Sorption and desorption of bicyclopyrone on soils

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Abstract

Bicyclopyrone is an herbicide that is marketed for the control of herbicide-resistant weeds. However, there is a lack of extensive data on its sorption and factors that control its sorption in the soil system. In this study, we evaluated a series of 25 different soils, with a variety of properties to determine if an empirical relationship could be developed to predict the sorption coefficient for bicyclopyrone. Overall, there were no statistically significant relationships observed with organic carbon, cation exchange capacity, or clay content. There was a moderate negative correlation with soil pH ($R = -0.61$). Additionally, Freundlich isotherm analysis suggests that the partitioning coefficient ($K_D$) value could adequately characterize the sorption behavior for the range of soils evaluated here.

1 INTRODUCTION

Bicyclopyrone {1R,5S)-3-[hydroxy-[2-(2-methoxyethoxy-methyl)-6-(trifluoromethyl)pyridin-3-yl]methylidene]bicyclo[3.2.1]octane-2,4-dione; BCP)} is a selective herbicide that inhibits 4-hydroxyphenylpyruvate dioxygenase (HPPD) in susceptible plants. It was first registered by Syngenta Crop Protection, LLC for use in the USA in 2015 and in Canada around the same time. Bicyclopyrone is typically used in mixtures and is marketed under the trade names of Talinor and Acuron (Syngenta) for the control of broadleaf and grass weeds in maize (Zea mays L.), barley (Hordeum vulgare L.), and wheat (Triticum aestivum L.) crops. In particular, it is promoted for use against weeds that have developed resistance to glyphosate, acetolactate synthase (ALS) inhibitors, and auxinic herbicides (Benoit, Soltani, Hooker, Robinson, & Sikkema, 2019; Kumar, Liu, Boyer, & Stahlman, 2019; Sarangi & Jhala, 2017; Striegel et al., 2020). Products containing BCP may be applied pre-emergence or post-emergence (e.g., Benoit, 2019); however, superior control has been observed with post-emergence application (Burriss et al., 2018).

Little is published in the peer-reviewed literature regarding the environmental fate of BCP. It is reported to have variable persistence in soils (half-lives of 20–357 d) and is subject to photolysis but not hydrolysis in aqueous solutions (FAO, 2017). Bicyclopyrone has a pKa of 3.06 (AMVMA, 2017) and is reported to be moderately persistent in soil.
Sorption of BCP to soil is reported to be hysteretic and highly variable, with organic carbon–normalized sorption coefficients \( \left( K_{oc} \right) \) ranging from 0 to 500, and little correlation between sorption and soil organic carbon content has been observed (APVMA, 2017).

Sorption–desorption in soils is one of the key factors controlling the availability of herbicides, which has implications not only for weed management but also for the tendency of herbicides to leach and carry over to sensitive crops. Because of BCP’s low sorption in some soils, product labels include advisories against applying BCP to permeable soils and soils with shallow water tables (Syngenta Crop Protection, 2017). Limited assays showed that carryover of BCP applied alone did not inhibit growth of select subsequent cover crops (Brooker, Sprague, & Renner, 2020), but mixtures including BCP inhibited development of a rye \( (Secale cereale \ L.) \) cover crop under some conditions (Pridie, Clay, & Shaffer, 2020). Given the limited information regarding the sorption–desorption of BCP in soils, we report here the sorption and desorption of BCP in a wide variety of soils to better characterize the environmental fate of this herbicide.

### 2 MATERIALS AND METHODS

#### 2.1 Soils

A total of 25 soils were collected across multiple soil series with diverse characteristics (see Table 1). Soils were collected from the 0-to-10-cm depth interval, dried at 105 °C for 24 h, sieved to 2 mm, and analyzed for total carbon and nitrogen by combustion (Elementar Variomax Cube), pH (in 1:1 deionized water slurry), cation exchange capacity, and soil texture.

#### 2.2 Batch \( k_D \) determination—Single concentration

Bicyclopyrone sorption was determined on each soil in triplicate using the batch equilibration method with radiolabeled BCP. The \(^{14}\text{C}\) spiking solution for BCP was prepared by diluting \(^{14}\text{C}\)-bicyclopyrone \( \text{[pyridinyl-3-}^{14}\text{C]} \); specific activity = 95.3 \( \mu \)Ci mg\(^\text{−1}\); 8,880 Bq mmol\(^{−1}\); 99.5% purity] with unlabeled BCP (Syngenta Crop Protection, LLC), which resulted in a stock solution of 10 mg L\(^{−1}\) with an overall activity of 1,090 Bq mL\(^{−1}\) (65,450 disintegrations min\(^{−1}\) ml\(^{−1}\)). A 0.5-ml aliquot of this spiking solution was added to 9.5 ml of 0.01 M CaCl\(_2\) to achieve a 10-ml solution volume. This solution (0.5 mg L\(^{−1}\) BCP) was added to 1 g of soil in a 20-ml glass scintillation vial for a series of 25 different USDA soil series. Samples were then placed horizontally on a reciprocal shaker and allowed to equilibrate for 24 h (180 rev min\(^{−1}\)) in the dark. Following centrifugation (20 min, 1,500 \( \times \) g), 2 ml of supernatant was removed and filtered (0.45 \( \mu \)m). Then a 1-ml aliquot of the filtered solution was mixed with 5 ml of scintillation cocktail \[\text{EcoLite}(+); \text{MP Biomedicals, LLC}\] and analyzed for \(^{14}\text{C}\) by liquid scintillation counting (LSC) (HITACHI AccuFLEX LSC-8000, GMI Ramsey; 10-min counting window). No statistically significant sorption of the BCP to scintillation vials, syringes, or syringe filters was observed (98–100% recovery; data not shown). The sorbed concentration of BCP on the soil was estimated by the following:

\[
C_s = \frac{(C_i - C_e)}{m} V
\]

where \( C_i \) is the initial concentration (mg L\(^{−1}\)), \( C_e \) is the equilibrium concentration (mg L\(^{−1}\)), \( V \) is the total volume of the liquid phase (L), and \( m \) is the mass of the soil (g). The equilibrium concentration was determined by the LSC of the liquid phase using the following equation:

\[
C_e = \frac{(\text{LSC}_e - \text{Blank}) \times C_i}{\text{LSC}_i}
\]

where LSC\(_e\) is the disintegrations per minute of the sample following equilibration with the soil, Blank is the disintegrations per minute of the scintillation cocktail and vial alone, \( C_i \) is the liquid phase concentration of the initial standard (mg L\(^{−1}\)), and LSC\(_i\) is the disintegration of the corresponding BCP standards (without soil added). The partitioning coefficient \( (K_D) \) was estimated by the following:

\[
K_D = \frac{C_s}{C_e}
\]

#### 2.3 Sorption isotherms—Multiple concentrations

Sorption isotherms were generated for 7 of the 25 soils, which were selected based on the initial single-concentration screening to cover a range of observed \( K_D \) values. The isotherm was
TABLE 1 Table of soil properties, sorption coefficient ($K_D$), desorption coefficient ($K_D$), and Freundlich isotherm model coefficients determined in this study

| USDA Soil Series | OC (%) | N | Sand | Clay | CEC cmol kg$^{-1}$ | pH | Avg. Sorption ($K_D$) | SD | Avg. Desorption ($K_D$) | SD | $K_f$ | $1/n$ | $R^2$ |
|------------------|--------|---|------|------|-------------------|----|----------------------|----|------------------------|----|-------|-------|-------|
| Alvin            | 1.10   | 0.05 | 77   | 3    | 7.9               | 4.7 | 0.74                  | 0.03 | 0.99*                  | 0.02 |        |       |       |
| Barnes           | 2.85   | 0.21 | 48   | 18   | 32.5              | 6.0 | 0.54                  | 0.17 | 0.74                   | 0.20 |        |       |       |
| Bluford          | 0.79   | 0.07 | 37   | 4    | 12.9              | 6.4 | 0.18                  | 0.07 | 0.16                   | 0.02 | 0.187  | 1.27  | 0.939 |
| Cisne-A          | 1.09   | 0.11 | 27   | 17   | 19.1              | 6.1 | 0.06                  | 0.06 | 0.10                   | 0.03 |        |       |       |
| Cisne-E          | 0.79   | 0.07 | 31   | 17   | 20.0              | 4.8 | 2.31                  | 0.14 | 3.23*                  | 0.38 |        |       |       |
| Coxville         | 2.63   | 0.18 | 42   | 15   | 3.7               | 5.2 | 2.41                  | 0.07 | 1.64                   | 0.98 | 0.998  |       |       |
| Crane            | 2.50   | 0.15 | 15   | 26   | 26.1              | 4.6 | 1.88                  | 0.07 | 2.60*                  | 0.18 |        |       |       |
| Drummer          | 5.21   | 0.27 | 43   | 8    | 25.2              | 7.0 | 0.69                  | 0.02 | 1.21*                  | 0.19 | 0.556  | 1.07  | 0.957 |
| Fayette          | 1.68   | 0.11 | 25   | 10   | 15.9              | 5.8 | 0.61                  | 0.12 | 1.02*                  | 0.19 |        |       |       |
| Hubbard          | 0.95   | 0.03 | 84   | 7    | 6.3               | 6.2 | 0.75                  | 0.10 |                       |     |        |       |       |
| Huey             | 0.93   | 0.09 | 31   | 14   | 16.4              | 5.8 | 0.12                  | 0.12 | 0.09                   | 0.18 |        |       |       |
| Ipava            | 1.38   | 0.08 | 21   | 15   | 19.9              | 5.7 | 0.61                  | 0.07 | 0.97                   | 0.21 |        |       |       |
| Langhei          | 2.53   | 0.13 | 51   | 20   | 58.7              | 7.9 | 0.38                  | 0.27 |                       |     |        |       |       |
| Maryland         | 3.63   | 0.32 | 50   | 20   | 54.7              | 7.8 | 0.97                  | 0.06 |                       |     |        |       |       |
| Oakville         | 1.54   | 0.10 | 89   | 3    | 10.0              | 4.2 | 4.19                  | 0.32 | 5.81*                  | 0.47 | 3.999  | 0.93  | 0.992 |
| Osco             | 1.47   | 0.15 | 26   | 15   | 16.5              | 5.8 | 1.08                  | 0.03 | 1.56*                  | 0.04 |        |       |       |
| Oska-Marting     | 1.34   | 0.11 | 10   | 43   | 31.7              | 4.9 | 2.82                  | 0.05 | 4.23*                  | 0.05 |        |       |       |
| Portneuf         | 0.48   | 0.01 | 15   | 65   | 40.2              | 7.6 | 0.39                  | 0.11 |                       |     | 0.206  | 1.16  | 0.930 |
| Rollins-Cloquet  | 0.85   | 0.02 | 85   | 4    | 2.2               | 5.1 | 2.95                  | 0.10 | 4.49*                  | 0.33 |        |       |       |
| Swygert          | 2.46   | 0.14 | 30   | 29   | 24.3              | 6.1 | 0.71                  | 0.08 | 1.17*                  | 0.18 |        |       |       |
| Tifton           | 0.70   | 0.02 | 80   | 11   | 1.4               | 5.9 | 0.28                  | 0.10 | 0.45                   | 0.24 |        |       |       |
| Verndale         | 1.40   | 0.19 | 75   | 15   | 7.5               | 6.1 | 0.69                  | 0.19 |                       |     |        |       |       |
| Vilas            | 0.22   | 0.01 | 87   | 10   | 8.9               | 5.9 | 1.40                  | 0.19 |                       |     |        |       |       |
| Waukegan         | 2.50   | 0.20 | 19   | 28   | 21.1              | 6.0 | 0.88                  | 0.08 | 1.31*                  | 0.70 | 0.791  | 0.98  | 0.990 |
| Zimmerman        | 0.50   | 0.01 | 95   | 3    | 2.6               | 5.8 | 0.15                  | 0.07 | 0.09                   | 0.04 | 0.265  | 1.12  | 0.886 |

*CEC, cation exchange capacity; $K_f$, Freundlich constant; N, total nitrogen; OC, organic carbon.

*Indicates a significant difference between the sorption and desorption $K_D$ values.

created using initial BCP solution concentrations of 0.1, 0.5, 1, 2.5, 5, 10, and 20 mg L$^{-1}$. Individual samples were run in duplicate using methods analogous to the single concentration batch $K_D$ determination described above. Equilibrium liquid ($C_e$) and solid ($C_s$) concentrations were then analyzed by fitting to linear forms of four different sorption models: Langmuir, Freundlich, Temkin, and the Dubinin–Radushkevich models (Horsfall, Spiff, & Abia, 2004; Hunt & He, 2015).

2.4 Desorption studies

Desorption studies were conducted for a subset of 17 soils that ranged from 0.5 to 5.2% organic carbon. First, BCP was sorbed following the procedures described in the single-concentration batch $K_D$ determination except that a 5-ml aliquot of supernatant was removed after the first 24-h equilibration period and the initial adsorption was determined. Desorption of the herbicides was accomplished by replacing the 5-ml aliquot removed from the equilibrated vial with 5 ml of fresh 0.01 M CaCl$_2$ containing no BCP. The vials were vortexed to disperse the soil sample into solution, mechanically shaken as previously described for 24 h, and then recentrifuged. The concentration of BCP present in the aqueous solution after the 24-h desorption period was determined by LSC, as previously described. The newly established $K_D$ was then calculated and compared with the original adsorption $K_D$.

2.5 Statistical analysis

All data for the $K_D$ determination were conducted in triplicate, with means and standard deviations of the measurements
3 RESULTS AND DISCUSSION

Data for the soil physical and chemical properties, along with the determined BCP $K_D$ at 0.5 mg L$^{-1}$, are shown in Table 1. The $K_D$ ranged from 0.06 to 4.19 L kg$^{-1}$ for the soils evaluated. Of the measured soil properties, only soil pH was significantly correlated to $K_D$ ($R = -0.61, p < 0.05$). The other soil properties evaluated, including soil organic carbon (OC) and clay content, were not significantly correlated to the measured BCP-$K_D$ values. The $K_{OC}$ values were not calculated since OC was not a primary sorption mechanism, which is typically assumed for agrochemical sorption processes (Braschi, Gessa, & Blasioli, 2011). The sole correlation of BCP sorption and pH suggests that BCP mobility would be the lowest in acidic soils, and the compound would not necessarily be retained in alkaline soils regardless of the OC content. Results from other triketone herbicides including mesotrione and sulcotrione show an increase in sorption with decreasing pH (Dumas et al., 2017; Dyson, Beulke, Brown, & Lane, 2002). Dumas et al. (2017) reported that for sulcotrione and mesotrione, clay content is often correlated with sorption, with OC having a lesser impact. A lack of correlation with soil organic matter suggests that sorption $K_D$ values (not OC-normalized
$K_{OC}$ on specific soils are needed to accurately predict BCP soil residues for potential carryover and off-field movement assessments, as has been observed for other triketone herbicides (Barchanska et al., 2017).

The desorbed $K_D$ values are shown in Table 1. There was a strong correlation between the $K_D$ (sorption) and the $K_D$ (desorption) ($R^2 = .994$; $p < .05$). The only factor that was significantly correlated with desorption $K_D$ was again the soil pH ($R = −.76$; $p < .05$). There was a significant increase in the value of $K_D$ with the single step desorption for 11 of the 17 soils (Table 1). For soils with a $K_D$ sorption value of $>1$ L kg$^{-1}$, there was significant hysteresis with the desorption $K_D$ higher than the sorption $K_D$. Additionally, no relationship was observed between any of the measured soil properties and the ratio of the sorption $K_D$ to the desorption $K_D$, indicating that hysteresis could not be predicted based on soil properties. Overall, there was an average of 30% desorption of the initially sorbed BCP across all the soils evaluated in the single desorption step in 24 h. Studies have shown that sorption of other triketone herbicides is at least partially reversible (Dumas et al., 2017).

The sorption data fit to the four isotherm models are presented in Figure 1. The Freundlich isotherms provided the best fit for the seven selected soils; the model fitting coefficients are presented in Table 1. This improved fit of the Freundlich isotherm suggests a large degree of heterogeneity in the soil binding sites for BCP (Adamson & Gast, 1967). The values for the Freundlich constant, $K_f$, ranged from 0.2 to 3.99 and were well correlated with the previously determined $K_D$ values ($R^2 = .969$). The values of 1/$n$ ranged from 0.93 to 1.27; however, there was no clear relationship between 1/$n$ and $K_f$ as is typically observed for chemical sorption across a range of soil types (e.g., Ebato, Yonebayashi, & Kosaki, 2001).

With the exception of soil pH, no correlation was statistically significant between the soil properties assessed here and the soil BCP-$K_D$ value. The $K_D$ of BCP spanned nearly two orders of magnitude in the agricultural soils tested (Table 1), and we determined that a soil-specific sorption $K_D$ (not the OC-normalized $K_{OC}$) may be more appropriate for parameterizing environmental fate or water quality models to predict potential BCP soil residues and off-field movement. Additional research is needed to better predict the conditions that present an increased risk of environmental contamination by BCP.

**DATA AVAILABILITY STATEMENT**

Data for this article are available at doi:10.5061/dryad.70rxwdbwd.

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**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

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