Environmental Pollution 189 (2014) 92–97

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Assessing biochar's ability to reduce bioavailability of aminocyclopyrachlor in soils

Jennifer L. Rittenhouse*, Pamela J. Rice, Kurt A. Spokas, William C. Koskinen

Agricultural Research Service, U.S. Department of Agriculture, 439 Borlaug Hall, 1991 Upper Buford Circle, St. Paul, MN 55108, United States

ARTICLE INFO

Article history:
Received 22 October 2013
Received in revised form
18 February 2014
Accepted 21 February 2014

Keywords:
Auxin
Herbicide
Aminocyclopyrachlor

ABSTRACT

Aminocyclopyrachlor is a pyrimidine carboxylic acid herbicide used to control broadleaf weeds and brush. Amending soil with activated charcoal is recommended to prevent off-site transport of aminocyclopyrachlor and non-target plant damage. We used the batch-equilibrium method to determine the concentration of aminocyclopyrachlor in a pseudo-steady state with biochar, soil, and biochar-soil systems (<10% biochar by weight). We observed that aminocyclopyrachlor is mobile in soils. Soil incorporation of activated charcoal removed nearly all of the aqueous aminocyclopyrachlor thereby limiting its bioavailability to non-target flora. On the other hand, biochars were less effective than activated charcoal. Biochar produced from olive mill waste feedstock was the most effective biochar that we assessed for reducing the aqueous herbicide concentration. Although these biochars reduced the aminocyclopyrachlor concentration, they would not be practical remediation media due to the extraordinarily high application rates required to reduce the concentration by 50% (2.13×10^5 kg ha^{-1} -7.27×10^5 kg ha^{-1}).

Published by Elsevier Ltd.

1. Introduction

Aminocyclopyrachlor (6-amino-5-chloro-2-cyclopropyl-4-pyrimidine carboxylic acid) is a new auxin herbicide in the pyrimidine carboxylic acid class of chemicals (Fig. 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).

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 physicochemical 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 et al., 2011). Due to its low sorption, aminocyclopyrachlor is mobile in soil after application (Oliveira 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 37–103 d and in non-vegetated field studies the soil half-life is 72–128 d. Studies have also observed minimal 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-

* Corresponding author.
E-mail address: Jennifer.Rittenhouse@ars.usda.gov (J.L. Rittenhouse).

http://dx.doi.org/10.1016/j.envpol.2014.02.022
0269-7491/Published by Elsevier Ltd.

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, 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.

2. Materials and methods

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.

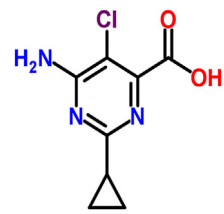

Fig. 1. Chemical structure of aminocyclopyrachlor.

Soils were submitted to Midwest Laboratories (Omaha, NE, USA) for analysis of cation exchange capacity (C.E.C.), organic matter (%O.C.), 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 loss of weight on ignition method. Soil texture was determined by the hydrometer method. A summary of the soil properties is provided in Table 1.

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 2). We also compared the wood chip 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 5–58% ash, 16–88% 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.

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 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 2.

2.3. Herbicide

Physicochemical 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 0.01 N $CaCl_2$ 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 stored at 4 °C in darkness then brought to ambient temperature prior to use. The solution radioactivity was ~150 Bq mL^{-1}.

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

Table 1
Physicochemical properties of Minnesota soils.

Soil type	C.E.C. (meq/100 g)	O.C. (%)	Sand (%)	Silt (%)	Clay (%)	Texture	pH (in $CaCl_2$)
Becker 0–15 cm depth	7.5	1.6	78	12	10	Sandy loam	5.60 ± 0.05
Becker 15–30 cm depth	7.5	1.2	82	10	8	Loamy sand	5.72 ± 0.03
Lamberton 0–15 cm depth	21.6	2.7	32	32	36	Clay loam	6.36 ± 0.02
Lamberton 15–30 cm depth	21.4	2.1	34	36	40	Clay loam	6.99 ± 0.05
Rosemount 0–15 cm depth	16.5	3.2	28	54	18	Silt loam	6.99 ± 0.07
Rosemount 15–30 cm depth	16.6	2.8	22	58	10	Silt loam	7.15 ± 0.06

Table 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
Corn stover	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

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. 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).

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 ч 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 ($t^{soil}{}_{1/2}$) × (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.

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. Results and discussion

3.1. Leachability of aminocyclopyrachlor

Our assessment of biochar use for the removal of aminocyclopyrachlor began by calculating the leaching potential of the herbicide in soil. The K_{oc} values of the evaluated soils ranged from 9.8 to 39 in the surface soils and 8.0 to 23 in the subsurface soils, as shown in Table 3. Despite the range in K_{oc} 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 surface soil, which was ranked "high" when the 37-day half-life is used in the GUS calculation (GUS = 3.8). From these data, we concluded that aminocyclopyrachlor is mobile in soil following application to turf, as other studies have already demonstrated as well (Oliveira 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).

3.2. Reducing the aqueous herbicide concentration by biochar

We compared 7 biochars, with varied chemical and physical properties (Table 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} (Fig. 2). Wood chip (WC) biochar reduced the

Table 3
Aminocyclopyrachlor concentrations and leachability in Minnesota soils.

Soil type	Concentration remaining in solution (ng ml^{-1})	Kd[a] (mL g^{-1})	KOC[b] (mL g^{-1})	GUS value[c] ($t_{1/2}$ = 37 d)	GUS value[c] (t1/2 = 103 d)	Leaching potential
Becker 0–15 cm depth	24 ± 0.93	0.63 ± 0.03	39 ± 2.1	3.8	4.8	High to very high
Becker 30–45 cm depth	12 ± 0.11	0.28 ± 0.00	23 ± 0.21	4.1	5.3	Very high
Lamberton 0–15 cm depth	14 ± 0.95	0.34 ± 0.03	13 ± 0.95	4.6	5.8	Very high
Lamberton 30–45 cm depth	7.6 ± 0.17	0.17 ± 0.00	8.0 ± 0.18	4.9	6.2	Very high
Rosemount 0–15 cm depth	13 ± 3.5	0.31 ± 0.10	9.8 ± 3.0	4.7	6.1	Very high
Rosemount 30–45 cm depth	16 ± 3.0	0.40 ± 0.08	14 ± 3.1	4.5	5.7	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})).

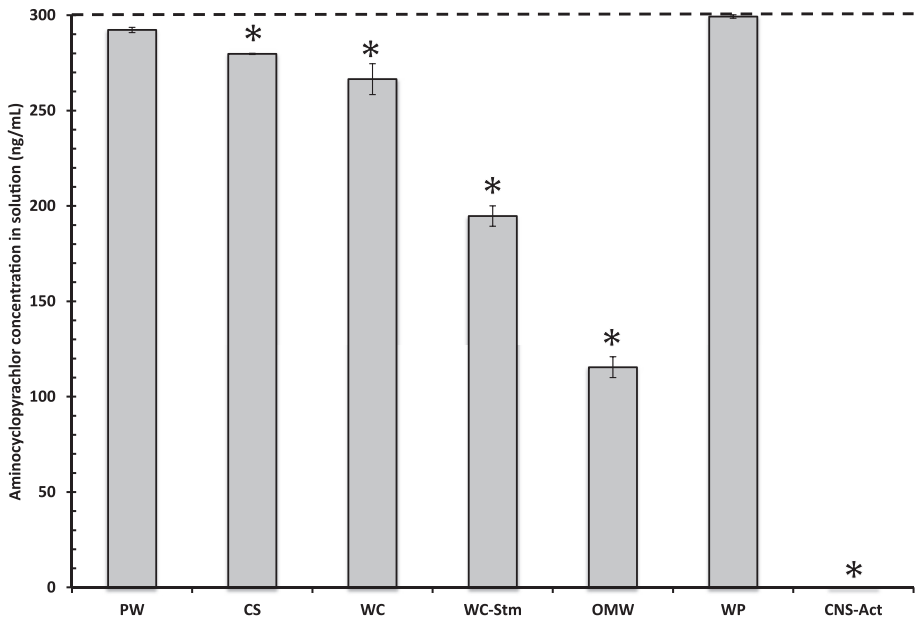

Fig. 2. Concentration (ng ml^{-1}) of aminocyclopyrachlor in solution following batch-equilibrium studies with biochars. Dashed line indicates initial solution concentration. Gray bars indicate solution concentrations from the biochar systems. Stars indicated which solution concentrations from the biochar systems are significantly different from the initial solution concentration. Biochar feedstock abbreviations: PW = pinewood; CS = corn stover; WC = wood chip; WC-Stm = steam-activated wood chip; OMW = olive mill waste; WP = wood pellet; CNS-Act = coconut shell activated charcoal.

herbicide concentration to 266 ± 8.10 ng mL^{-1} and corn stover (CS) biochar reduced it to 280 ± 0.32 ng mL^{-1}. Two biochars, pinewood (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.

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}) (Fig. 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.

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 sown to reduce the leachability of herbicides in Minnesota soils (Spokas et al., 2009). In contrast, we found that removal of aminocyclopyrachlor form 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) (Fig. 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), corn stover (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 (Ahmad 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

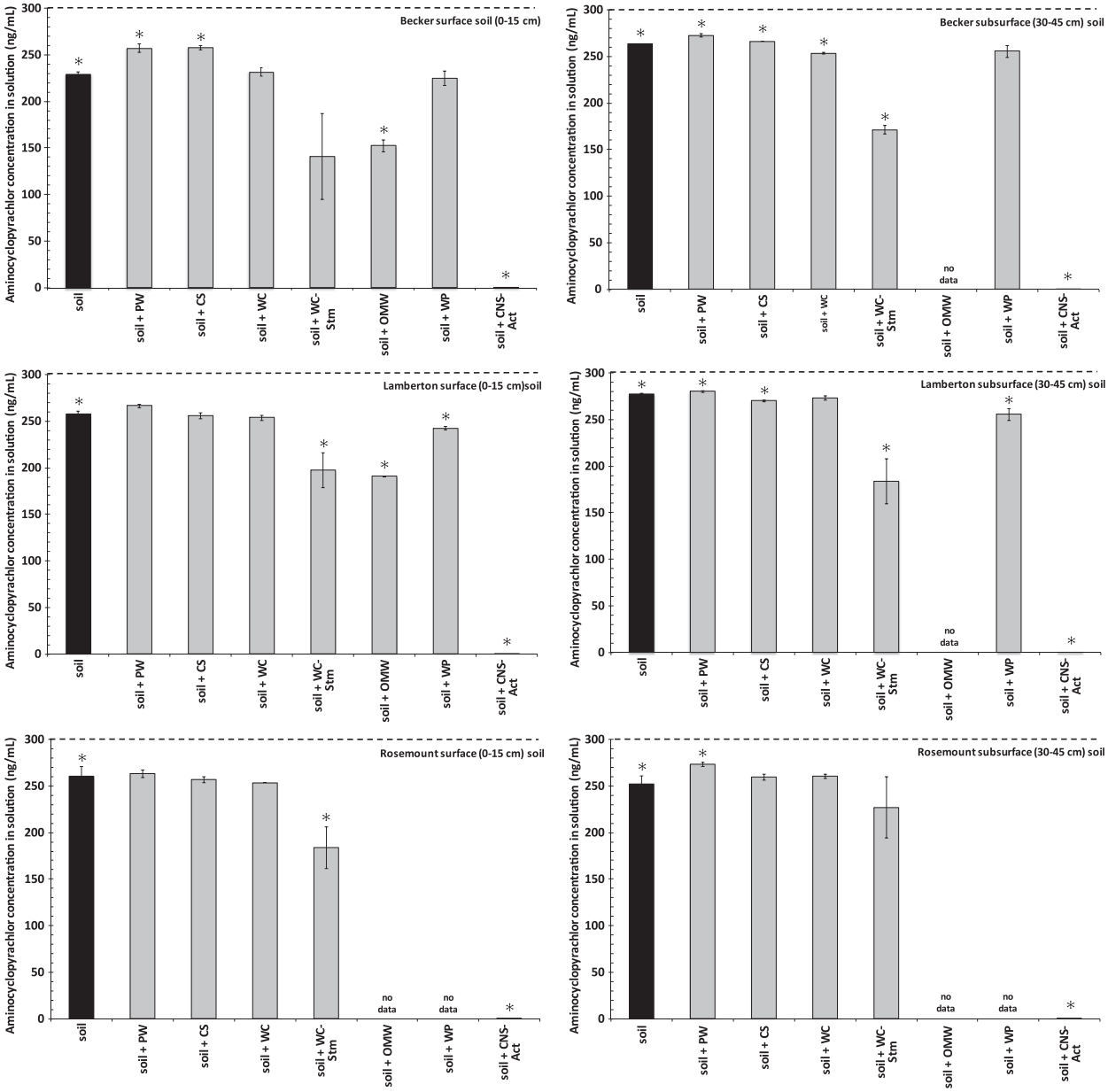

Fig. 3. Concentration (ng ml^{-1}) of aminocyclopyrachlor in solution following batch-equilibrium studies with biochar-amended soils. Dashed line indicates initial solution concentration. Black bars indicate solution concentrations from the soil-only systems. Stars above the black bars indicate the solution 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 = corn stover; WC = wood chip; WC-Stm = steam-activated wood chip; OMW = olive mill waste; WP = wood pellet; CNS-Act = coconut shell activated charcoal.

Table 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
Corn stover	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

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. 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 2.59–11.2 $\times$ 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.

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 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.

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, 2011. Fall 2011 Guidelines for Planting Trees on Properties That Have Been Treated With Imprelis Herbicide. DuPont Professional Products, Wilmington, DE.

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: Kortekamp, Andreas (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 Sediments 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. International Weed Science Society, Fayetteville, AR, p. 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, p. 8.

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 centipede grass. 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 Glob. Change 11, 403–427.

Lewis, D.F., 2012. North Carolina State, PhD Dissertation. Environmental Fate and Biological Impact of Aminocyclopyrachlor 343 in Turfgrass and Neighboring Systems, vol. 344, p. 152.

Lima, I.M., McAloon, A., Boateng, A.A., 2008. Activated carbon from broiler litter: process description and cost of production. Biomass Bioenergy 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 Bioenergy 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 Cent. 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., March 17, 2010. Aminocyclopyrachlor: Human Health Risk Assessment for Proposed Uses as an Herbicide. USEPA Office of Prevention, Pesticides and Toxic Substances.

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 Manag. 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. Environ. 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. Office of Prevention, Pesticides and Toxic Substances, Washington, DC, pp. 1–34.

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

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 Cent. 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, 310–331.