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

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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% ($2.13 \times 10^5$ kg ha$^{-1}$ –$7.27 \times 10^5$ kg ha$^{-1}$).

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## 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-

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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.

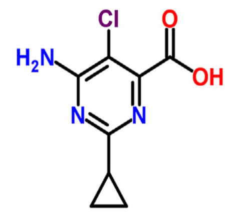


**Fig. 1.** Chemical structure of aminocyclopyrachlor.

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 $1.03 \times 10^5$ 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 ($9.0 \times 10^{-5}$) 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 ($6.92 \times 10^{-6}$ 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 |