Adsorption kinetics of the herbicide safeners, benoxacor and furilazole, to activated carbon and agricultural soils

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Abstract
Chloroacetamide herbicides, namely acetochlor and metolachlor, are common herbicides used on corn and soybean fields. Dichloroacetamide safeners, namely benoxacor and furilazole, are commonly used in formulations containing chloroacetamide herbicides. Extensive reports on adsorption of chloroacetamide herbicides are available, yet little information exists regarding adsorption potential of co-applied safeners. Herein, the adsorption and desorption characteristics of selected herbicide safeners to granular activated carbon (GAC) and in agricultural soils are reported. Further, soil column studies were performed to understand the leaching behaviour of the herbicide Dual II Magnum. Equilibrium sorption experiments of safeners to three agricultural soils and one GAC showed that adsorption was best fitted by the Freundlich isotherm. The Freundlich adsorption constant, Kf, for benoxacor and furilazole sorption onto three agricultural soils ranged from 0.1 to 0.27 and 0.1 to 0.13 (mg/g) × (mg/L)^(1/n), respectively. The Kf for benoxacor and furilazole to GAC was 6.4 and 3.4 (mg/g) × (mg/L)^(1/n), respectively, suggesting more favorable sorption of benoxacor to GAC than furilazole to GAC. The sorption to soils was reversible as almost 40%–90% of both safeners was desorbed from three soils. These results were validated in four replicated soil column studies, where S-metolachlor was shown to leach similarly to the safener benoxacor, originating from the herbicide formulation. The leaching of S-metolachlor and benoxacor was influenced by soil texture. Cumulatively, these results show that safeners will move through the environment to surface waters similarly to the active ingredients in herbicides, but may be removed during drinking water treatment via GAC.

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Introduction

Chloroacetamide based herbicide formulations commonly contain dichloroacetamides (Rosinger et al., 2012; Jablonkai, 2013). The dichloroacetamides increase the activity of glutathione S-transferase isozymes yielding the less phytotoxic enzyme-herbicide conjugate in crops thus reducing herbicide injury of crops (Miller et al., 1996; Riechers et al., 2010; Rosinger et al., 2012). When added to herbicide formulations, dichloroacetamides are referred to as herbicide “safeners” (Farago et al., 1994) and are included on herbicide labels as “inert” or “other ingredients” (Sivey et al., 2015). Two common dichloroacetamide safeners, namely benoxacor and furilazole, were recently detected in surface waters of the Mid-Western United States at concentrations up to 190 ng/L (Woodward et al., 2017). The reported detection of safeners in surface water, likely occurs due to runoff from agricultural fields on which chloroacetamide-based herbicides had been applied. These chloroacetamide based herbicides are widely used in the United States on corn, soybean and wheat crops. Further, there is likely limited photodegradation of these compounds on the surface of agricultural soils (Poudel Acharya and Weidhaas, 2018) prior to rainfall or irrigation induced runoff. While research literature extensively covers the environmental fate of several chloroacetamide herbicides and their potential for adsorption in particular (Weber and Peter, 1982; Wang et al., 1999) there is a dearth of information regarding adsorption of safeners that are co-applied with these herbicides.

Adsorption and desorption phenomena in the soil can be used to predict the leaching and distribution behaviour of herbicides and safeners (Si et al., 2009). A chemical compound in the soil-water matrix can be sorbed by various mechanisms including electrostatic interaction, ion exchange, hydrogen bonding, cation bridging and hydrophobic interactions (Kah and Brown, 2006). The application rate of any herbicide for effective weed control also depends on the adsorption-desorption processes of the herbicide in the given type of soil. The adsorbate plays a significant role in the adsorption-desorption processes. Soil texture and organic matter affect the adsorption and desorption characteristics (Long et al., 2014).

The fate and transport of herbicides metolachlor (Obrigawitch et al., 1981) and acetochlor (Linn et al., 1993) have been thoroughly investigated. For herbicide safeners to be effective, the movement of safeners through the soil profile should be similar to the movement of the active ingredients (e.g., S-metolachlor) present in the herbicide formulation (Nelson and Penner, 2007). One study on leaching of active ingredient isoxaflutole and the associated safener furilazole, through the soil profile showed that furilazole leached more slowly than the isoxaflutole (Nelson and Penner, 2007). There is no literature covering the fate of the inert ingredients, specifically the herbicide safeners benoxacor and furilazole when in combination with active ingredients metolachlor and acetochlor, respectively. One objective of this study is to evaluate the adsorption and desorption characteristics of benoxacor and furilazole in agricultural soils so as to predict the potential for runoff from farms and infiltration to groundwater. The second objective is to determine the adsorption and desorption of these safeners to granular activated carbons (GAC) typically used in drinking water treatment plants. Finally, we conducted a study to look into the leaching behaviour of S-metolachlor and benoxacor originating from the herbicide formulation Dual II Magnum.

1. Materials and methods

1.1. Reagents

Benoxacor (CAS #98730-04-2, 99% purity), furilazole (CAS # 121776-33-8, 99% purity) and S-metolachlor (CAS # 87392-12-9, 99% purity) were obtained from Sigma-Aldrich (USA). The herbicide formulation Dual II Magnum was purchased from Intermountain Farmers Association (USA). Dual II Magnum consisted of S-metolachlor as the active ingredient (82.4%) and benoxacor (<5%) included in the other ingredients (17.6%). The mobile-phase compounds, water (HPLC grade) and acetonitrile (HPLC grade), were purchased from Fisher Scientific, Inc. (USA).

1.2. Analytical method

All the samples were syringe-filtered through nylon filters with 0.45 μm pore size (FisherBrand, USA), and were analyzed via HPLC on a Shimadzu LC-2030 (USA) equipped with a UV detector. The stationary phase was a Luna Omega C18 column (150 mm × 4.6 mm ID with 3 μm particles, Phenomenex, USA). The mobile phase was acetonitrile and water at a flow rate of 0.75 mL/min with 10 μL sample injection volumes. The retention time of benoxacor was 5.02 min and the monitored wavelength was 253 nm. The retention time of furilazole was 4.92 min and the monitored wavelength was 218 nm. S-metolachlor was monitored at a wavelength of 220 nm and had a retention time of 7.59 min. The column compartment temperature was maintained at 40°C. Lab Solutions software from Shimadzu (USA) was used for identification and quantification of the safeners and S-metolachlor. The analytical detection limits were 0.01 mg/L for the safeners and 0.1 mg/L for metolachlor.

1.3. Soil and GAC preparation and characterization

Three different soils (1, 2 and 3) were used in these studies to determine safener soil adsorption characteristics. The top 7 cm of soils (i.e., in the A soil horizon) were collected from a wildlife management area (soil 1) and two agricultural fields (soils 2 and 3) in the Jefferson and Bonneville counties of Idaho. Soil 1 was collected from an undisturbed marsh. Soil 2 was collected from an agricultural field that had been under cultivation for more than 100 years and was planted in alfalfa at the time of sampling. Soil 3 was collected from an undisturbed marsh. Soil 2 was collected from an agricultural field that had been under cultivation for more than 75 years and was lying fallow after harvest of wheat. No information was available regarding the application of pesticides to the fields in prior years. The soils were air-dried for 48 hr, then ground with a mortar and pestle. Each soil sample was sieved through a 2 mm sieve and stored at room temperature in a
plastic bag until further testing. The sieved soils were used for all further adsorption-desorption experiments. For the soil column studies three additional soils were collected from three locations: from a dig site on the University of Utah campus (soil 4), a field in Centerville Utah (soil 5), and a hayfield in Huntsville Utah (soil 6) respectively. The soils were brought to the lab, air-dried and then sieved through a 2 mm sieve and stored until use. The sand for the soil column was commercial sand, sieved through a 2 mm sieve, air-dried and acid washed to remove organics following previously published methods (Bolster et al., 2009; Mantha et al., 2017). All six soils were characterized for texture, pH and organic matter. The specific surface area of soil 1, 2 and 3 was measured with a BET (Brunauer-Emmett-Teller) analyzer using the ASTM D3663-03 method using nitrogen gas (Brame and Griggs, 2016).

To determine if benoxacor and furilazole were present in the agricultural soils prior to use in these studies, the ultrasonic extraction procedure of the EPA method 3550C (USEPA, 2007) was used. One g of soil was mixed with 10 mL of hexane, and the samples were extracted twice by ultra-sonication for 15 min in an ultrasonic water bath (Branson, USA). After extraction, the samples were centrifuged at 8000 r/min for 6 min. The samples were then syringe filtered into the vial for analysis of benoxacor and furilazole through the HPLC. It was found that the soil used in these studies did not contain any of the safeners after collection from the field.

The GAC used in these studies was untreated, granulated activated charcoal made from a peat bog (Sigma Aldrich, USA). This GAC was a Norit Carbon, commonly used in towers to purify gases and liquids. The vendor previously characterized the GAC as having a BET surface area of 600–800 m²/g with a particle size of 0.85–2.4 mm (8–20 mesh). The GAC was rinsed with deionized water until the rinse water was completely clear and then dried overnight at 105°C. The same batch of rinsed GAC was used for all sorption experiments. Surface morphology of the GAC was visualized using scanning electron microscopy (SEM) with a Hitachi TM3030 Plus Tabletop SEM microscope (USA) at a 100×, 800× and 1800× magnification (Fig. 1).

1.4. **Soil pH, organic matter content, and size characterization**

Soil pH was measured according to the Method 9045D (Black et al., 1965). Five g of soil was added to 5 mL of deionized water and the mixture was shaken on a shaker table for about 15 min and then allowed to equilibrate for 1 hr. A pH meter (VWR, USA) was used to take the pH readings. The readings were taken at a room temperature of 21.2°C. Three replications were measured. Organic matter content of the soil was determined using the loss upon ignition ASTM D-2974-87 method (ASTM, 2014). The organic matter was converted to organic carbon percent by using the standard conversion where percent organic carbon content is 1.72 times the percent organic matter (Douglas, 2010). Soil particle size was determined using the hydrometer, ASTM 152 H method (Bouyoucos, 1962). Replicate, 40 g quantities of oven dried soil (105°C) was passed through a No. 10 mesh sieve (<2.0 mm) and used to determine percent sand, silt and clay.

1.5. **GAC sorption and desorption**

A batch equilibrium experiment (OECD, 2000) was conducted to study the adsorption-desorption of benoxacor and furilazole to
GAC. The stock solutions containing 3, 8 and 12 mg/L of benoxacor and 8, 26, and 32 mg/L of furilazole were made in deionized water. Various masses of GAC (5, 10, 20, 50, and 100 mg) were weighed in baked Pyrex bottles, and 100 mL of stock solution was added to each bottle. The bottles were placed on a shaker table at room temperature (22 °C) and were kept in the dark to prevent photodegradation. Control bottles were prepared similarly, but without GAC. Concentrations of safeners in the solution were determined at 1, 3, 6, 20, 48, 94, and 168 hr.

The pseudo-first-order and pseudo-second-order model were examined for fit to the experimental GAC sorption data using previously published methods (Sun et al., 2012). The linear expression of the pseudo first-order model is expressed as Eq. (1):

\[
\ln (q_t - q_e) = \ln (q_e) - k_1 \times t
\]

(1)

The linear expression of the pseudo second-order model is expressed as Eq. (2):

\[
t/\left(q_t\right) = 1/\left(k_2 \times q_e^2\right) + t/\left(q_e\right)
\]

(2)

where, \(q_t\) (mg/g) and \(q_e\) (mg/g) are the mass of benoxacor or furilazole sorbed per unit mass of sorbent at equilibrium and time, \(t\) (hr), respectively. The \(q_t\) at a time, \(t\), was calculated as Eq. (3):

\[
q_t = (c_0 - c_t) \times V/M_a
\]

(3)

where, \(C_0\) (mg/L) is the concentration of safener at an initial time; \(C_t\) (mg/L) is a concentration of safener at time, \(t\); \(V\) (L) is the volume of the solution and \(M_a\) (g) is the mass of GAC used. The coefficient of determination, \(R^2\), was used to select the most appropriate kinetic model using previously published methods (Ho, 2006).

After the sorption study was completed, the supernatant was removed carefully after centrifugation, retaining the GAC, and 10 mL of deionized (DI) water was added to the bottles. The GAC was mixed with DI water on a shaker table for 24 hr, at which point the concentration of safeners in solution was determined. Desorption was calculated by subtracting the mass of safeners in the solution after 24 hr of desorption equilibrium from the mass of safeners still adsorbed to the GAC as determined by the mass balance of safeners.

1.6 Soil sorption and desorption

Soil adsorption and desorption studies were performed following a similar experimental protocol as the GAC sorption. A preliminary experiment was conducted to find the equilibrium time for the sorption of safeners onto the soil. The soil to reach equilibrium was 72 hr for all soils. Various masses of soil were weighed (1, 2, 3 and 5 g) and 15 mL of various concentrations of safeners prepared in 0.01 mol/L CaCl2 solution. The initial concentration of benoxacor was varied from 4 to 21 mg/L while furilazole concentrations varied from 1 to 48 mg/L. The concentrations after 72 hr was determined by HPLC and were fitted to sorption isotherms. Desorption studies were conducted immediately after sorption by carefully removing the supernatant by centrifugation while retaining the soil. Five mL of methanol was added to the soils and shaken for 72 hr at 140 r/min at 22 °C. Concentrations of safener in methanol were estimated by HPLC and were used to determine the mass desorbed from the soil. Methanol was used as extraction solvent since no desorption was observed with water in an earlier study with GAC (data not shown). A standard curve for benoxacor and furilazole dissolved in methanol was determined to use in analyzing soil desorption results. Controls, not including soils, were included in the study and did not show any loss of safeners due to biodegradation or other abiotic mechanisms.

1.7 Sorption and desorption isotherms

Three sorption models (i.e., Linear, Freundlich and Langmuir) were tested to determine which best fit the sorption of benoxacor and furilazole to the GAC and agricultural soils. Based on the goodness of fit (\(R^2\) value, the Freundlich isotherm was determined to most appropriately model the safener sorption in these studies. The Freundlich sorption isotherm is

\[
\log(q_e) = \log(K_f) + 1/n \times \log(C_0)
\]

(4)

where, \(C_0\) (mg/L) is the aqueous equilibrium phase solute concentration, \(K_f\) ((mg/g) × (mg/L)/(L/n)) is the Freundlich constant that gives a measure of the adsorbent capacity and \(n\) gives a measure of the intensity of sorption or desorption (Dada et al., 2012). The goodness of fit was based on the coefficient of determination (\(R^2\)).

1.8 Soil column leaching study

The leaching behaviour of Dual II Magnum, a herbicide formulation containing benoxacor and metolachlor, was studied in four different replicate columns, one acid washed sand column and three different soil types (soils 4, 5 and 6). The soils were air-dried, ground and sieved through a 2 mm sieve (USA standard testing sieves, Size 10, ASTM). The columns consisted of 36 cm long and 5.7 cm internal diameter polyvinyl chloride (PVC) cylinders. The bottom of the PVC columns was closed using glass fiber wool to retain soil while permitting the flow of water and herbicide formulation. The glass fiber wool was kept at the bottom of the column with a steel wire mesh and tightened with a steel screw and nut. The bottom 2.5 cm of the column was filled with gravel for good drainage followed by a small amount of glass fiber. The column was then filled with the soil selected for that treatment up to a depth of 15 cm.

The water displacement method was used to measure the porosity of soil columns. The empty PVC cylinder and PVC cylinders with soils or sand were submerged in water. Porosity was calculated based on the difference in volumes of water displaced between the empty PVC column and the packed PVC column. Porosity was determined just before starting the soil column experiments.

The Dual II Magnum formulation was diluted 104-fold prior to adding one liter to the top of the columns. A total
of 6 or 7 pore volumes of the water passing through each soil column was collected. The samples collected were syringe filtered (0.45 μm nylon filters, Fisher Scientific, Inc., USA) and the pesticide compounds, benoxacor and S-metolachlor, were analyzed via HPLC. The electrical conductivity (VWR, USA) was measured in all collected samples.

Destructive sampling of the soil in the soil columns was done immediately after the cessation of gravity flow from the columns. All the soil columns used in the study were segregated into four different sections, each approximately 3.8 cm in length. The four separate layers were then homogenized independently and ground using a mortar and pestle. Approximately 0.5 g of soil subsample was taken from each section and extraction of S-metolachlor and benoxacor was performed. The extraction of S-metolachlor and benoxacor from the soil was done by adding 5 mL of acetonitrile to 0.5 g of soil. The solution was then shaken in a shaker at 180 r/min for 20 min. The solution was then syringe filtered (0.45 μm nylon filters, Fisher Scientific, Inc., USA) and the pesticide compounds, benoxacor and S-metolachlor, were analyzed via HPLC.

1.9. Data analysis

SigmaPlot 11® (Systat Software Inc., USA) was used to produce plots. Pearson Product Moment correlation coefficient of soil properties with adsorption coefficients was calculated with Sigma Stat with a p = 0.05.

2. Results

2.1. Soil characterization

The soils (1, 2, and 3) used in adsorption and desorption studies were characterized for texture, pH, organic matter and surface area. The organic matter (OM) percentage varied from 4.1% to 6.9% for three soils (Table 1). The clay percentage ranged from 31% to 55% and the sand percentage ranged from 15% to 40%. The BET surface area for the soils 1, 2, and 3 were 64, 24, and 8 m²/g, respectively. Soils 4, 5, and 6 used for soil column studies were also characterized for pH, organic matter and texture (Table 1). The organic matter content of soil 4, 5, and 6 was between 1.9% and 6.8%, respectively. Soil 4 had the lowest content of clay percentage (23.9%) followed by soil 5 (38.2%) and soil 6 (44.8%) with the soil texture of sandy clay loam, clay loam and clay respectively.

2.2. GAC sorption and desorption of benoxacor and furilazole

The pseudo-second order sorption kinetics were found to fit the GAC sorption data (Fig. 2) suggesting that the sorption rate is controlled by chemical sorption and the sorption capacity is proportional to the number of active sites on the sorbent (Ho and McKay, 1999). Kinetic parameters and the coefficients of determination are shown in Table 2. The Freundlich adsorption isotherm of benoxacor and furilazole onto GAC is shown in Fig. 3. The Freundlich constants, Kf and n, and the corresponding coefficient of determination R² for sorption and desorption are given in Table 3. From sorption kinetics on GAC (Fig. 2), the equilibrium concentration for both the safeners was reached at less than 24 hr. The Ce ranged from 0.03 to 2 mg/L for benoxacor and from 0.6 to 11 mg/L for furilazole. The goodness of fit criterion R² for the Freundlich sorption isotherm was 0.88 and 0.91 for benoxacor and furilazole, respectively, showing that this isotherm is a good fit for the given experimental conditions. The adsorption capacity constant, Kf, for benoxacor and furilazole to GAC is 6.4 and 3.4 (mg/g) × (mg/L)¹/n, respectively. The parameter to measure the intensity of sorption, n, for benoxacor and furilazole was 1.4 and 0.80, respectively, suggesting furilazole has more favorable sorption than benoxacor onto GAC. Desorption intensity, n, for benoxacor was close to one for GAC, indicating that desorption was independent of concentration for the range of concentrations examined in this study. A mass balance was performed on the amount of safener at the beginning and after sorption and desorption. A wide range of benoxacor (3%–99%) was adsorbed to GAC while only 1.5%–16% of it was desorbed based on mass balance calculations. For furilazole, the adsorption percentage ranges from 65% to 97%, and was irreversible for most drinking water applications as less than 0.02% (mass basis) was desorbed when de-ionized water was used.

2.3. Batch study soil sorption and desorption of benoxacor and furilazole

Pseudo-second order sorption kinetics were found to fit the sorption of benoxacor to soils 1, 2 and 3 (Table 2 and Fig. 2c).

### Table 1 – Soil characteristics for soils used for isotherms (soils 1, 2 and 3) and for soil column leaching (soils 4, 5 and 6).

<table>
<thead>
<tr>
<th>Parameter (n)</th>
<th>Unit</th>
<th>Soil 1</th>
<th>Soil 2</th>
<th>Soil 3</th>
<th>Soil 4</th>
<th>Soil 5</th>
<th>Soil 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>OM (2)</td>
<td>%</td>
<td>6.9 (0.05)</td>
<td>4.1 (0.18)</td>
<td>4.8 (0.99)</td>
<td>1.9 (0.1)</td>
<td>5.3 (0.1)</td>
<td>6.8 (0.2)</td>
</tr>
<tr>
<td>OC (2)</td>
<td>%</td>
<td>12.0 (0.11)</td>
<td>7.0 (0.43)</td>
<td>8.2 (0.20)</td>
<td>3.3 (0.17)</td>
<td>9.1 (0.17)</td>
<td>11.8 (0.34)</td>
</tr>
<tr>
<td>pH (3)</td>
<td>SU</td>
<td>7.1 (0.01)</td>
<td>8.1 (0.04)</td>
<td>7.7 (0.01)</td>
<td>7.1 (0.03)</td>
<td>7.0 (0.03)</td>
<td>6.8 (0.06)</td>
</tr>
<tr>
<td>BET (3)</td>
<td>m²/g</td>
<td>63.6 (0.7)</td>
<td>23.6 (0.3)</td>
<td>7.6 (0.2)</td>
<td>NM</td>
<td>NM</td>
<td>NM</td>
</tr>
<tr>
<td>Clay (2)</td>
<td>%</td>
<td>55.5 (1.4)</td>
<td>35.5 (2.8)</td>
<td>31.7 (0.01)</td>
<td>23.9 (1.8)</td>
<td>38.2 (3.6)</td>
<td>44.5 (1.8)</td>
</tr>
<tr>
<td>Silt (2)</td>
<td>%</td>
<td>29.1 (1.3)</td>
<td>24.1 (2.8)</td>
<td>30.5 (1.3)</td>
<td>20.1 (1.8)</td>
<td>31.8 (0.1)</td>
<td>30.5 (1.8)</td>
</tr>
<tr>
<td>Sand (2)</td>
<td>%</td>
<td>15.5 (0.1)</td>
<td>40.4 (0.01)</td>
<td>37.8 (1.3)</td>
<td>55.9 (0.1)</td>
<td>30 (3.2)</td>
<td>24.9 (3.6)</td>
</tr>
<tr>
<td>Soil class</td>
<td></td>
<td>Clay</td>
<td>Clay loam</td>
<td>Clay loam</td>
<td>Sandy clay loam</td>
<td>Clay loam</td>
<td>Clay</td>
</tr>
</tbody>
</table>

Mean (standard deviation), n: number of replicate analyses.
Sorption of benoxacor to the soils reached equilibrium within 94 hr. The adsorption and desorption isotherms of benoxacor and furilazole to the three soils are shown in Fig. 4. The adsorption and desorption isotherm parameters for benoxacor and furilazole to the three different soils and GAC are shown in Table 3. The Freundlich sorption isotherm was found to be the best fit for both benoxacor ($R^2 = 0.80$ to $0.88$) and furilazole ($R^2 = 0.8$ to $0.90$) for the various soils. The $K_f$ values for benoxacor sorption onto three soils ranged from 0.1 to 0.27. The $K_f$ values for furilazole sorption ranged from 0.1 to 0.13. The intensity of sorption ($n$) ranged between 0.6 to 2.4 and 1.2 to 1.4 for benoxacor and furilazole, respectively, for three soils. Soil 1 has $n < 1$ for benoxacor indicating that sorption is favorable in this soil; this soil has almost 7% OM, 55% of clay, and a higher BET surface area. For furilazole, soil 2 had a desorption concentration below the detection limit and is therefore not reported.

### 2.4. Correlation of sorption parameters with soil properties

The Pearson product moment correlation between the adsorption coefficients, $K_f$ and $n$, and the soil properties (pH, organic carbon percent, and clay percent) was determined. A significant correlation was found between the percentage of organic carbon and the adsorption parameter for benoxacor.
There was no significant relationship among other variables.

2.5. Column study

The results of leaching of formulation Dual II Magnum through replicated sand columns and three different soil columns is shown in Fig. 5. Both benoxacor and S-metolachlor exhibit similar transport rates through the soil columns. Breakthrough of the herbicide and safener were delayed compared to the conservative tracer (1 mol/L NaCl). Further, increasing clay content increased the retardation of S-metolachlor and benoxacor transport as evidenced by the delay in a breakthrough for soil 6, a clay soil (Fig. 5d) compared to soil 4, a sandy clay loam soil (Fig. 5b). Increasing clay content in soils also resulted in greater sorption of both metolochlor and benoxacor as shown in Fig. 6. Herbicide and safener distribution on the soil after leaching showed that most benoxacor and S-metolachlor was found on top of the column in case of soil 6 which has the highest percentage of clay (Fig. 6). In the case of soil 4 which is a sandy clay loam soil, most of the compounds were found at the bottom of the column. Therefore, the leaching of the herbicide and safener are both influenced by the soil texture, particularly clay content of the soil. Also, the amount of both of the compounds sorbed to the soil after the leaching experiment was also affected by the clay content of the soil.

3. Discussion

3.1. Sorption of safeners to GAC during water treatment

It is important to understand the mechanism of adsorption and desorption of any chemical compound for predicting the environmental fate of contaminants. The mechanism of adsorption is both a physical and chemical process that holds the safeners at the interface between the liquid and solid phases. The common mechanism of the adsorption of safeners onto GAC (non-polar) is the stronger attractive forces between the carbon surface and the safener (non-polar) than the forces between the safener and water (polar) (DeSilva, 2000). Since furilazole is moderately soluble and benoxacor is not very soluble (Poudel Acharya and Weidhaas, 2018), the adsorption capacity ($K_f$) is higher for benoxacor than for furilazole, as expected. The $K_f$ and $n$ values estimated for the dichloroacetamides benoxacor and furilazole in these soils were lower than those reported for the chloroacetamides metolachlor (i.e., $K_f$ from 0.3 to 6.1 when $n$ is 1.06 (Kodešová et al., 2011)) and acetochlor (i.e., $K_f$ from 5 to 12 when $n$ ranges from 1.01 to 1.27 (Bedmar et al., 2011)). Others have suggested an inverse linear relationship between the adsorption coefficient and water solubility in organic pollutants (Kleineidam et al., 2002). The higher adsorption capacity of benoxacor compared to furilazole, might also be because benoxacor is smaller than furilazole. A previous study

![Fig. 3 - Sorption of benoxacor and furilazole to granular activated carbon. $C_0$ benoxacor: 3, 8 and 12 mg/L; $C_0$ furilazole: 8, 26 and 32 mg/L. The 95% confidence limit on the regressions are shown as dashed lines.](image-url)

Table 3 – Adsorption and desorption isotherm parameters for benoxacor and furilazole associated with three soils and a granulated activated carbon.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Comp</th>
<th>$C_e$ range (mg/L)</th>
<th>Adsorption</th>
<th>Desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sorbed (%)$^a$</td>
<td>$K_f^b$</td>
</tr>
<tr>
<td>GAC</td>
<td>B</td>
<td>0.03–2</td>
<td>92 (7)</td>
<td>6.4</td>
</tr>
<tr>
<td>GAC</td>
<td>F</td>
<td>0.6–11</td>
<td>81 (12)</td>
<td>3.4</td>
</tr>
<tr>
<td>Soil 1</td>
<td>B</td>
<td>0.2–8.5</td>
<td>57 (20)</td>
<td>0.10</td>
</tr>
<tr>
<td>Soil 2</td>
<td>B</td>
<td>0.4–11.3</td>
<td>76 (17)</td>
<td>0.27</td>
</tr>
<tr>
<td>Soil 3</td>
<td>B</td>
<td>1.4–19.5</td>
<td>43 (18)</td>
<td>0.17</td>
</tr>
<tr>
<td>Soil 1</td>
<td>F</td>
<td>0.3–18.7</td>
<td>42 (14)</td>
<td>0.13</td>
</tr>
<tr>
<td>Soil 2</td>
<td>F</td>
<td>2.7–36.8</td>
<td>19 (8)</td>
<td>0.10</td>
</tr>
<tr>
<td>Soil 3</td>
<td>F</td>
<td>4.5–45.5</td>
<td>27 (19)</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Comp: compound; B: benoxacor; F: furilazole; N: number of observations; BQL: below quantitation limit.

$^a$ Average (standard deviation) of initial mass of safener sorbed to soils or GAC and percentage of initial mass sorbed that was recovered with methanol extraction for soils or DI water extraction for GAC. $^b$ $(mg/g) \times (mg/L)^{1/n}$. 
Salman et al., 2011) showed that the adsorption differences are due to molecular size. In contrast, the sorption intensity, $n$, of furilazole onto GAC was less than one which indicated that furilazole sorption was favorable. These results suggest that GAC can be used for the removal of benoxacor and furilazole in the treatment system and during any chemical spills. This study shows that clean water will not drive desorption of safeners from the GAC. While there was not a quantifiable desorption of furilazole from the GAC in these studies, this may be due to the limited concentration ranges used in this study that did not cover the solubility range up to 232 mg/L. Had higher concentrations been used in these studies, safener desorption may have been detected.

Since both safeners have been found in Mid-Western Streams (Woodward et al., 2017) these safeners may be present in drinking water systems. However, studies herein suggest GAC can be used to remove these safeners thus minimizing the risk humans. Additional work on the occurrence of safeners in source waters and drinking water systems along with the assessment of the toxicity of safeners in aquatic organisms and to humans is necessary. These studies also suggest GAC could be a good alternative for the cleanup of sites during the accidental spillage of these safeners. Others have reported on the use of GAC to remove the pesticides carbofuran and bentazon from aqueous solution (Salman et al., 2011).

### 3.2. Understanding safener agricultural and environmental fate

Adsorption and desorption of compounds from various materials directly influence the compounds persistence, transport into and mobility in groundwater (Cohen et al., 1986). In the batch studies herein, the sorption intensity, $n$, for the soils 2 and 3 and for both safeners were greater than one, indicating less favorable sorption. Adsorption of benoxacor and furilazole in three tested soils (soils 1, 2, and 3) was found to be weak. Further, the desorption of both safeners from all soils was less than the amount initially adsorbed similar to that reported for acetochlor (Hiller et al., 2009). Although these

<table>
<thead>
<tr>
<th>Soil properties (Correlation coefficient, p value)</th>
<th>pH</th>
<th>Organic carbon percent</th>
<th>Clay percent</th>
<th>BET area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_f / C^2$ benoxacor</td>
<td>0.99, 0.06</td>
<td>$-0.99$, 0.046</td>
<td>$-0.87$, 0.32</td>
<td>$-0.83$, 0.37</td>
</tr>
<tr>
<td>$K_f / C^2$ furilazole</td>
<td>$-0.59$, 0.598</td>
<td>0.71, 0.491</td>
<td>0.94, 0.22</td>
<td>0.96, 0.16</td>
</tr>
</tbody>
</table>
Fig. 5 – Breakthrough curves of benoxacor and metolachlor following the application of commercial formulation Dual II Magnum along with electrical conductivity. The solid and open symbols represent two columns of the same soil type. Plot a represents the sand column, plot b, c and d are for soils 4, 5 and 6 respectively.
results could not conclude the adsorption-desorption behavior was hysteretic various others have reported hysteresis behavior for acetochlor (Tatarkova et al., 2014) and metolachlor (Otero et al., 2012). Column studies showed breakthrough of benoxacor and S-metolachlor at similar times and some sorption of benoxacor to the soils. Therefore, both batch and column studies suggest there is a potential for safener leaching to groundwater, especially at higher application rates. Safener migration to groundwater is especially likely if rainfall occurs soon after application of herbicide formulations containing these safeners. This safener transport is likely influenced by soil properties.

It has long been known that metolachlor can leach into groundwater (Masse et al., 1994). In some cases metolachlor has been found to be weakly adsorbed to the soil, suggesting it can move downward with percolating water (Wu et al., 2011). In contrast, varying reports of acetochlor leaching have been published. For example, early reports suggested acetochlor and two of its metabolites could infiltrate to a depth of 70 cm when applied to luvisol and calcisol soils (Baran et al., 2004). Yet, later reports suggested no migration of acetochlor in Haplic Chernozem soils in field trials (Jursík et al., 2013). To date, no studies have been reported on the leaching of benoxacor from soils and only one study investigated furilazole leaching. Specifically, it was found that furilazole leached from the area of herbicide application when applied together with isoxaflutole (Nelson and Penner, 2007).

The properties of soils selected for the batch study were not found to be significantly correlated with adsorption and desorption parameters of safeners except for organic carbon. This might be because the three soils did not differ enough with respect to organic matter (i.e., differing by only 5%) and clay percentage (i.e., soils 1, 2 and 3 being clays or clay loams) to have a significant difference in adsorption. Extensive research has been done studying the influence of soil properties on adsorption and desorption of various pesticides, sometimes with widely contrasting results. Adsorption of metolachlor and acetochlor was shown to be positively correlated with soil organic matter (Obrigawitch et al., 1981; Weber and Peter, 1982; Si et al., 2009), clay content (Kodešová et al., 2011), and the surface area of soils (Peter and Weber, 1985) and negatively correlated with clay content (Bedmar et al., 2011). The relative percentage of sand, silt, and clay in the soil affect the persistence of herbicides in soil through processes like adsorption-desorption, biodegradation, and leaching (Wu et al., 2011). Future studies with soils varying properties, with regards to organic carbon and texture, would be able to address the influence of soil properties on the adsorption and desorption of safeners. Also, conducting the experiments at various temperatures, soil moisture contents, and pH is necessary to model the various scenarios that occur in actual field conditions.

4. Conclusions

In summary, these results show that the adsorption-desorption of the safeners was best fit with the Freundlich isotherm. The adsorption capacity and intensity parameters suggest that GAC can be used for the removal of benoxacor and furilazole in the treatment system and during any chemical spills. Both batch and column studies suggest there is a potential for safener leaching to groundwater, especially at higher application rates. The soil properties did not have an influence on the adsorption of safeners except for organic carbon and the adsorption parameter \( n \) for benoxacor. Future studies on soils with varying properties with regards to organic carbon and texture would be able to address the influence of soil properties on the adsorption and leaching behavior of safeners. These studies aid in the understanding of the potential fate and transport of herbicide safeners co-applied with active herbicide ingredients during agricultural management.

**REFERENCES**


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**Fig. 6** – Distribution of S-metolachlor (a) and benoxacor (b) along the soil columns after leaching through the soil column with herbicide formulation Dual II Magnum.


USEPA, 2007. SW-846 Method 3500C: Ultrasonic extraction, part of test methods for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges and wastes. Available at: https://www.epa.gov/hw-sw846/sw-846-

