S.C., Wartelle, L.H., Rodgers, J.E., 2010. Immobilization of heavy metal ions (Cu-II, Cd-II, Ni-II, and Pb-II) by broiler litter-derived biochars in water and soil. J. Agric. Food Chem. 58, 5538-5544.

U.S. Environmental Protection Agency. 2009. Guidance for selecting input parameters in modeling the environmental fate and transport of pesticides, version 2.1, October 22, 2009.

U.S. Environmental Protection Agency. 2009. National primary drinking water regulations. EPA 816-F-09-004.

U.S. Environmental Protection Agency, 2010. Pesticide fact sheet, July 26, 2010. Conditional registration, 2010; 108 pp.

USEPA/OPPTS. 2010. Ecological Risk Assessment for the Section 3 New Chemical Registration of Aminocyclopyrachlor on Non-Crop Areas and Turf. EPA-HQ-OPP-2009-0789-0004. Washington, DC: Environmental Protection Agency, Off Prevent Pest Tox Sub http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2009-0789-0004. Accessed: December 29, 2014.

U.S. Environmental Protection Agency, Jun. 27, 2012. Imprelis and Investigation of Damage to Trees. Pesticides: Regulating Pesticides. http://www.epa.gov/pesticides/regulating/imprelis.html. Aug. 27, 2013.

U.S. Geological Survey, 2014. National water-quality assessment program: 2011 Pesticide use maps. http://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2011&map=INDAZIFLAM&hilo=L&disp=Indaziflam. Accessed: December 29, 2014.

Wauchope, R.D., Yeh, S., Linders, J. BHJ, Kloskowski, R. Tanaka, K., Rubin, B., Katayama, A., Kordel, W., Gerstl, Z., Lane, M., Unsworth, J.B. 2002. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pest Manag. Sci. 58, 419-445.

Westra, P., Nissen, S., Gaines, T., Bekun, B., Lindenmayer, B., Shaner, D., 2008.
Aminocyclopyrachlor for invasive weed management and restoration grass safety in the
Central Great Plains. North Central Weed Sci. Soc. Proc. 63:203.

Yelverton, F. H., Worsham, A. D., Peedin, G. F., 1992. Activated carbon reduces
tobacco (*Nicotiana tabacum*) injury from soil-applied herbicides. Weed Technol. 6, 310–
31.

Chapter 2

Assessing Biochar's Ability to Reduce Bioavailability of

Aminocyclopyrachlor in Soils

3.1. Introduction

Aminocyclopyrachlor (6-amino-5-chloro-2-cyclopropyl-4-pyrimidinecarboxylic acid) is a new auxin herbicide in the pyrimidine carboxylic acid class of chemicals (Figure 3.1.) (Claus et al., 2008; Bukun et al., 2010). The US-Environmental Protection Agency (USEPA) approved aminocyclopyrachlor registration in August 2010 for the control of broadleaf weeds and brush on non-cropland and turf (USEPA, 2010).

Figure 3.1. Chemical structure of aminocyclopyrachlor
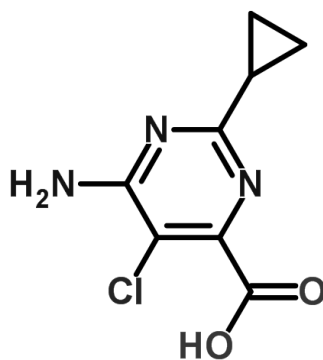
Aminocyclopyrachlor stimulates detrimental plant tissue growth and accompanying vascular inhibition, which are characteristic control mechanisms of synthetic auxin herbicides (Flessner et al., 2011). This allows for management of a wide range of weed species. Aminocyclopyrachlor has high efficacy at low applications rates, with most susceptible weed

species controlled at 70-100 g ha^{-1} (Finkelstein et al., 2009; Westra et al., 2008). Some plant species are controlled at even lower rates (8.7 g ha^{-1}) when co-applied with methylated seed oil (Koepke-Hill et al., 2012). In addition, its residues in soil can provide weed control for several months following application and the residues in previously treated turf clippings can also provide significant weed control (Kniss and Lyon, 2011; Strachan et al., 2011). Despite this effective control of plants, aminocyclopyrachlor has a low toxicity profile for mammals and wildlife (Rupp et al., 2011; Ryman et al., 2010).

Aminocyclopyrachlor has the potential to leach through soil as indicated by its physiochemical properties that classify it as environmentally persistent, soluble in water, and non-volatile. Furthermore, soil organic matter content, soil clay content, and soil pH influence aminocyclopyrachlor sorption (Cabrera et al., 2012; Oliveira Jr et al., 2011). Due to its low sorption, aminocyclopyrachlor is mobile in soil after application (Oliveira Jr et al, 2011). Of additional concern, plant roots were shown to take up residual concentrations of aminocyclopyrachlor in soil (Bukun et al., 2010; Lindenmayer et al., 2009; Rick et al., 2008). Aminocyclopyrachlor residues have been detected at soil depths of 70-90 cm 1 yr after application, confirming that the compound is in fact persistent and easily leached (Ryman et al., 2010). A field study conducted in the United States and Canada observed the half-life of aminocyclopyrachlor in soil is between 22 and 126 d (Ryman et al. 2010). Similarly, Finkelstein et al. (2009) reported the soil half-life of aminocyclopyrachlor applied to turf is 37 to 103 d and in non-vegetated field studies the soil half-life is 72 to 128 d. Studies have also observed minimal microbial mineralization (Lewis, 2012).

Currently, there is interest in reducing potential off-site transport of aminocyclopyrachlor in soils through management practices, as well as potential remediation options for

aminocyclopyrachlor-impacted soils. It has been shown that aminocyclopyrachlor use has resulted in damage to tree species including spruce, pine, and honey locust (Patton et al., 2013; USEPA, 2012). Activated charcoal (AC) is commonly used as a protecting agent for herbicide injury to plants in soil (Coffey and Warren, 1969; Johnson, 1976; Strek et al., 1981; Ogbonnaya and Semple, 2013). Until April 2012, incorporation of AC while planting was suggested to protect young tree and evergreen root balls from aminocyclopyrachlor exposure (Anonymous, 2011). However, the efficacy of AC amendments as a remediation tool for various herbicide residues can be inconsistent, often resulting in the herbicide-impacted agricultural field being left fallow or alternative crops being grown until the herbicide residues have dissipated (Bovey and Miller, 1969; Yelverton et al., 1992; Foo and Hameed, 2010). In addition, AC would be an expensive soil amendment for field-scale use (Lima et al., 2008). Biochars are relatively new amendments also being used for reduction of potential off-site transport or for remediation purposes (Jones et al., 2011).

Given the low potential for aminocyclopyrachlor degradation in soil, incorporating biochar into soil could be a useful management practice to remove or immobilize the herbicide. Biochar is the "solid residual remaining after the thermo-chemical transformation of biomass whose main intended purpose is as a means of carbon sequestration" (Lehmann et al., 2006; Spokas, 2010; Cabrera-Mesa and Spokas, 2011; Spokas et al., 2012). Activated charcoals are black carbons that are further conditioned for sorption applications (Mozammel et al., 2002). AC is thermochemically activated following pyrolysis. Biochar has been shown to sorb a variety of chemicals and this ability is a combined function of its production temperature, surface area, and percent carbon content (Beesley et al., 2011; Cabrera-Mesa and Spokas, 2011; Chen and Yuan, 2011; Jones et al., 2011; Kookana, 2010; Sarmah et al., 2010; Uchimiya et al., 2010). However,

34

the practical assessment of different biochar types and proposed field application rates to achieve aminocyclopyrachlor remediation goals has not been adequately examined.

The overall goal of this assessment was to evaluate the effect of biochar amendments on the reduction of aminocyclopyrachlor in an aqueous soil solution. The herbicide concentration reduction was compared between three Minnesota soils, biochars derived from various feedstocks, activated charcoal, steam activated biochar, and soils amended with either biochar or activated charcoal. Results of this comparison will help evaluate the utility of biochar amendments to mitigate the off-site movement of aminocyclopyrachlor.

3.2. Materials and Methods

3.2.1. Soils

Surface (0-15 cm) and subsurface (15-30 cm) soils were collected from three research locations in Minnesota, USA. The soil at the Sand Plain Research Farm (Becker, MN) is classified as a Hubbard loamy sand (sandy, mixed, frigid Entic Hapludoll), whereas the Southwest Research and Outreach Center (Lamberton, MN) soil is a Webster clay loam (fine, loamy, mixed, mesic Typic Haplaquoll) and soil from the Rosemount Research and Outreach Center at UMore Park (Rosemount, MN) is a Waukegon silt loam (fine-silty, mixed, mesic Typic Hapludoll). All soil was air-dried and passed through a 2 mm sieve prior to use.

Soils were submitted to Midwest Laboratories (Omaha, NE, USA) for analysis of cation exchange capacity (C.E.C.), organic matter (%O.M.), and soil texture. The pH of the soil in a 0.01 M $CaCl_2$ solution was measured in-house. The summation of cations method was used for C.E.C. analysis (Midwest Laboratories, Omaha, NE). Soil organic matter was analyzed using the

35

loss of weight on ignition method. Soil texture was determined by the hydrometer method. We calculated the percentage organic matter by multiplying the reported %O.M. by 0.58. A summary of the soil properties is provided in Table 3.1.

Table 3.1. Physicochemical properties of Minnesota soils.

Soil	C.E.C. (meq/100 g)	O.C. (%)	Sand (%)	Silt (%)	Clay (%)	Texture	pH (in CaCl₂)
Becker 0-15 cm depth	7.5	0.93	78	12	10	Sandy loam	5.60 ± 0.05
Becker 15-30 cm depth	7.5	0.70	82	10	8	Loamy sand	5.72 ± 0.03
Lamberton 0-15 cm depth	21.6	1.57	32	32	36	Clay loam	6.36 ± 0.02
Lamberton 15-30 cm depth	21.4	1.22	34	36	40	Clay loam	6.99 ± 0.05
Rosemount 0-15 cm depth	16.5	1.86	28	54	18	Silt loam	6.99 ± 0.07
Rosemount 15-30 cm depth	16.6	1.62	22	58	10	Silt loam	7.15 ± 0.06

3.2.2. Biochars

A variety of parent materials and production processes were represented in the selected biochars; including woodchips, corn stover, and olive mill waste produced under various temperatures ranging from 490 to 700°C (Table 3.2.). We also compared the woodchip biochar, activated by steam (2 h at 120°C and 1.03×10^5 Pa) and activated charcoal from coconut shells

first produced at 450°C then activated at 1100°C. These biochars and activated charcoal contained 5 to 58% ash, 16 to 88% carbon, and surface area ranging from 0.52 to 62 $m^2\,g^{-1}$ for the biochars and 956 $m^2\,g^{-1}$ for the activated carbon. The oxygen-to-carbon molar ratio for activated carbon (9.0×10^{-5}) was much lower than those for biochars (0.08 - 0.28), which shows that the AC was a more stable black carbon form than the biochars.

Table 3.2. Characteristics of black carbons.

Feedstock	Abbrev.	Production temperature (°C)	Surface area ($m^2\,g^{-1}$)	Ash content (%)	Carbon content (%)	O:C molar ratio	pH (in $CaCl_2$)
pine wood	PW	490	0.52	58	35	0.11	7.33 ± 0.24
cornstover	CS	490	0.82	57	37	0.08	9.00 ± 0.01
wood chip	WC	~500	1.6	5.0	74	0.18	6.61 ± 0.03
wood chip (steam activated)	WC-Stm		29				6.47 ± 0.16
olive mill waste	OMW	700	34	77	16	0.28	11.17 ± 0.38
wood pellet	WP	650	62	6.4	73	0.19	6.81 ± 0.09
coconut shells (activated charcoal)	CNS-Act	450/1100	956	14	88	9.0×10^{-5}	6.93 ± 0.06

We did not grind or sieve the biochars, as this an unlikely effort prior to field application when utilized for field-scale remediation. Although the biochar particle sizes were not

analytically homogenized, the same size fraction of biochar was used for each treatment and its replicates. This could lead to some variation in the results, but we were targeting as-delivered biochar particle sizes since this is the most likely form that would be applied to agricultural fields.

Surface areas of the biochars were analyzed by Pacific Surface Science Inc. (Oxnard, CA, USA) using 5 point sorption isotherm B.E.T. N_2 surface area tests. Biochar pH was measured in a 0.01 M $CaCl_2$ solution. Hazen Research Inc. (Golden, CO, USA) analyzed the biochars by ultimate analysis (ASTM D3176-09) for percentage of ash, carbon, nitrogen, sulfur, hydrogen, and oxygen (by difference). A summary of biochar properties is presented in Table 3.2.

3.2.3. Herbicide

Physiochemical properties of aminocyclopyrachlor include weak acidity ($pK_a = 4.65$), molecular weight of 213.6 g mole^{-1}, lack of lipophilicity (log $K_{OW} = -2.48$), water solubility (3.13-4.20 g L^{-1}), and low vapor pressure (6.92×10^{-6} Pa at 20°C) (Ryman et al., 2010).

DuPont (Wilmington, DE, USA) kindly provided the analytical and ^{14}C-labeled aminocyclopyrachlor (pyrimidine-2-^{14}C-aminocyclopyrachlor). The standard solutions were prepared in 0.01N $CaCl_2$ at a concentration of 0.30 mg L^{-1}, although the typical application rates range between 0.01 mg L^{-1} and 0.18 mg L^{-1}. The standards were refrigerated at 4°C in darkness then brought to ambient temperature prior to use. The solution radioactivity was ~150 Bq mL^{-1}.

3.2.4. Batch-equilibrium study

Aminocyclopyrachlor concentrations were determined after each system achieved a pseudo-steady state using the batch-equilibration method. Replicate samples were prepared by adding 10 g of soil, 1 g of biochar or activated charcoal, or 10 g of soil plus 1 g biochar or activated charcoal into a 50 mL glass centrifuge tube with a Teflon-lined cap. The soil-biochar

samples were thoroughly mixed. Blank samples of standard solution (20 mL of 0.30 mg L^{-1} ^{14}C-aminocyclopyrachlor), containing neither soil nor char amendments, showed no evidence of chemical sorption to the laboratory glassware (99.1% recovery). To every tube, we added 20 mL of 0.30 mg L^{-1} ^{14}C-aminocyclopyrachlor. The samples were capped and shaken manually for approximately 30 s, then placed horizontally on a tabletop shaker overnight (~18 h). Equilibrium was determined from preliminary kinetic studies (data not shown). The tubes were centrifuged at 1280 × g for 30 min, after which 3 mL of supernatant was removed using a glass pipette. A 1 mL subsample was transferred into a scintillation vial along with 5 mL of scintillation cocktail (EcoLyte, cocktail, ICN Biomedicals, Costa Mesa, CA) and vortexed. The solution was analyzed for ^{14}C-aminocyclopyrachlor by liquid scintillation counting (Packard 1500; Packard Tri-Carb, Downers Grover, IL). The remaining supernatant was analyzed for pH (Orion Research Expandable IonAnalyzer EA 920; Orion, Cambridge, MA).

3.2.5. Calculations

A distribution coefficient, K_d (mL g^{-1}), was determined for each soil using the equation: $K_d = [C_s]/[C_e]$, where C_s (ng g^{-1}) is the concentration of chemical sorbed after equilibrium and C_e (ng mL^{-1}) is the concentration of chemical in solution after equilibrium. Preliminary studies possessed no observable degradation during the sample equilibration. For each soil, a pesticide organic carbon coefficient, K_{OC} (mL g^{-1}), was calculated from: $K_{OC} = (K_d / \%OC \times 100)$, where %OC is the percentage of organic carbon content in the soil or biochar-amended soil mixture.

Groundwater Ubiquity Scores (GUS) for surface and subsurface soils were calculated using the equation: $GUS = \log(t^{soil}_{1/2}) \times (4 - \log(K_{OC}))$, where $t^{soil}_{1/2}$ is the herbicide half-life (d) in soil (Gustafson 1989). We used the GUS index to determine whether aminocyclopyrachlor was

persistent or mobile (GUS >1 is mobile). Half-lives calculated in existing studies were used (Finkelstein et al., 2009).

Lastly, we estimated the rate of biochar application required to remove 50% of the aminocyclopyrachlor from a soil-water system. This was accomplished by measuring and averaging concentrations (ng ml^{-1}) of aminocyclopyrachlor remaining in solution from the surface and subsurface soil for each biochar treatment, calculating the percentage of aminocyclopyrachlor removed from the soil-biochar system (1 g of biochar plus 10 g of soil), then calculating the amount of biochar needed to remove 50% of the herbicide and converting our findings to a field-scale application rate (kg ha^{-1}), assuming a soil bulk density of 1.2 g cm^{-3} and a tillage incorporation depth of 15 cm. We assumed that there is a linear relationship between the concentration of aminocyclopyrachlor applied and the concentration of aminocyclopyrachlor in the soil-water and that sorption is concentration independent.

3.2.6. Statistics

Two statistical software programs were used to analyze the data. Unpaired t-tests were performed using GraphPad Software (www.graphpad.com/quickcalcs/ttest1) to determine the statistical differences between the standard solution, soils, biochars, and biochar-amended soils. Potential correlations of soil properties on the solution concentration of aminocyclopyrachlor were compared using a linear regression model and ANOVA with R (www.r-project.org). The same analyses were used to examine the role of biochar properties on the observed aqueous herbicide concentration.

3.3. Results and Discussion

3.3.1. Leachability of aminocyclopyrachlor

40

Our assessment of biochar use for the removal of aminocyclopyrachlor began by calculating the leaching potential of the herbicide in soil. The Koc values of the evaluated soils ranged from 17 to 68 in the surface soils and 14 to 40 in the subsurface soils, as shown in Table 3.3. Despite the range in Koc values and aminocyclopyrachlor half-lives, the leaching potential of aminocyclopyrachlor ranged from high (GUS = 3.0-4.0) to very high (GUS > 4.0). In fact, the only soil not ranked as "very high" is the Becker soil, which was ranked "high" when the 37-day half-life is used in the GUS calculation. From these data, we concluded that aminocyclopyrachlor is mobile in soil following application to turf, as other studies have already demonstrated as well (Oliveira Jr et al., 2011). Aminocyclopyrachlor leaching is a concern because of the low concentrations of this herbicide at which plant injury can occur (<0.1 μg L^{-1}; Patton et al. 2013).

Table 3.3. Aminocyclopyrachlor concentrations and leachability in Minnesota soils.

Soil type	Concentration remaining in solution (ng ml^{-1})	K_d[A] (mL g^{-1})	K_{OC}[B] (mL g^{-1})	GUS value[C] ($t_{1/2}$ = 37 d)	GUS value[C] ($t_{1/2}$ = 103 d)	Leaching potential
Becker 0-15 cm depth	24 ± 0.93	0.63 ± 0.03	68 ± 3.2	3.40	6.98	high to very high
Becker 30-45 cm depth	12 ± 0.11	0.28 ± 0.00	40 ± 0.0	3.76	6.89	high to very high
Lamberton 0-15 cm depth	14 ± 0.95	0.34 ± 0.03	22 ± 1.9	4.18	6.80	very high
Lamberton 30-45 cm depth	7.6 ± 0.17	0.17 ± 0.00	14 ± 0.0	4.48	6.74	very high
Rosemount 0-15 cm depth	13 ± 3.5	0.31 ± 0.10	17 ± 5.4	4.36	6.76	very high
Rosemount 30-45 cm depth	16 ± 3.0	0.40 ± 0.08	25 ± 4.9	4.09	6.82	very high

[A] K_d = [C_s]/[C_e], where C_s is the concentration of chemical sorbed after equilibrium and C_e is the concentration of chemical in solution after equilibrium.
[B] K_{OC} = (K_d / OC), where OC is the soil organic carbon content.
[C] GUS = log ($t^{soil}_{1/2}$) × (4 − log (K_{OC}))

3.3.2. Reducing the aqueous herbicide concentration by biochar

We compared 7 biochars, with varied chemical and physical properties (Table 3.2.), in an

aqueous aminocyclopyrachlor solution to see which biochars reduced the herbicide concentration
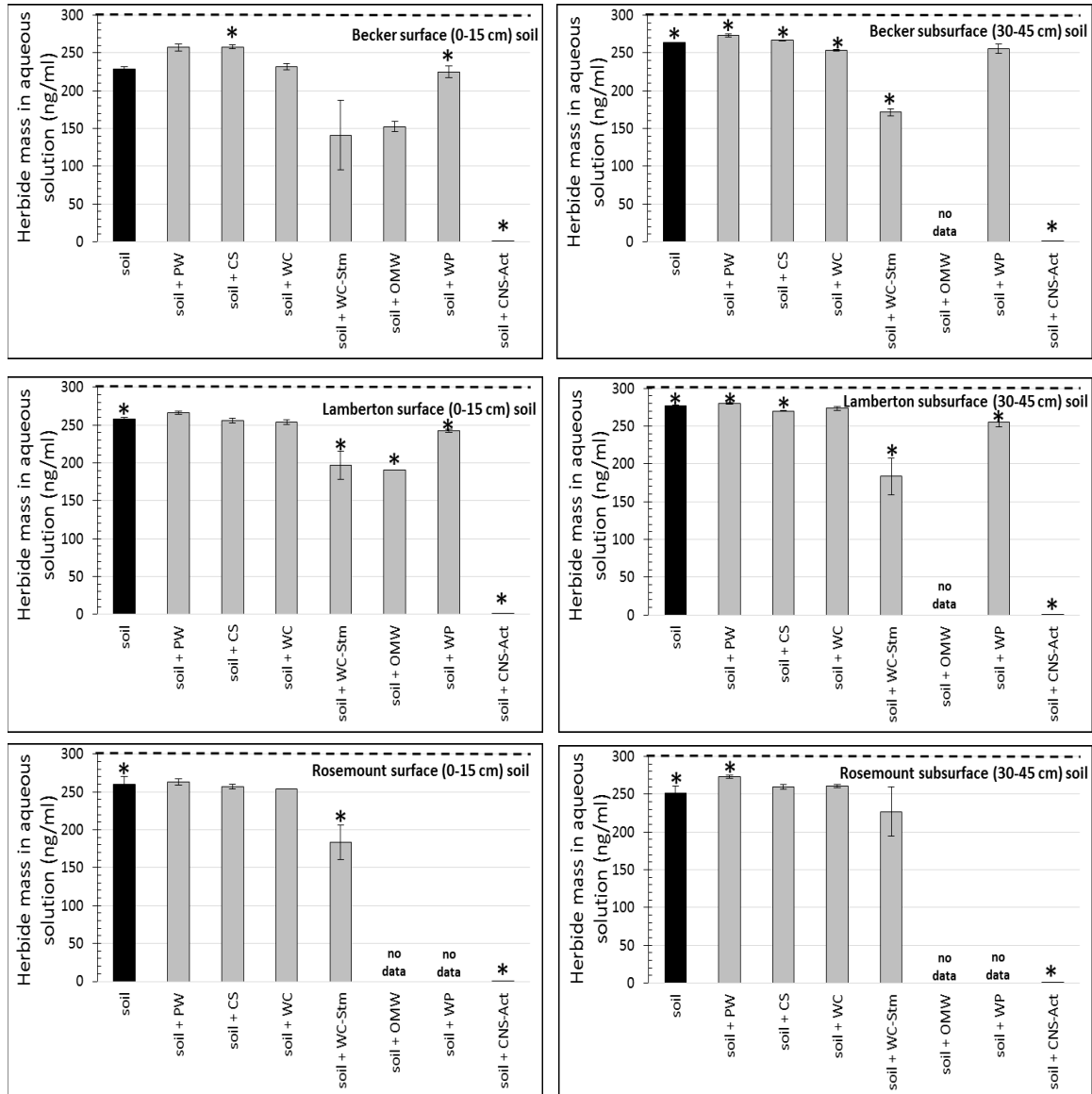
in solution. The initial concentration of aminocyclopyrachlor in solution was 300 ng mL^{-1}. We found that adding activated charcoal from coconut shell feedstock (CNS-Act) to the solution reduced the concentration to 0.07 ± 0.05 ng mL^{-1}, olive mill waste (OMW) biochar reduced the concentration to 115 ± 5.46 ng mL^{-1}, and steam-activated wood chip (WC-Stm) biochar reduced it to 195 ± 5.33 ng mL^{-1} (Figure 3.2). Wood chip (WC) biochar reduced the herbicide concentration to 266 ± 8.10 ng mL^{-1} and cornstover (CS) biochar reduced it to 280 ± 0.32 ng mL^{-1}. Two biochars, pine wood (PW) and wood pellet (WP), did not have any significant impacts on the aqueous herbicide concentration. By comparing the WC and the WC-Stm, we observed an increase of 31% in the removed amount of aminocyclopyrachlor from the solution phase as a result of the steam activation.

Figure 3.2. Concentration (ng ml^{-1}) of aminocyclopyrachlor in solution following batch-equilibrium studies with biochars. Dashed line indicates initial solution concentration. Gray bars indicate solution concentrations from the biochar systems. Stars indicated which solution concentrations from the biochar systems are significantly different from the initial solution concentration. Biochar feedstock abbreviations: PW = pinewood; CS = cornstover; WC = wood chip; WC-Stm = steam-activated wood chip; OMW = olive mill waste; WP = wood pellet; CNS-Act = coconut shell activated charcoal.
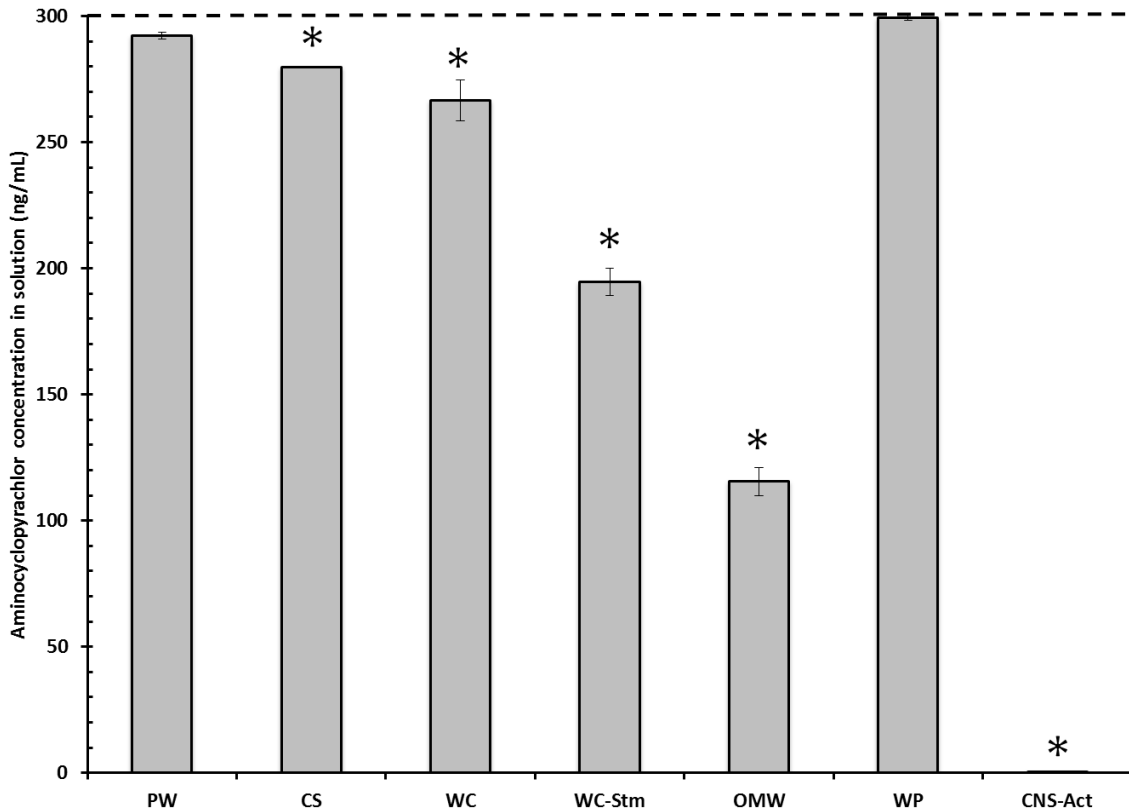
The concentration of aminocyclopyrachlor in solution after reaching a pseudo-steady state with the soils was slightly lower in the surface soils (Becker: 229 ± 3 ng mL^{-1}; Lamberton: 258 ± 3 ng mL^{-1}; Rosemount: 260 ± 11 ng mL^{-1}) than the subsurface soils (Becker: 263 ± 0.3 ng mL^{-1}; Lamberton: 277 ± 0.5 ng mL^{-1}; Rosemount: 252 ± 9 ng mL^{-1}) (Figure 3.3.). Despite the numerical differences, these differences between the Rosemount surface and subsurface soils were not statistically significant ($p>0.05$), but were for the Becker and Lamberton soils.

Figure 3.3. Concentration (ng ml^{-1}) of aminocyclopyrachlor in solution following batch-equilibrium studies with biochar-amended soils. Dashed line indicates initial solution concentration. Black bars indicate solution concentrations from the soil-only systems. Stars above the black bars indicate the solution concentration in the soil system is significantly different from the initial solution concentration. Gray bars indicate solution concentrations from the biochar-amended soil systems. Stars above the gray bars indicated which solution concentrations from the biochar-amended soils are significantly different from solution concentrations of the soil alone. Biochar feedstock abbreviations: PW = pinewood; CS = cornstover; WC = wood chip; WC-Stm = steam-activated wood chip; OMW = olive mill waste; WP = wood pellet; CNS-Act = coconut shell activated charcoal.

Prior to this investigation, we anticipated the evaluated biochars would readily adsorb aminocyclopyrachlor, and addition of these biochars to the soil would noticeable decrease the concentration of aminocyclopyrachlor in solution since hardwood biochar has been shown to reduce the leachability of herbicides in Minnesota soils (Spokas et al., 2009). In contrast, we found that removal of aminocyclopyrachlor from solution with biochar and biochar-amended soils was variable. The most effective amendment evaluated was the activated charcoal from coconut shell feedstock (CNS-Act). After incorporating CNS-Act into the soils, little to no aminocyclopyrachlor remained in the solution. In all six soils, less than 0.5 ng mL^{-1} of aminocyclopyrachlor was in solution where the initial concentration was 300 ng mL^{-1} (99.98% removal) (Figure 3.3.). It is possible that AC possesses a high number of sorption sites, which render the competition from dissolved soil organic matter inconsequential.

Overall, the biochar-amended soils were less effective in removing aminocyclopyrachlor from solution than the activated charcoal (CNS-Act). Amending soils with biochar produced from pinewood (PW), cornstover (CS), wood chips (WC), wood pellet (WP) had little effect on the resulting aminocyclopyrachlor solution concentrations. When compared to soil alone, the additional removal of the herbicide from solution with the biochar-amended soil was usually not statistically significant. These soil amendment results are similar to our assessment of the PW, CS, WC, and WP biochars alone. Similar to the biochar alone results, the steam activation of WC did remove an additional 10-40% of the aminocyclopyrachlor when compared to the soil-only. However, it should be noted that activation would be a poor choice for remediation due to its higher production costs and direct competition with the activated charcoal markets (Lima et al., 2008).

The biochar produced from OMW feedstock resulted in the lowest concentration of aminocyclopyrachlor remaining in solution. Due to limited material availability, OMW-amended soil was only studied in Becker and Lamberton surface soils. The results were similar in magnitude to that of the WC-Stm but the two treatments are statistically different ($p<0.05$). The OMW has the highest production temperature, percentage ash content, and pH with the lowest O:C molar ratio of the biochars we studied, excluding here the WC-Stm and CNS-Act. Our results show that the concentration of aminocyclopyrachlor remaining in solution is correlated ($p<0.05$) to biochar production temperature ($R^2=0.61$) and solution pH ($R^2=0.74$). This study did not find a correlation between concentration and biochar surface area or ash content although surface area has been suggested as a controlling factor of biochar-herbicide sorption (Cabrera-Mesa and Spokas, 2011). However, the relationship with biochar surface area could be biased by the lack of intermediate surface area values (i.e. 10-100's $m^2\ g^{-1}$) in this assessment. Interestingly, when we include the CNS-Act, correlations ($p<0.05$) between the concentration and biochar properties resulted in surface area ($R^2=0.67$) and ash content ($R^2=0.74$) becoming the significant correlations, thus agreeing with recent reviews (Amad et al., 2014; Chen et al., 2008; Graber et al., 2012).

For the soil samples, cation exchange capacity ($R^2=0.74$), percentage sand content ($R^2=0.91$), and pH ($R^2=0.80$) were statistically correlated for the surface soils ($p<0.05$). Given these strong correlations, it is interesting that 10% biochar additions have such an observable impact on the concentration of aminocyclopyrachlor in solution. The addition of biochar altered these correlations similar to the trends of biochar-only systems. The one similarity between the soils tested and the biochars was the correlation with pH, which is not surprising because aminocyclopyrachlor is a weak acid. Increasing the pH will increase the anionic species of the

herbicide thus potentially decreasing the potential for sorption because of less molecular species present in solution.

3.3.3. Biochar application rate estimates

The purpose of our assessment was to investigate biochar amendments that would reduce the concentration of aminocyclopyrachlor in solution. This concentration represents a surrogate for the bioavailable or leachable amount of aminocyclopyrachlor. From our data, the concentration of aminocyclopyrachlor in the aqueous phase is primarily controlled by biochar than soil type. In our study, the aqueous concentrations of aminocyclopyrachlor of the biochar and biochar-soil system were similar. Given the fact that aminocyclopyrachlor can be harmful to nontarget flora (Patton et al. 2013), it is beneficial to determine the hypothetical application rate of biochars that could reduce the herbicide bioavailability. For both the surface and subsurface soil, the estimated application rate of CNS-Act required to reduce the aminocyclopyrachlor in soil by 50% is 9.15×10^4 kg ha^{-1} (Table 4). For the remaining biochars, the surface soil application rate range is from 2.13 to 7.27×10^5 kg ha^{-1} and the range for subsurface soil is 2.59 to 11.2×10^5 kg ha^{-1}. We conclude that although there is almost no aminocyclopyrachlor remaining in the aqueous phase when CNS-Act is mixed with soil, it is not a feasible method for remediation given the extraordinarily high application rate required.

Table 3.4. Biochar application rate (kg ha^{-1}) required to remove 50% of aminocyclopyrachlor from soils.

Feedstock	Surface soil application rate (kg ha^{-1})	Subsurface soil application rate (kg ha^{-1})
pine wood	7.27×10^5	11.2×10^5
cornstover	6.36×10^5	7.93×10^5
wood chip	5.10×10^5	7.32×10^5
wood chip (steam activated)	2.18×10^5	2.59×10^5
olive mill waste	2.13×10^5	no data
wood pellet	4.13×10^5	6.16×10^5
coconut shells (activated charcoal)	9.15×10^4	9.15×10^4

3.4. Conclusions

This was the first study to assess the practical use of biochar as a remediation tool to reduce bioavailable and leachable aminocyclopyrachlor in soils using biochar. We confirmed that aminocyclopyrachlor would leach in three Minnesota soils, as illustrated by the GUS index. We found that the biochars, with the exception of OMW biochar, were of limited use as a soil amendment for reducing the aqueous concentration of aminocyclopyrachlor. The two biochars, OMW and WC-Stm, were the most effective although the reduction was less than expected. These data suggest that despite biochar possessing an aromatic carbon structure, the biochar surface characteristics are not chemically or physically optimized for aminocyclopyrachlor

49

sorption. Steam activation increases sorption capacities as a post-processing activation process.

Overall, due to the high application rates required to reduce the concentration of

aminocyclopyrachlor by 50%, the economic feasibility for biochar's aminocyclopyrachlor

remediation will be limited, expect for limited small-scale or specialty applications.

3.5. References

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99, 19-33.

Anonymous. Fall 2011 guidelines for planting trees on properties that have been treated with Imprelis herbicide. DuPont Professional Products, Wilmington, DE. 2011.

Beesley L., Moreno-Jiménez, E., Gomez-Eyles, J.L., Harris, E., Robinson, B., Sizmur, T., 2011. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. Environ. Pollut. 159, 3269-3282.

Bovey, R., Miller, F., 1969. Effect of activated carbon on phytotoxicity of herbicides in tropical soil. Weed Sci. 17, 189-192.

Bukun, B., Lindenmayer, B., Nissen, S.J., Westra, P., Shaner, D.L., Brunk, G., 2010. Absorption and translocation of aminocyclopyrachlor and aminocyclopyrachlor-methyl ester in Canada thistle (*Cirsium arvense*). Weed Sci. 58, 96-102.

Cabrera-Mesa, A., Spokas, K., 2011. Impacts of biochar (black carbon) additions on the sorption and efficacy of herbicides, in: Andreas Kortekamp ed., Herbicides and Environment, In Tech. pp. 315-340.

Cabrera, A., Trigo, C., Cox, L., Celis, R., Hermosin, M.C., Cornejo, J., Koskinen, W.C., 2012. Sorption of the herbicide aminocyclopyrachlor by cation-modified clay minerals. Eur. J. Soil Sci. doi: 1111/j.1365-2389.2012.01466.x

Chen, B., Zhou, D., Zhu, L., 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needs with different pyrolytic temperatures. Environ. Sci. Technol. 42, 5137-5143.

Chen B., Yuan, M., 2011. Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar. J. Soils Sed. 11, 62-71.

Claus, J., Turner, R., Armel, G., Holliday, M., 2008. DuPont aminocyclopyrachlor (proposed common name) (DPX-MAT/KJM44) herbicide for use in turf, IWC, bare-ground, and brush markets. Proceedings of the 5th International Weed Science Congress, Volume 1. Fayetteville, AR: International Weed Science Society, pp. 654.

Coffey, D.L., Warren, G.F., 1969. Inactivation of herbicides by activated carbon and other adsorbents. Weed Sci. 17, 16-19.

Finkelstein, B.L., Armel, R.G., Bolgunas S.A., Clark, D.A., Claus, J.S., Crosswicks, R.J., Hirata, C.M., Hollinghaus, G.J., Koeppe, M.K., Rardon, P.L., Wittenbach, V.A., Woodward, M.D., 2009. DuPont DPX-MAT28 herbicide. Technical Bulletin. Reorder No.: K15023. E.I. du Pont de Nemours and Company 8 p.

Flessner, M.L., Dute, R.R., McElroy, J.S., 2011. Anatomical response of St. Augustinegrass to aminocyclopyrachlor treatment. Weed Sci. 59, 263-269.

Foo, K.Y., Hameed, B.H., 2010. Detoxification of pesticide waste via activated carbon adsorption process. J Hazard Mater. 175, 1-11.

Graber, E.R., Tsechansky, L., Gerstl, Z., Lew, B., 2012. High surface area biochar negatively impacts herbicide efficacy. Plant Soil 353, 95-106.

Gustafson, D.I., 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. Environ Toxicol Chem. 8, 339-357.

Johnson, B.J. 1976. Effect of activated charcoal on herbicide injury during establishment of centipedegrass. Agron. J *68,* 802-805.

Jones D.L., Edwards-Jones, G., Murphy, D.V., 2011. Biochar mediated alterations in herbicide breakdown and leaching in soil. Soil Biol. Biochem. 43, 804-813.

Kniss, A.R., Lyon, D.J., 2011. Winter wheat response to preplant applications of aminocyclopyrachlor. Weed Technol. 25, 51-57.

Koepke-Hill, R.M., Armel, G.R., Brosnan, J.T., Breeden, G.K., Vargas, J.J., Mueller, T.C., 2012. Control of silk tree (*albizia julibrissin*) with aminocyclopyrachlor and other herbicides. Weed Sci. 60, 345-349.

Kookana, R.S., 2010. The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review. Soil Res. 48, 627-637.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems – a review. Mitig Adapt Strategy Global Change. 11, 403-427.

Lewis, D. F., 2012 Environmental fate and biological impact of aminocyclopyrachlor 343 in turfgrass and neighboring systems. North Carolina State, PhD Dissertation. 344 pp.152.

Lima, I. M., McAloon, A., Boateng, A. A., 2008. Activated carbon from broiler litter: Process description and cost of production. Biomass Bioenerg. 32, 568-572.

Lindenmayer, L., Westra, P., Brunk, G., 2009. Soil interactions with DOX-KJ44 and DPX-MAT28. Proc. Weed Sci. Soc. Am. 62, 515.

Mozammel, H., Masahiro, O., Bhattacharya, S., 2002. Activated charcoal from coconut shell using $ZnCl_2$ activation. Biomass Bioenerg. 22, 397-400.

Ogbonnaya, U., Semple, K., 2013. Impact of biochar on organic contaminants in soil: A tool for mitigating risk? Agron J. 3, 349-375.

Oliveira Jr, R.S., Alonso, D.G., Koskinen, W.C., 2011. Sorption-desorption of aminocyclopyrachlor in selected Brazilian soils. J. Agric. Food Chem. 59, 4045-4050.

Patton, A.J., Ruhl, G.E., Creswell, T.C., Wan, P., Scott, D.E., Becovitz, J.D., Weisenberger, D.V., 2013. Potential damage to sensitive landscape plants from wood chips of aminocyclopyrachlor damaged trees. Weed Technol. 27, 803-809.

Rick, S. K., Turner, R.G., Meredith, J.H., 2008. Biology review of aminocyclopyrachlor. North Central Weed Sci. Soc. Proc. 63, 202.

Rupp, R.N., Edwards, M., Harbour, J., Meredith, J.H., Rick, S.K., 2011. Weed control with aminocyclopyrachlor in pastures and rangeland. Proc. Weed Sci. Soc. Am. Abstr. 49, Abstract 244.

Ryman, J., Miller, J.S., Morton, T., 2010. Aminocyclopyrachlor: Human health risk assessment for proposed uses as an herbicide. USEPA Office of Prevention, Pesticides and Toxic Substances. March 17, 2010.

Sarmah A.K., Srinivasan, P., Smernik, R.J., Manley-Harris, M., Antal, M.J., Downie, A., van Zwieten, L., 2010. Retention capacity of biochar-amended New Zealand dairy farm soil for an estrogenic steroid hormone and its primary metabolite. Aust. J. Soil Res. 48, 648-658.

Spokas, K.A., Koskinen, W.C., Baker, J.M., Reicosky, D.C., 2009. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. Chemosphere 77, 574-581.

Spokas, K.A., 2010. Review of the stability of biochar in soils; predictability of O:C molar ratios. Carbon Manage. 1, 289-303.

Spokas, K. A., Cantrell, K. B., Novak, J. M., Archer, D. W., Ippolito, J. A., Collins, H. P., Boateng, A. A., Lima, I. M., Lamb, M. C., McAloon, A. J., Lentz, R. D., Nichols, K.

A., 2012. Biochar: A synthesis of its agronomic impact beyond carbon sequestration. J. Envioron Qual. 41, 973-989.

Strachan, S.D., Nanita, S.C., Ruggiero, M., Casini, M.S., Heldreth, K.M., Hageman, L.H., Flanigan, H.A., Ferry, N.M., Pentz, A.M., 2011. Correlation of chemical analysis of residual levels of aminocyclopyrachlor in soil to biological responses in alfalfa, cotton, soybean, and sunflower. Weed Technol. 25, 239-244.

Strek, H.J., Weber, J.B., Shea, P.J., Mrozek Jr., E., Overcash, M.R., 1981. Reduction of polychlorinated biphenyl toxicity and uptake of carbon-14 activity by plants through the use of activated carbon. J. Agric. Food. Chem. 29, 288-293.

Uchimiya M., Lima, I.M., Klasson, K.T., Chang, S.C., Wartelle, L.H., Rodgers, J.E., 2010. Immobilization of heavy metal ions (Cu-II, Cd-II, Ni-II, and Pb-II) by broiler litter-derived biochars in water and soil. J. Agric. Food Chem. 58, 5538-5544.

U.S. Environmental Protection Agency, 2010. Ecological risk assessment for the section 3 new chemical registration of aminocyclopyrachlor on non-crop areas and turf. Washington, DC: Office of Prevention, Pesticides and Toxic Substances, pp 1-34.

U.S. Environmental Protection Agency, Jun. 27, 2012. Imprelis and Investigation of Damage to Trees. Pesticides: Regulating Pesticides. http://www.epa.gov/pesticides/regulating/imprelis.html. Aug. 27, 2013.

Westra, P., Nissen, S., Gaines, T., Bekun, B., Lindenmayer, B., Shaner, D., 2008. Aminocyclopyrachlor for invasive weed management and restoration grass safety in the Central Great Plains. North Central Weed Sci. Soc. Proc. 63:203.

Yelverton, F. H., Worsham, A. D., Peedin, G. F., 1992. Activated carbon reduces tobacco (*Nicotiana tabacum*) injury from soil-applied herbicides. Weed Technol. 6, 310–31.

Chapter 4

Conclusions

This research was conducted to better understand the sorption-desorption of two new herbicides, this work also evaluated biochar's ability at reducing aminocyclopyrachlor bioavailability. It was found that aminocyclopyrachlor sorbed very little to soil, with K_d values being less than 1 ml g^{-1}, as there seemed to be little interaction between the sorbent (herbicide) and sorbate (soil). The determination of K_d values is intended to aid in chemical fate and transport models, such as those used by regulatory agencies. The soil environment is slightly negatively charged so a molecule such as aminocyclopyrachlor, which is not readily ionizable (Nanita et al, 2009), would be unlikely to bind to soil particles and thus bioavailable. It has been shown that aminocyclopyrachlor can damage sensitive plant species, such as tomatoes, when present in the soil at very low concentrations (< 0.1 ppb) (Patton et al, 2013). Another study suggested that aminocyclopyrachlor residuals are biologically active for up to 2 years following application (Westra et al, 2008). Aminocyclopyrachlor was classified as highly mobile and because it slowly degrades its use should be limited to areas lacking sensitive vegetation and areas that are not prone to flooding where it has a greater chance of moving offsite.

Indaziflam K_d values varied by soil type and ranged from 6.17-22.70 mL g^{-1}. It is not clear which soil properties dominated the herbicide sorption processes. The leaching potential of indaziflam was classified as moderately mobile, similar to 2,4-D (Spadotto 2002). This is primarily due to the long chemical half-life which exceeds 150 d. Although

indaziflam is not as drastic of a leacher as aminocyclopyrachlor, this work provided evidence that offsite transport of indaziflam is possible so caution should be taken when applying indaziflam-containing products to soils near waterways where it would be carried downstream and impact non-target ecosystems.

Consequences of high pesticide mobility include polluted surface or groundwater, contaminated soil, or unintended damage to non-target organisms, such as trees in the case of aminocyclopyrachlor. After removal of aminocyclopyrachlor-damaged trees, in 2011 the chemical manufacturer recommended using activated charcoal to protect the root ball of replacement trees. This led us to question the efficacy of biochar for reducing the amount of bioavailable aminocyclopyrachlor in soil because it was shown to be an effective sorption media for other weak acid herbicides (Clay and Malo, 2012). We found that the activated charcoal removed most of the aminocyclopyrachlor in the soil-water, but the biochars and activated biochar, which varied by surface area, did not sorb as much aminocyclopyrachlor as we expected. Overall, biochars were considered a poor remediation tool for reducing the concentration of bioavailable aminocyclopyrachlor because in order to reduce this concentration by 50% one would need to apply 9.15×10^4 kg ha^{-1} of activated charcoal or $2.13\text{-}11.2 \times 10^5$ kg ha^{-1} of biochar. Neither application rate would be economically feasible. It would be advantageous to compare aminocyclopyrachlor sorption to alternative biochars in order to find a suitable soil amendment to reduce the herbicide mobility.

Additional research of the sorption-desorption mechanisms of aminocyclopyrachlor and indaziflam in soil is also recommended. This would provide clarity on soil parameters that consistently predict mobility of these two herbicides in any soil. As mentioned in the earlier chapters, the relationships between soil properties and sorption-desorption were generally unclear. This information would be helpful in determining whether a location of intended application is suitable for aminocyclopyrachlor or indaziflam application because understanding local pesticide fate and transport is necessary to protect the greater ecosystem as well as downstream waters.

Bibliography

Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S., Ok, Y.S., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99, 19-33.

Alonso, D.G., Koskinen, W.C., Oliveira Jr, R.S., Constantin, J., Mislankar, S., 2011. Sorption-desorption of indaziflam in selected agricultural soils. J. Agric. Food Chem. 59, 13096-13101.

Alva, A. K.; Singh, M. 1990. Effects of soil-cation composition on reactions of four herbicides in a candler fine sand. Water, Air, Soil Pollut. 52, 175-182.

Anonymous. Fall 2011 guidelines for planting trees on properties that have been treated with Imprelis herbicide. DuPont Professional Products, Wilmington, DE. 2011.

Bayer Environmental Science. 2014. Bayer Spect(i)cle FLO™ [product label]. Research Triangle Park, North Carolina, USA.

Beesley L., Moreno-Jiménez, E., Gomez-Eyles, J.L., Harris, E., Robinson, B., Sizmur, T., 2011. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. Environ. Pollut. 159, 3269-3282.

Bovey, R., Miller, F., 1969. Effect of activated carbon on phytotoxicity of herbicides in tropical soil. Weed Sci. 17, 189-192.

Bukun, B., Lindenmayer, B., Nissen, S.J., Westra, P., Shaner, D.L., Brunk, G., 2010. Absorption and translocation of aminocyclopyrachlor and aminocyclopyrachlor-methyl ester in Canada thistle (*Cirsium arvense*). Weed Sci. 58, 96-102.

Cabrera-Mesa, A., Spokas, K., 2011. Impacts of biochar (black carbon) additions on the sorption and efficacy of herbicides, in: Andreas Kortekamp ed., Herbicides and Environment, In Tech. pp. 315-340.

Cabrera, A., Trigo, C., Cox, L., Celis, R., Hermosin, M.C., Cornejo, J., Koskinen, W.C., 2012. Sorption of the herbicide aminocyclopyrachlor by cation-modified clay minerals. Eur. J. Soil Sci. doi: 1111/j.1365-2389.2012.01466.x

Chen, B., Zhou, D., Zhu, L., 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needs with different pyrolytic temperatures. Environ. Sci. Technol. 42, 5137-5143.

Chen B., Yuan, M., 2011. Enhanced sorption of polycyclic aromatic hydrocarbons by soil

amended with biochar. J. Soils Sed. 11, 62-71.

Claus, J., Turner, R., Armel, G., Holliday, M., 2008. DuPont aminocyclopyrachlor (proposed common name) (DPX-MAT/KJM44) herbicide for use in turf, IWC, bareground,and brush markets. In: Proceedings of the 5th International Weed Science Congress, vol. 1. InternationalWeed Science Society, Fayetteville, AR, p. 654.

Clay, S.A., Malo, D.D. 2012. The influence of biochar production on herbicide sorption characteristics, Herbicides – Properties, Synthesis and Control of Weeds, Dr. Mohammed Nagib Hasaneen (Ed.), ISBN: 978-953-307-803-8, InTech, DOI: 10.5772/31492. Available from: http://www.intechopen.com/books/herbicides-properties-synthesis-and-control-of-weeds/the-influence-of-biochar-production-on-herbicide-sorption-characteristics. Accessed February 9, 2015.

Coffey, D.L., Warren, G.F., 1969. Inactivation of herbicides by activated carbon and other adsorbents. Weed Sci. 17, 16-19.

E.I. DuPont de Nemours and Company. 2011. DuPont™ Streamline® herbicide [product label]. Wilmington, Delaware, USA.

E.I. DuPont de Nemours and Company. 2012. DuPont land management: Use of DuPont™ Perspective®, Streamline®, and Viewpoint® herbicides near trees and shrubs. Wilmington, Delaware, USA.

Finkelstein, B.L., Armel, R.G., Bolgunas S.A., Clark, D.A., Claus, J.S., Crosswicks, R.J., Hirata, C.M., Hollinghaus, G.J., Koeppe, M.K., Rardon, P.L., Wittenbach, V.A., Woodward, M.D., 2009. DuPont DPX-MAT28 herbicide. Technical Bulletin. Reorder No.: K15023. E.I. du Pont de Nemours and Company 8 p.

Flessner, M.L., Dute, R.R., McElroy, J.S., 2011. Anatomical response of St. Augustinegrass to aminocyclopyrachlor treatment. Weed Sci. 59, 263-269.

Foo, K.Y., Hameed, B.H., 2010. Detoxification of pesticide waste via activated carbon adsorption process. J Hazard Mater. 175, 1-11.

Graber, E.R., Tsechansky, L., Gerstl, Z., Lew, B., 2012. High surface area biochar negatively impacts herbicide efficacy. Plant Soil 353, 95-106.

Goetz, A.J., Wehtje, G., Walker, R.H., Hajek, B. 1986. Soil solution and mobility characterization of imazaquin. Weed Sci. 34, 788-793.

Gustafson, D.I., 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. Environ. Toxicol. Chem. 8, 339-357.

Finkelstein, B.L., Armel, R.G., Bolgunas, S.A., Clark, D.A., Claus, J.S., Crosswicks, R.J., Hirata, C.M., Hollinghaus, G.J., Koeppe, M.K., Rardon, P.L., Wittenbach, V.A., Woodward, M.D., 2009. DuPont DPX-MAT28 Herbicide. Technical Bulletin. Reorder No.: K15023. E.I. du Pont de Nemours and Company, p. 8.

Jhala, A.J. and Singh, M. 2012. Leaching of indaziflam compared with residual herbicides commonly used in Florida citrus. Weed Technol. 26, 602-607.

Johnson, B.J. 1976. Effect of activated charcoal on herbicide injury during establishment of centipedegrass. Agron. J *68,* 802-805.

Jones D.L., Edwards-Jones, G., Murphy, D.V., 2011. Biochar mediated alterations in herbicide breakdown and leaching in soil. Soil Biol. Biochem. 43, 804-813.

Kniss, A.R., Lyon, D.J., 2011. Winter wheat response to preplant applications of aminocyclopyrachlor. Weed Technol. 25, 51-57.

Koepke-Hill, R.M., Armel, G.R., Brosnan, J.T., Breeden, G.K., Vargas, J.J., Mueller, T.C., 2012. Control of silk tree (*albizia julibrissin*) with aminocyclopyrachlor and other herbicides. Weed Sci. 60, 345-349.

Kookana, R.S., 2010. The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: a review. Soil Res. 48, 627-637.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems – a review. Mitig Adapt Strategy Global Change. 11, 403-427.

Lewis, D. F., 2012 Environmental fate and biological impact of aminocyclopyrachlor 343 in turfgrass and neighboring systems. North Carolina State, PhD Dissertation. 344 pp.152.

Lewis, D.F., Jeffries, M.D., Gannon, T.W., Richardson, R.J., Yelverton, F.H. 2014. Persistence and Bioavailability of Aminocyclopyrachlor and Clopyralid in Turfgrass Clippings: Recycling Clippings for Additional Weed Control. Weed Science: July-September 2014, Vol. 62, No. 3, pp. 493-500.

Lima, I. M., McAloon, A., Boateng, A. A., 2008. Activated carbon from broiler litter: Process description and cost of production. Biomass Bioenerg. 32, 568-572.

Lindenmayer, L., Westra, P., Brunk, G., 2009. Soil interactions with DOX-KJ44 and DPX-MAT28. Proc. Weed Sci. Soc. Am. 62, 515.

Minnesota Department of Agriculture, 2014. Pesticide sales information. http://www2.mda.state.mn.us/webapp/lis/chemsold_results.jsp. Accessed: December 29, 2014.

Minnesota Pollution Control Agency. 2014. Water types and programs: surface water. http://www.pca.state.mn.us/index.php/water/water-types-and-programs/surface-water/index.html. Accessed: February 9, 2015.

Mozammel, H., Masahiro, O., Bhattacharya, S., 2002. Activated charcoal from coconut shell using $ZnCl_2$ activation. Biomass Bioenerg. 22, 397-400.

Nanita, S.C., Pentz, A.M., Grant, J., Vogl, E., Devine, T.J., Henze, R.M. 2009. Mass spectrometric assessment and analytical methods for quantitation of the new herbicide aminocyclopyrachlor and its methyl analogue in soil and water. Anal. Chem. 81, 797-808.

National Park Service. 2015. Mississippi River facts. http://www.nps.gov/miss/riverfacts.htm. Accessed: February 9, 2015.

National Ocianic and Atmospheric Administration. 2012. NOAA scientists: Midwest drouth brings fourth smallest Gulf of Mexico 'dead zone' since 1985. July 27, 2012. http://www.noaanews.noaa.gov/stories2012/20120727_midwestdrought.html. Accessed: February 9, 2015.

OECD, 2000. OECD guidelines for the testing of chemicals, adsorption/desorption using a batch equilibrium method OECD Test Guideline, vol. 106. OECD Publications, Paris.

Ogbonnaya, U., Semple, K., 2013. Impact of biochar on organic contaminants in soil: A tool for mitigating risk? Agron J. 3, 349-375.

Oliveira Jr, R.S., Alonso, D.G., Koskinen, W.C., 2011. Sorption-desorption of aminocyclopyrachlor in selected Brazilian soils. J. Agric. Food Chem. 59, 4045-4050.

Oliveira Jr, R.S., Alonso, D.G., Koskinen, W.C., Papiernik, S.K. 2013. Comparative sorption, desorption and leaching potential of aminocyclopyrachlor and picloram. J. Environ. Sci. Heal. B 48, 1049-1057.

Patton, A.J., Ruhl, G.E., Creswell, T.C., Wan, P., Scott, D.E., Becovitz, J.D., Weisenberger, D.V. 2013. Potential damage to sensitive landscape plants from wood chips of aminocyclopyrachlor damaged trees. Weed Technol. 27, 803-809.

Rick, S. K., Turner, R.G., Meredith, J.H., 2008. Biology review of aminocyclopyrachlor. North Central Weed Sci. Soc. Proc. 63, 202.

Rupp, R.N., Edwards, M., Harbour, J., Meredith, J.H., Rick, S.K., 2011. Weed control with aminocyclopyrachlor in pastures and rangeland. Proc. Weed Sci. Soc. Am. Abstr. 49, Abstract 244.

Ryman, J., Miller, J.S., Morton, T., 2010. Aminocyclopyrachlor: Human health risk assessment for proposed uses as an herbicide. USEPA Office of Prevention, Pesticides and Toxic Substances. March 17, 2010.

Sarmah A.K., Srinivasan, P., Smernik, R.J., Manley-Harris, M., Antal, M.J., Downie, A., van Zwieten, L., 2010. Retention capacity of biochar-amended New Zealand dairy farm soil for an estrogenic steroid hormone and its primary metabolite. Aust. J. Soil Res. 48, 648-658.

Spadotto, C.A. 2002. Screening method for assessing pesticide leaching potential. Pesticidas: R.Ecotoxicol. e Meio Ambiente, Curitiba.12, 69-78

Spokas, K.A., Koskinen, W.C., Baker, J.M., Reicosky, D.C., 2009. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. Chemosphere 77, 574-581.

Spokas, K.A., 2010. Review of the stability of biochar in soils; predictability of O:C molar ratios. Carbon Manage. 1, 289-303.

Spokas, K. A., Cantrell, K. B., Novak, J. M., Archer, D. W., Ippolito, J. A., Collins, H. P., Boateng, A. A., Lima, I. M., Lamb, M. C., McAloon, A. J., Lentz, R. D., Nichols, K. A., 2012. Biochar: A synthesis of its agronomic impact beyond carbon sequestration. J. Envioron Qual. 41, 973-989.

Strachan, S.D., Nanita, S.C., Ruggiero, M., Casini, M.S., Heldreth, K.M., Hageman, L.H., Flanigan, H.A., Ferry, N.M., Pentz, A.M., 2011. Correlation of chemical analysis of residual levels of aminocyclopyrachlor in soil to biological responses in alfalfa, cotton, soybean, and sunflower. Weed Technol. 25, 239-244.

Strek, H.J., Weber, J.B., Shea, P.J., Mrozek Jr., E., Overcash, M.R., 1981. Reduction of polychlorinated biphenyl toxicity and uptake of carbon-14 activity by plants through the use of activated carbon. J. Agric. Food. Chem. 29, 288-293.

Trigo, C., Koskinen, W.C., Kookana, R.S. 2014. Sorption-desorption of indaziflam and its three metabolite in sandy soils. J. Environ. Sci. Heal. B 49, 836-843.

Uchimiya M., Lima, I.M., Klasson, K.T., Chang, S.C., Wartelle, L.H., Rodgers, J.E., 2010. Immobilization of heavy metal ions (Cu-II, Cd-II, Ni-II, and Pb-II) by broiler litter-derived biochars in water and soil. J. Agric. Food Chem. 58, 5538-5544.

U.S. Environmental Protection Agency. 2009. Guidance for selecting input parameters in modeling the environmental fate and transport of pesticides, version 2.1, October 22, 2009.

U.S. Environmental Protection Agency. 2009. National primary drinking water regulations. EPA 816-F-09-004.

U.S. Environmental Protection Agency, 2010. Pesticide fact sheet, July 26, 2010. Conditional registration, 2010; 108 pp.

USEPA/OPPTS. 2010. Ecological Risk Assessment for the Section 3 New Chemical Registration of Aminocyclopyrachlor on Non-Crop Areas and Turf. EPA-HQ-OPP-2009-0789-0004. Washington, DC: Environmental Protection Agency, Off Prevent Pest Tox Sub http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2009-0789-0004. Accessed: December 29, 2014.

U.S. Environmental Protection Agency, Jun. 27, 2012. Imprelis and Investigation of Damage to Trees. Pesticides: Regulating Pesticides. http://www.epa.gov/pesticides/regulating/imprelis.html. Aug. 27, 2013.

U.S. Geological Survey, 2014. National water-quality assessment program: 2011 Pesticide use maps. http://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2011&map=INDAZIFLAM&hilo=L&disp=Indaziflam. Accessed: December 29, 2014.

Wauchope, R.D., Yeh, S., Linders, J. BHJ, Kloskowski, R. Tanaka, K., Rubin, B., Katayama, A., Kordel, W., Gerstl, Z., Lane, M., Unsworth, J.B. 2002. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pest Manag. Sci. 58, 419-445.

Westra, P., Nissen, S., Gaines, T., Bekun, B., Lindenmayer, B., Shaner, D., 2008. Aminocyclopyrachlor for invasive weed management and restoration grass safety in the Central Great Plains. North Central Weed Sci. Soc. Proc. 63:203.

Yelverton, F. H., Worsham, A. D., Peedin, G. F., 1992. Activated carbon reduces tobacco (*Nicotiana tabacum*) injury from soil-applied herbicides. Weed Technol. 6, 310–31.