ALFALFA, CUCUMBER, DRY BEAN, AND SUGARBEET RESPONSE TO BICYCLOPRYONE AND MESOTRIONE

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ABSTRACT

ALFALFA, CUCUMBER, DRY BEAN, AND SUGARBEET RESPONSE TO BICYCLOPRYONE AND MESOTRIONE

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Bicyclopyrone and mesotrione are HPPD-inhibiting herbicides (Group 27) registered for use in corn. Greenhouse and field experiments were conducted to evaluate alfalfa, cucumber, black bean, kidney bean, and sugarbeet response to bicyclopyrone and mesotrione. In the greenhouse, cucumber, black bean, kidney bean, and sugarbeet were more sensitive to mesotrione compared with bicyclopyrone. Sugarbeet was the most sensitive crop to bicyclopyrone and mesotrione followed by alfalfa with cucumbers being the most tolerant. In field research, bicyclopyrone at 50 and 100 g ha^{-1} (1 and 2X rate), and mesotrione at 210 g ha^{-1} were applied in early June to V4 corn at two locations in 2015 and 2016. The following spring, alfalfa and sugarbeet were planted in mid-April, cucumber and dry edible bean were planted in mid-June and crop response was measured. In 2016, injury was less than 20% for all crops, regardless of herbicide treatment at either location. However, at East Lansing 2017 sugarbeet was severely injured and did not survive where mesotrione was applied the previous year. Sugarbeet and kidney bean injury was 15 and 5%, respectively, from the 2X rate of bicyclopyrone. Neither mesotrione or bicyclopyrone affected crop growth or yield at Richville in 2017. While there were differences in soils at the two locations, rainfall within the first 30 days following application most likely contributed to differences in herbicide carryover. From this research it appears that alfalfa, dry bean, or cucumber can be planted the year following mesotrione or bicyclopyrone application. However, sugarbeet should not be planted the year following applications of mesotrione or bicyclopyrone and the crop rotation restriction should be 18 months or longer.

Dedicated to my wife Natasha, my brother Jacob, and my parents Doug and Bev Wilkinson

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

LITERATURE REVIEW

Introduction

Bicyclopyrone is a newest registered 4-hydroxyphenylpyruvate dioxygenase (HPPD) inhibiting herbicide (WSSA Group 27) (Dunne 2012). Bicyclopyrone is a member of the triketone chemical family. This family of compounds was discovered through targeted synthesis of leptospermone originally discovered in the root systems of the bottlebrush plant (*Callistemon citrinus* (Cornes 2006). Bicyclopyrone has preemergence (PRE) and postemergence (POST) activity on both large and small-seeded broadleaf weeds, as well as some grasses (Chen et al. 2018). Bicyclopyrone premixed with s-metolachlor and mesotrione, with and without atrazine is marketed as Acuron and Acuron Flexi (Anonymous 2016a; Anonymous 2018a), respectively, in corn (*Zea mays* L.) and is combined with bromoxynil and sold under the trade name of Talinor (Anonymous 2016b) in wheat (Triticum aestivum). In 2022, it may also be registered as a solo product in minor crops (Chen et al. 2018). The use rate of bicyclopyrone in premixtures is 50 g ha^{-1}. Bicyclopyrone is very similar in chemical structure and activity to another triketone herbicide, mesotrione, which is widely used across the United States in corn (Dunne 2012). However, bicyclopyrone had greater safety to many minor crops when compared with mesotrione (Chen et al. 2018; Felix et al. 2007; Riddle et al. 2013), and in many cases, there is greater than a 12-month rotation interval for planting other crops following mesotrione applications. Currently, there is little known about the persistence of bicyclopyrone and its effects on rotational crops.

Alfalfa (*Medicago sativa* L.), cucumber (*Cucumis sativus* L.), dry bean (*Phaseolus vulgaris* L.), and sugarbeet (*Beta vulgaris* L.) are economically important crops to Michigan. In

2019, Michigan growers planted 331,600 ha of alfalfa, 9,570 ha of cucumber, 38,400 ha of black bean, 1,200 ha of kidney bean, and 65,560 ha of sugarbeet (USDA 2020). Each of these crops have known sensitivities to mesotrione (Felix et al. 2007; Soltani et al. 2007; Riddle et al. 2013; Robinson 2008). Among crop production in the United States, Michigan ranks as one of the top four states in marketable alfalfa, cucumber, black bean, kidney bean, and sugarbeet and ranks first in production in both black bean and pickling cucumber (USDA 2020). Due to the diverse number of crops grown in Michigan and possibilities for herbicide carryover, mesotrione and most of the HPPD inhibiting herbicides are generally limited to use in corn-soybean (*Glycine max* L.), and corn-soybean-wheat rotations. The current rotation restrictions for mesotrione is 10 months prior to planting alfalfa and 18 months for cucumber, dry bean, and sugarbeet (Anonymous 2018b). If the rotation restrictions for bicyclopyrone are shorter than the rotation restrictions for mesotrione to sensitive crops, bicyclopyrone could replace mesotrione where sensitive crops are planted in rotation.

HPPD-inhibiting Herbicides

The Group 27, HPPD-inhibiting herbicides are named because they bind to the 4-hydroxyl-phenyl-pyruvate dioxygenase (HPPD) enzyme within the plant (Dunne 2012). Currently, the HPPD inhibiting herbicides consist of four chemical families: isoxazoles, pyrazoles, pyrazolones, and triketones (Wang et al. 2014). The HPPD-inhibiting herbicides are part of the non-heme Fe (II)-dependent dioxygenase family with the ability to convert 4-hydroxphenylpyruvate (HPPA) into a homogentisate (HGA) (Cornes 2006; Kupper et al. 2018). Homogentisate is a key compound for the biosynthesis of plastoquinone, which is essential to produce phytoene desaturase, a critical enzyme for carotenoid biosynthesis (Wang et al. 2014).

Carotenoids are needed to protect chlorophyll and plant cell membranes during photosynthesis (Cornes 2006). The disruption of photosynthesis caused by HPPD inhibitors results in the white or bleached appearance of sensitive plants (Riddle et al. 2013). HPPD-inhibiting herbicides could aid in controlling mayweed chamomile (*Anthemis cotula L.*) and prickly lettuce (*Lactuca serriola L.*) in corn and small grain production fields were resistance to ALS inhibitors, auxin receptors, and photosystem II inhibitors have been discovered (Martin et al. 2018).

Isoxazoles. Isoxaflutole was one of the first HPPD-inhibiting herbicides discovered that is still widely used in corn and sugar cane (*Saccharum officinarum* L.) production throughout the world (Papiernik et al. 2007). Isoxaflutole was registered in 1998 and is used as a preemergence herbicide to control grass and broadleaf weeds (Papiernik et al. 2007; Sprague et al. 1997; Taylor-Lovell et al. 2002). Once isoxaflutole is absorbed by the plant it is converted to diketonitrile (DKN) which is toxic to the plant (Papiernik et al. 2007). Diketonitrile degrades overtime into an inactive benzoic acid product (Mougin et al. 2000). The amount and speed of degradation or metabolism in the plant determines isoxaflutole selectivity, with susceptible plants metabolizing isoxaflutole at a slower rate. Susceptible plants exhibit the classic HPPD-inhibiting herbicide symptoms of white leaf tissue, followed by necrotic tissue, and leading to plant death (Mougin et al. 2000). Isoxaflutole currently has a 10-month rotation restriction for alfalfa grown in all geographies and sugarbeet grown east of the Mississippi river (Anonymous 2019a). There is an 18-month rotation restriction for cucumber and dry bean. However, this is contingent on receiving 38 cm of rain following isoxaflutole application to the rotational crop planting. Isoxaflutole is water soluble (6.8 mg/L) and cannot be applied on soils where the water table is in the top 7.6 cm of soil (Papiernik et al. 2007; Shaner 2014). The high leaching potential of isoxaflutole reduces the carryover potential from season to season (Papiernik et al. 2007).

Pyrazoles. Pyrasulfotole is a member of the pyrazole chemical family and is registered for postemergence use in small grains, and for preemergence use in timothy (Reddy et al. 2012). Pyrasulfotole provides excellent broadleaf weed control in small grains and is generally sold as a premixture with bromoxynil to increase the spectrum of broadleaf weed control (Fromme et al. 2012; Reddy et al. 2012). Pyrasulfotole inhibits plastoquinone biosynthesis that leads to a decrease in carotenoids, therefore stopping the plant's ability to complete photosynthesis (Reddy et al. 2012). Bleaching of plant tissue and eventual tissue death results as the plant cannot complete the photosynthesis process. Pyrasulfotole is decomposed in the soil by microorganisms (Wardell Boersma et al. 2019). As soil pH increases, pyrasulfotole is more available in the soil for plant absorption (Wardell Boersma et al. 2019). Crop rotation restrictions for pyrasulfotole tend to be shorter compared with other HPPD-inhibiting herbicides and are 4 months for alfalfa, 9 months for dry edible bean and sugarbeet, and 12 months for cucumber (Anonymous 2016c; Wardell Boersma et al. 2019).

Pyrazolones. Topramezone is currently the only HPPD-inhibiting herbicide registered in the United States in the pyrazolone chemical family (Grossman and Ehrhardt 2007). Topramezone was discovered by BASF in 2005 and is used for selective postemergence weed control in field and sweet corn (Rahman et al. 2014; Soltani et al. 2007a). Topramezone primarily provides broadleaf weed control, however when it is tank-mixed with atrazine there is a synergistic affect that enhances both broadleaf and annual grass weed control (Bollman et al. 2008; Soltani et al.

2007b). Like other HPPD-inhibitors, topramezone prevents carotenoid biosynthesis, causing leaf bleaching, plant necrosis, and plant death (EPA 2005). Topramezone is primarily decomposed by microorganisms in the soil but also through adsorption to soil particles when the soil is acidic (EPA 2005). In bare ground studies, topramezone had a 3 to 29 d time to 50% dissipation (DT_{50}) value which is longer than most HPPD inhibitors (EPA 2005). Due to the longer persistence in the soil, the crop rotation restriction for alfalfa is 9 months and 18 months for cucumber, dry bean, and sugarbeet (Anonymous 2017).

Triketones. There are currently three herbicide active ingredients registered for use in the United States in the triketone chemical family. These include mesotrione, tembotrione, and most recently bicyclopyrone (Sprague 2020). One of the first triketone herbicides developed and still widely used in the United States is mesotrione (Mitchell et al. 2001). Mesotrione was developed by Syngenta Crop Protection and released as a herbicide in 2001 for control of small-seeded broadleaf and some grass weeds in corn (Dunne 2012; Felix et al. 2007; Riddle et al. 2013). Mesotrione is a synthetic herbicide derived from the bottlebrush plant (Cornes 2006). The bottlebrush plant was found to produce leptospermone which had herbicidal properties, but it was unsuitable as a commercial herbicide. While mesotrione is primarily used as a corn herbicide it is registered for use in several other minor crops in the United States, including asparagus (*Asparagus officinalis L.*), rhubarb (*Rheum rhabarbarum L.*), and several fruits (Anonymous 2018b). Corn has shown a natural tolerance to mesotrione by rapidly metabolizing mesotrione into inactive products through the cytochrome P450 enzyme (Dumas et al. 2017). Mesotrione has a half-life of between 3 and 65 d, but degradation is slowed in soils with more acidic pH values due to greater soil adsorption (Dyson et al. 2002). Mesotrione is not very mobile in soil or soluble in water and therefore is seldom found below 10 cm depth in the soil profile. Also, mesotrione is the most persistent in sandy to sandy loam soils and less persistent in clay soils (Riddle et al. 2013). Mesotrione crop rotation restrictions are 18-months for cucumber, dry bean, and sugarbeet, and 10-months for alfalfa (Anonymous 2018b).

Tembotrione is another triketone herbicide for use in corn (Williams and Pataky 2008). Tembotrione was first registered by Bayer Crop Science in 2009. Tembotrione is often used to control small-seeded broadleaf and some annual grass weeds (Bollman et al. 2008). Tembotrione is primarily a postemergence herbicide that inhibits the plant's ability to create essential enzymes needed to complete photosynthesis (Kupper et al. 2017). Though tembotrione is labeled for use in corn, tembotrione has caused severe phototoxicity and plant death to certain sweet corn varieties (Williams and Pataky 2008). Tembotrione is often characterized as a compound that is non-volatile, highly soluble, and stable in water (Kupper et al. 2017). Tembotrione can be absorbed by plants at twice the rate as mesotrione but has a half-life as short as 12 h in ideal conditions (Kupper et al. 2017). This shorter half-life allows for less plant absorption at lower temperatures when compared with mesotrione which has a longer half-life (Kupper et al. 2017). While a reduced half-life can negatively affect weed control with tembotrione, this characteristic makes it a safer option for crop rotation to sensitive crops. Tembotrione has similar rotation restrictions as mesotrione with a 10-month rotation restriction to alfalfa and an 18-month rotation restriction to cucumber, dry bean, and sugarbeet (Anonymous 2019b).

The newest member of the triketone chemical family is bicyclopyrone. Bicyclopyrone was developed by Syngenta Crop Protection and was registered for use in 2015 (Accinelli et al. 2015). Bicyclopyrone controls small and large seeded broadleaf weeds, as well as a few grasses in field corn, sweet corn, popcorn, sugarcane, and wheat (Baalouch et al. 2012). Currently, bicyclopyrone is only registered for use in premixtures to control a broader weed spectrum, and to aid in controlling glyphosate-resistant weeds (Sarangi and Jhala 2017). Bicyclopyrone is primarily used as a preemergence herbicide, but it has postemergence activity as well (Accinelli et al. 2014). Currently, very little information is published on the carryover potential of bicyclopyrone, except for a study published by Dunne (2012) that examined the carryover potential of bicyclopyrone to soybean across the Midwest. In this study, the only consistent carryover from bicyclopyrone to soybean was at the two farthest north locations in Michigan and South Dakota when bicyclopyrone was applied at 200 and 400 g ha^{-1}, 4 and 8X the labeled use rate. Soil characteristics at these two locations were very different. The only conclusion Dunne (2012) was able to make was that the potential for bicyclopyrone carryover was related to the shorter growing seasons, that reduced soil microbial activity that is needed for bicyclopyrone degradation.

Figure 1.1. Chemical structures of HPPD-inhibiting herbicides in the isoxazole, pyrazole, pyrazolone, and triketone chemical families.

Bicyclopyrone **Mesotrione** **Tembotrione**

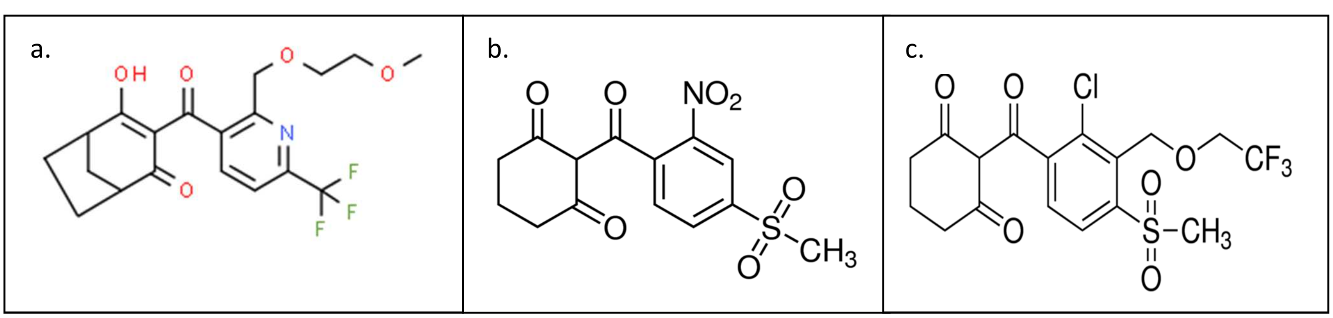
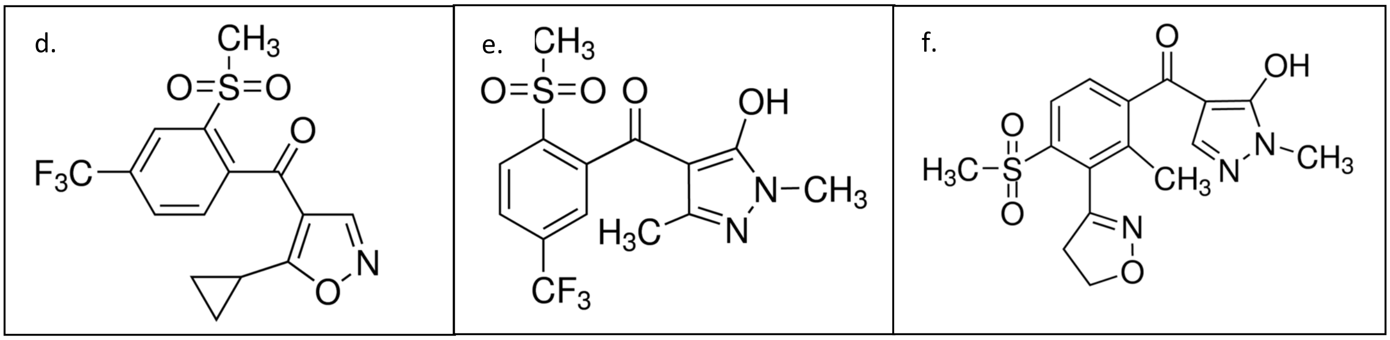


Figure 1.1(cont'd)

Isoxaflutole **Pyrasulfotole** **Topramezone**



Factors Affecting Herbicide Persistence

Herbicides are the most used pesticide in conventional agricultural production systems across the United States. When choosing a herbicide several key factors need to be considered prior to application including crop tolerance, weed susceptibility, expected length of weed control, and rotational crop restrictions (Felix et al. 2007; Riddle et al. 2012; Robinson et al. 2006). Herbicide active ingredients differ in their chemical half-lives and the half-life of an herbicide determines the likelihood of a herbicide's ability to persist from one-season to the next (Bailey 2003). Herbicides with longer half-lives provide extended weed control throughout a season, but at a certain point longer persisting herbicides start to affect the next season's crop. Crops response to herbicide residues differs greatly based on crop species and cultivars. This is especially noticeable with herbicide carryover to dry edible bean (Felix et al. 2007; Robinson et al. 2006; Soltani et al. 2007b). Soltani et al. (2007b) found that white bean was more tolerant to mesotrione residues followed by black bean, and then kidney and cranberry bean, showing that both white and black bean could be planted the season following mesotrione applications to corn. Other crops also have varying degrees of susceptibility to mesotrione residues. Riddle et al. (2013) examined mesotrione carryover to sugarbeet, cucumber, green bean, peas (*Pisum sativum*

L.), and soybean over a two-year period. Sugarbeet injury from mesotrione ranged from 6 to 100%, while cucumber was more tolerant. Differences in these responses are often influenced by herbicide half-lives in soils and are dependent on soil type, organic carbon, soil pH, and most importantly weather.

Herbicide properties. The potential for a herbicide to carry over to the following season's rotational crop starts with the physical and chemical properties of the herbicide. The physical characteristics of a herbicide are measured using the log Kow, water solubility, soil adsorption coef, Koc, and pKa (Dunne 2012; Dyson et al. 2002; Taylor-Lovell et al. 2000). Log Kow is used to predict the adsorption of a herbicide to soil and other living organisms. The log Kow is also inversely related to water solubility. For example, the log Kow for bicyclopyrone and mesotrione is 1.58 and 1.49, respectively (Dunne 2012). The water solubility of these herbicides at 25 C is 138.7 and 157.5 for bicyclopyrone and mesotrione, respectively. Based on the log Kow and water solubility values, bicyclopyrone is slightly less water soluble than mesotrione, suggesting that it would take more rainfall to move bicyclopyrone through the soil profile compared with mesotrione. Due to the high solubility value and low soil adsorption coefficient, bicyclopyrone fluxes in the soil profile, allowing it to move through the soil profile following heavy rainfall or irrigation event, and potentially moving back into the top 1 cm of the soil profile (Hand et al. 2015). Bicyclopyrone is relatively mobile in soil with a Koc of 13.11 at pH 6 (Dunne 2012). Both bicyclopyrone and mesotrione are weak acids with a pKa values of 3.06 and 3.1, respectively. Weak acids can break bonds from the uncharged forms to anionic forms as pH increases (Dyson et al. 2002). Based on similar pKa, Kow, and water solubility values between bicyclopyrone and mesotrione it can be hypothesized that bicyclopyrone will likely have a similar carryover potential as mesotrione.

Soil Characteristics. Agricultural soils are comprised of sand, silt, clay, and organic matter (Dyson et al. 2002). The amount of sand, silt, and clay determines the texture of the soil. Agricultural fields are not uniform and can be comprised of many soil types and topographies. Topographical changes can lead to changes not only in soil textures, but in soil pH and organic matter. These soil characteristics not only factor into crop production, but into herbicide dissipation or degradation.

Soil Texture. Soil texture is the physical size ranges of particles that comprise the soil profile primary composed of different percentages of sand, silt, and clay (Fernandez-Illescas et al. 2001). These three textural groups are further broken down into 12 different classes based on the percentages of sand, silt, and clay. The 12 textural classes include: sandy clay, clay loam, silty clay, sandy clay loam, loam, silty clay loam, sandy loam, silt loam, loamy sand, clay, sand, and silt (Fernandez-Illescas et al. 2001). Each of these textural classes have different porosity values. The porosity of a soil refers to the macro- and micro-pores of the soil that water filters through. In agricultural settings macropores allow for substances to be moved through the soil profile that are dissolved in water. Soils with more macropores have increased movement of herbicides through the soil profile and out of a plant's rooting zone. Herbicides are also able to bind to soil particles (Wardell Boersma et al. 2019). Each herbicide binds differently to soil particles making them either available or unavailable for plant uptake and environmental degradation. For example, Loux and Reese (1993) were able to determine that imazethapyr was more available in a silt loam soil compared with a clay soil using unaged soil samples. Imazethapyr was also more likely to carryover in fine and medium soils with high organic matter, like clay and silt soils compared with coarse textured soils with low organic matter, thus showing the importance of the soil textural class and organic matter when predicting herbicide carryover.

Soil pH. Soil pH can also be a predictor for herbicide degradation and likely plays a significant role in the carryover potential and crop response of rotational crops (Felix et al. 2007; Shaner et al. 2012). Chaubane et al. (2005) determined that mesotrione desorption was as high as 30% with alkaline soils (high soil pH) compared with soils with lower pH. The potential for mesotrione carryover increases as soil pH decreases. Dunne (2012) reported mesotrione carryover to soybean could occur when soils were more acidic, below 5.5. Dunne (2012) also reported that when anhydrous ammonia is knifed into the soil, anhydrous ammonia can cause a localized pH decrease causing the soil to become more acidic. This would favor localized carryover concerns in field with mesotrione applications. Dyson et al. (2002) found that mesotrione sorption and degradation rates were equally proportioned to soil pH and soil organic carbon, as pH decreased mesotrione soil sorption values and the half-life of mesotrione increased. Like mesotrione, pyrasulfotole another HPPD-inhibiting herbicide, also had higher dissipation rates in soils with higher pH values (Shaner et al. 2012). Persistence was also higher for imazaquin, an ALS-inhibiting herbicide, when soil pH was low (Loux and Reese 1993). Loux and Reese (1993) attributed the increase in imazaquin present at lower soil pH to an increase in herbicide adsorption, which decreased the availability of microorganisms to breakdown imazaquin in the soil. However, as the soil pH increased, herbicides can form a stronger bond with soil particles and were less available for plants to absorb. This can reduce carryover from one season to the next and could allow for a more sensitive crops to be planted in the following season. Mesotrione has an acidic dissociation constant (pK_a) of 3.1 in soils, mesotrione can dissociate from molecular form to anionic form as the soil pH increases (Riddle et al. 2013). The acidic dissociation constant refers the strength of the acid. Chemical pKa values below -2 are strong acid, where pKa values of 2-12 are consider weak acids. As soil pH decreases, sorption by soil particles increases, reducing the amount of mesotrione available in plant available soil water, which reduces the ability for mesotrione to be in a liquid phase allowing for degradation of mesotrione (Shaner et al. 2012). Due to a 3.06 acidic dissociation constant (pKa), bicyclopyrone can be fully ionized in soils with pH values below 5 and bicyclopyrone could be expected to behave similarly to mesotrione in higher pH soils (Hand et al. 2015)

Soil Organic Matter. Organic matter is plant residue that has degraded over time and deposited in the soil (Lehmann and Kleber 2015). Plant tissue can be broken down by the environment and microorganisms in the soil (Barriuso et al. 1992). However, as the soil organic matter is slowly broken down by the environment, it can release small amounts of herbicides that have not been degraded by the environment or microorganisms (Lehmann et al. 1992). Herbicide effectiveness and herbicide residues are partially dependent on the adsorption and desorption properties of the soil (Barriuso et al. 1992). Soil organic matter and herbicide adsorption are known to play a role in the availability of herbicides and microorganisms in the soil profile, effecting the rate at which herbicides are decomposed (Barriuso et al. 1992; Stevenson 1972). Lehmann et al. (1992) discovered if soil organic matter was less than 1% of the total soil composition, it did not influence mesotrione residues, however if soil organic matter was higher than 1%, it tended to increase mesotrione availability in the soil. Soils characteristics of low pH, high clay, and organic matter content have resulted in greater binding and slower degradation of bicyclopyrone, resulting in greater crop injury (Chen et al. 2018; Dunne 2012; Dyson et al. 2002). Soil organic matter has been shown to play a role in the amount of herbicide carryover, but not as large of a role as soil pH (Dyson et al. 2002; Loux and Reese 1993; Shaner et al. 2012).

Cation Exchange Capacity. The cation exchange capacity (CEC) of a soil, which refers to the total capacity of a soil to hold exchangeable cations can affect herbicide carryover (Brown and Lemon 2018). The CEC can influence the soil's ability to buffer against soil acidification and hold onto soil nutrients (Carter 2000). Soils that are made up of a large quantity of clay or have higher percentages of organic matter have larger CEC values (Brown and Lemon 2018). Soils that are primarily composed of sand require a large percentage of organic matter to retain nutrients. If organic matter in a sandy soil is low, the CEC value will also be low. In a study conducted by Chen et al. (2018) on soils with low CEC and low organic matter, bicyclopyrone injured 'Thunder' cucumber and 'Noche' zucchini (*Cucurbita pepo* L.) and caused significant stand loss the season of application, however, this crop response was not represented in cucurbit yields. The low CEC and organic matter likely reduced soil adsorption of bicyclopyrone allowing for more availability for root absorption, leading to crop injury (Dunne 2012). Another soil-herbicide characteristic that can affect the transformation and transportation potential of herbicides, is the soil sorption coefficient value (Koc) (Reddy and Locke 1994). Koc is the interaction between the amount of chemical adsorbed by the soil and the amount of chemical that is dissolved by water that is available in the soil profile. The lower the Koc value for each chemical, the more mobile the chemical is in the soil profile (Dunne 2012; Reddy and Locke 1994). Bicyclopyrone has a Koc value of 13.11 and mesotrione has a Koc value of 141.7, which suggests that bicyclopyrone may be more mobile in the soil than mesotrione (Dunne 2012). The importance of the entire composition of the soil is an important factor to consider.

Environmental Factors

Temperature, precipitation, and photodegradation are all major factors that can affect herbicide degradation in the environment. Temperature and precipitation can greatly affect the concentration of a herbicide in the soil rooting zone as well as the activity of microorganisms in the soil. Sunlight also can degrade herbicides on the soil surface before being incorporated into the soil. Weather is an uncontrollable factor that effects herbicide effectiveness and residual activity starting the day of application.

Photodegradation and Precipitation. Photodegradation is the degradation of a herbicide by ultraviolet rays from the sun (Dumas et al. 2017). Photodegradation of a herbicide can occur in water, on soil surfaces, or on leaf surfaces. It has been estimated that 50% of bicyclopyrone is photodegraded in the first 3 to 11 d after application (Hand et al. 2015). During the degradation of mesotrione by sunlight, formulated mesotrione has a half-life of approximately 40 minutes, which can be accelerated by surfactants (Dumas et al. 2017). This means less herbicide would be available for incorporation into the soil profile by rainfall once it occurs. The time between herbicide application and rainfall has proven to be one of the most important periods for effective weed control and herbicide persistence in the soil (Shaner et al. 2012). Shaner et al. (2012) demonstrated that if the required amount of precipitation for incorporation of mesotrione did not occur within 7 days, not only was weed control reduced, but the persistence of the herbicide in the soil increased. Walker et al. (1992) noticed that the required number of days to reach 50% herbicide loss was increased by as many as 15 days during years with less than normal rainfall. Hand et al. (2015) found that herbicide persistence can be decreased in 3-11 d without proper rainfall. However, when overall rainfall was lower, the time to degrade alachlor 50% was longer than in seasons with higher rainfall. Herbicide breakdown slows as the soil profile dries out, however if the soil profile reaches anaerobic conditions with saturated soils, herbicide breakdown can slow down or completely stop (Hand et al. 2015). Under normal field conditions where periods of soil saturation and drought are common, mesotrione primarily stays in the top 10 cm of soil and seldom penetrates deeper into the soil profile (Rouchaud et al. 2001). Low soil moisture can also prevent efficient microbial and chemical degradation of herbicides that is primarily degraded by microorganisms (Alister and Kogan 2005; Loux et al. 1989). Alister and Kogan (2005) found that imidazolinone herbicides caused carryover issues 300 d after application in numerous rotational crops including sugarbeet when long water deficit periods happened after application. Rainfall or irrigation to incorporate herbicides after application is important to prevent herbicide dissipation. If an incorporating water event does not occur after an application, pesticides losses in the soil can be as high as 90% from volatilization depending on the chemical makeup and amount of time between application and rainfall (Carter 2000). For instances, volatility for atrazine and alachlor was 5 and 26% over the course of one month and 24 d, respectively. However, most herbicides are less volatile than some other pesticides like insecticides and fungicides. Carter (2000) also noted that herbicide losses in the soils range from 2-90% from volatilization, 0.001-0.25% from surface runoff, 1-5% from leaching, and 1-9% is possible from drain flow. The reason for this range is because herbicide movement in the soil is entirely dependent on the soil properties, herbicide properties, topography, geological characteristics, and land preparation practices. While neither mesotrione nor bicyclopyrone are considered water soluble in comparison to other herbicides, still a certain amount is lost through voids in the soil structure, which could prevent dissipation and degradation (Carter 2000). Clay soils can swell and shrink causing cracks in the soil profile. These macropores have the potential to be larger in soils with a high clay content and could lead to more possible herbicide losses through bypass flow routes for water movement (Carter 2000). Field tiles could accentuate this situation more by allowing faster water flow out of the soil profile carrying herbicides with the water. The amount potentially lost is dependent on the chemical properties of the herbicide.

Temperature. Air and soil temperature can greatly affect herbicide fate in the environment. As soil temperatures increase, microbial activity increases the degradation of herbicides in the soil (Durand et al. 2006). Increases in temperature, and increased water evaporation can dry out the soil profile at a faster rate, leading to lower germination of weeds. Lower weed populations absorb less herbicide from the soil, leaving more herbicide residues in the soil profile (Yu et al. 2013). Over the past few decades several studies that have been conducted to determine how temperature affects the half-lives of herbicides. Walker et al. (1992) reported that for every 5 C increase in temperature the half-life of alachlor decreased by a factor of two. Similar results were reported with isoxaflutole dissipation (Taylor-Lovell et al. 2002). With environmental changes causing warmer air temperatures during winters across the Midwest, increased microbial activity and herbicide degradations has been noticeably recorded (Bailey 2003). Like many of the variables that determine herbicide persistence, temperature should not be thought of as a single variable, temperature affects the rate of which herbicides degrade in the environment (Davidson et al. 2000). Studies have shown that as air and soil temperatures are lower during the winter months microbial activity dramatically slows down (Felix et al. 2007). Once soil temperatures approach freezing herbicide degradation can completely stop.

Microbial Degradation. The primary source of HPPD-inhibiting herbicide degradation is from soil microbes (Dunne 2012). In order for a herbicide like mesotrione to be degraded by microorganisms it must be available in the soil solution (Batisson et al. 2009; Dumas et al. 2017; Dyson et al. 2002; Shaner et al. 2012). Herbicides that are tightly bound to soil particles are less herbicide available for microbial degradation (Rouchaud et al. 1998; Shaner et al. 2012). As herbicide residues are metabolized by microorganisms, CO_2 and microbial biomass is produced (Sorenson et al. 2003). For microbial degradation to happen the soil conditions must be appropriate to support the microbial communities (Dumas et al. 2017). Microbial activity in soils tends to increase as soil organic matter increases (Hurle and Walker 1980). All soils have microbial communities, but not all soils have the same quantity of herbicide-degrading microorganisms which can greatly affect the rate at which herbicides are degraded (Batisson et al. 2009). Lewis et al. (1984) noticed that the adaptation of native soil microbial populations occurs as a result of exposure to herbicides. Microorganisms in the *Bacillus* family are commonly found in the environment and have been shown to degrade mesotrione (Durand et al. 2006). Recently, B*acillus* sp. 3B6 originally isolated from moisture in clouds was found to rapidly degrade mesotrione (Durand et al. 2006). Another *Bacillus* species that has been found to degrade mesotrione is *Bacillus* sp. Mes11 (Batisson et al. 2009). Both *Bacillus* species are very specific at degrading only mesotrione and no other herbicides in the triketone family. Even though it has not been tested, it is suspected these two *Bacillus* species will not degrade bicyclopyrone (Dumas et al. 2017). However, Batisson et al. (2009) speculates that the *Bacillus* species are attacking the molecules at the benzoyl 4-substituent which is absent from the chemical composition of other triketone herbicides but is present in bicyclopyrone. *Bradyrhizobium* sp. SR1 is another microorganism that persists in the soil and has shown to degrade sulcotrione and mesotrione which are both triketone herbicides (Dumas et al. 2017). Sorenson et al. (2003) found that the microbiological processes are an important step in the mineralization of the phenyl rings for herbicides in the phenylurea family. *Bradyrhizobium* sp. SR1, *Bacillus* sp. Mes11, and *Bacillus* sp. 3B6 are found to be part of the active microbial community in most soils and can transform mesotrione into 4-methylsulfonyl-2-nitrobenzoic (MNBA) and 2-amino-4-methylsulfonylbenzoic acid (AMBA) metabolites (Batisson et al. 2009). In laboratory studies, AMBA was found in the soil within 3 h of application (Batisson et al. 2009). Durand et al. (2006) showed that *Bacillus* sp. 3B6 is capable of remaining active even at temperatures as low as 17 C and most microorganisms are more active in soils with a neutral or basic soil pH (Batisson et al. 2009; Cox et al. 1996). There has been some interest in looking at applying fungi-inoculated bioplastic granules to fields to allow for increased application rates of bicyclopyrone and reduce its carryover potential (Acceinlli et al. 2015). The results indicated that inoculating a field with soil-inhibiting fungi *Beauveriabassiana, Rhizopus oryzae,* or *Trichoderma harzianum* was effective at reducing carryover from bicyclopyrone to soybean and field peas. This is only possible if the soil microorganisms can degrade the herbicides, assuming the herbicide is not tightly bound to soil particles (Acceinlli et al. 2015; Shaner et al. 2012). Microorganisms are the primary way most HPPD-inhibiting herbicides are degraded in the soil, but these microorganisms are very dependent on environmental factors that control the rate of microbial activity and the resulting herbicide dissipation.

Conclusion

The use of herbicides with residual activity can be an important aspect of weed control and herbicide-resistant weed management. Many residual herbicides can be used in corn-soybean or corn-soybean-wheat rotations since these crops are generally more tolerant to some of these herbicides. However, with specialty crops like alfalfa, cucumber, dry bean, and sugarbeet there are a limited number of herbicides registered for use and these crops tend to be more sensitive to herbicides with residual activity (Chen et al. 2018; Riddle et al. 2013; Sikkema et al. 2004). Bicyclopyrone, a HPPD-inhibiting herbicide, was developed to control large-seeded broadleaf weeds and some grasses in corn. Bicyclopyrone is absorbed by plants through both roots and shoots and can remain in the soil at an effective level for an unknown length of time (Cornes 2006; Dumas et al. 2017). Fortunately, bicyclopyrone shows tolerance to many specialty crops like specific cultivars of cucumber, zucchini, onion (*Allium cepa* L.), carrot (*Daucus carota* L.), and dill (*Anethum graveolens* L.) on muck soils, which is important since its chemical properties are similar to mesotrione (Chen et al 2018; Dunne 2012). Based on research done by Dyson et al. (2012) it can take between 5 and 6 half-life cycles before the residue of mesotrione is reduced to a rate that will no longer causes crop injury to sensitive crops, like sugarbeet. Many times, herbicide rotations to specialty crops are greater than 12 months due to the sensitivity to many residual herbicides. Due to a lack to available herbicide diversity in a specialty crop rotation because of carryover concerns, it is important to understand the potential risk of applying bicyclopyrone a year prior to planting specialty crops. However, there is currently a data gap concerning the carryover potential of bicyclopyrone, especially to specialty crops. Specialty crops tend to have a higher economic value and herbicide carryover to these high value crops is not tolerated.

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CHAPTER II

ALFALFA, CUCUMBER, DRY BEAN, AND SUGARBEET RESPONSE TO BICYCLOPRYONE AND MESOTRIONE

Abstract

Bicyclopyrone and mesotrione are a HPPD-inhibiting herbicide (Group 27) registered for use in corn. Mesotrione is sold alone or in premixture with other herbicides; bicyclopyrone is sold only in premixtures. There is limited data available on the response of other crops planted into fields where these herbicides were applied. Greenhouse and field experiments were conducted to evaluate alfalfa, cucumber, black and kidney bean, and sugarbeet response to bicyclopyrone and mesotrione. In the greenhouse, cucumber, black bean, kidney bean, and sugarbeet were more sensitive to mesotrione compared with bicyclopyrone. Sugarbeet was the most sensitive to both bicyclopyrone and mesotrione followed by alfalfa. Cucumbers were the most tolerant to bicyclopyrone and mesotrione followed by kidney bean and black bean. In field research, bicyclopyrone at 50 and 100 g ha^{-1} (1 and 2X rate), and mesotrione at 210 g ha^{-1} were applied in early June to V4 corn at two locations in 2015 and 2016. The following spring, alfalfa and sugarbeet were planted in mid-April and cucumber and dry edible bean in early-June and crop response was measured. In 2016, injury in all crops was less than 20%, regardless of herbicide treatment at either location. In 2017 at East Lansing, sugarbeet was severely injured and did not survive where mesotrione was applied the previous year. Sugarbeet and kidney bean injury was 15 and 5%, respectively from the 2X rate of bicyclopyrone. Neither mesotrione or bicyclopyrone affected crop growth or yield at Richville in 2017. Soil pH was 6.0 and soil organic matter was 4.2 to 4.5% at East Lansing and soil pH was 7.8 and soil organic matter 2.6% at Richville. While there were differences in soils at the two locations, rainfall within the first 30 days following application contributed to differences in herbicide carryover. At East Lansing,

rainfall was 20.5 and 2.8 cm within the first 30 days following application in 2015 and 2016, respectively, contributing to more herbicide carryover in the 2017 growing season than in the 2016 growing season. Rainfall at Richville had a 60% reduction in precipitation within the first 30 days however, no herbicide carryover was experienced. From this research it appears that alfalfa, dry bean or cucumber can be planted the year following mesotrione or bicyclopyrone application. However, sugarbeet should not be planted the year following applications of mesotrione or bicyclopyrone.

Introduction

Controlling weeds has become more challenging since the discovery of herbicide-resistant weeds. Many herbicides used to manage weeds have the potential to carryover and cause injury to crops planted in subsequent seasons (Chen et al. 2018; Dyson et al. 2002; Felix et al. 2007; Riddle et al. 2013). Understanding rotational crop sensitivity and the persistence of herbicides in soil prior to including their use in a weed management program is an important consideration for growers and agribusiness consultants.

Bicyclopyrone is the newest 4-hydroxyphenylpyruvate dioxygenase (HPPD) inhibiting herbicide (WSSA Group 27) used for weed control in corn (*Zea mays* L.), wheat (*Triticum aestivum*), barley (*Hordeum vulgare*), and Duram wheat (*Triticum durum*) (Dunne 2012; Martin et al. 2018; Peachy 2015). Similar to mesotrione, bicyclopyrone is a member of the triketone chemical family, and is a derivative of leptospermone, a compound originally discovered in the root systems of the bottlebrush plant (*Callistemon citrinus*) (Cornes 2006). Both bicyclopyrone and mesotrione control weeds by inhibiting carotenoids that are needed to protect chlorophyll and plant cell membranes during photosynthesis (Cornes 2006; Dunne 2012). The disruption of photosynthesis caused by HPPD inhibitors results in a white or bleached appearance of sensitive plants (Dunne 2012; Mougin et al. 2000).

The potential of an herbicide to carryover from one season to the next in sensitive crops is affected by soil type, soil pH, soil organic matter, weather, and herbicide characteristics. Mesotrione have shown the ability to persist in soil and injure crops planted in rotation (Dyson et al. 2002; Felix et al. 2007; Dunne 2012; Riddle et al. 2013). Felix et al. (2007) found significant injury in pickling cucumber planted the year following a preemergence or postemergence mesotrione application. Riddle et al. (2013) demonstrated sugarbeet sensitivity the following year from mesotrione applied preemergence to corn at 140 g ha^{-1} (2/3X) rate. Herbicides are more likely to persist in fine textured soils than in courser soils (Loux and Reese 1993). Soil pH and soil organic matter affect the likelihood of bicyclopyrone and mesotrione carryover. As the soil pH decreases and becomes more acidic, bicyclopyrone and mesotrione carryover becomes more likely (Chaubane et al. 2005; Shaner et al. 2012). While increased soil organic matter increases bicyclopyrone and mesotrione carryover (Barriuso et al. 1992; Durand et al. 2006; Dyson et al. 2002; Hand et al. 2015). Mesotrione persistence is longer in soils with low pH and high soil organic matter (Dyson et al. 2002; Felix et al. 2007; Riddle et al. 2013). Since bicyclopyrone and mesotrione are both primarily decomposed by microorganisms, weather can greatly affect the persistence of both bicyclopyrone and mesotrione in soils (Alister and Kogan 2005; Carter 2000; Dunne 2012). A lack of rainfall can greatly affect the persistence of herbicide by reducing the amount of herbicide incorporated into the soil profile and absorbed by the plants roots system. Mesotrione injured black and navy bean when rainfall following application was low and winter temperatures cooler than normal (Soltani et al. 2007). As the soil profile begins to dry out or become closer to freezing, microorganisms in the soil become less active, reducing the degradation of bicyclopyrone and mesotrione (Dumas et al. 2017; Riddle et al. 2013; Walker et al. 1992). Herbicide characteristics like water solubility, chemical hydrolysis, pKa, and half-life also affect the potential of a herbicide to carry over (Dunne 2012). Mesotrione's chemical properties suggest a herbicide that can persist in the soil for long periods of time (*Table 2.1*). The water solubility of mesotrione is 157.5 mg L^{-1} suggesting that mesotrione is not water soluble (Dunne 2012). The oil/water partitioning coefficient (Kow) of mesotrione is 1.49 and the pKa of mesotrione suggests it is a weak acid due to a value of 3.1. Mesotrione's Koc value of 141.7 suggests that it would bond tightly to the soil particles. The chemical properties of mesotrione pose a half-life of 5-62 days depending on conditions. Bicyclopyrone has very similar chemical properties to mesotrione. Bicyclopyrone's water solubility is 138.7 mg L^{-1} with a Kow value of 1.58 and a Koc of 13.11. Bicyclopyrone is also a weak acid with a pKa value of 3.06 and a half-life of 4-13 days. Bicyclopyrone and mesotrione are both weak acids with similar pKa values, suggesting that with a soil pH of 6.0, both herbicides would remain in an acidic form. The water solubility of bicyclopyrone is slightly higher than mesotrione making it more readily available for plant uptake. Furthermore, the Kow suggests that bicyclopyrone is 10 times less tightly absorbed to soils, suggesting more rapid uptake by plants in the field. Currently, there is little known about the persistence of bicyclopyrone, and sensitivity of crops planted in rotation (Chen et al. 2018). However, bicyclopyrone has greater crop safety to many minor crops when compared with mesotrione (Chen et al. 2018, Felix et al. 2007, Riddle et al. 2013), and in many cases, there is greater than a 12-month rotation interval following mesotrione applications. Currently, there is little known about the persistence of bicyclopyrone and its effects on rotational crops.

Therefore, the objectives of this research were to: 1) determine the relative sensitivity of alfalfa, cucumber, dry bean and sugarbeet to bicyclopyrone and mesotrione in the greenhouse and field, and 2) compare the persistence of mesotrione and bicyclopyrone on these crops at two field locations.

Materials and Methods

Greenhouse Experiment. Dose response experiments were conducted on alfalfa, cucumber, black bean, dark red kidney bean, and sugarbeet to compare the sensitivity of these crops to bicyclopyrone and mesotrione in three different soils. The soils examined included soil collected from the upper 10 cm of the no herbicide control plots from the 2015-2016 East Lansing and Richville field experiments described below, and soil supplied by the Michigan State University greenhouse (MSUGH) complex. The MSUGH soil was a steam-sterilized sandy loam field soil with a pH 7.4 and 3% organic matter collected near Charlotte, Michigan (42.5656 N; -84.8356 W). Pots (9 x 9 x 10 cm) were filled with the three soils, watered to field capacity for approximately 7-10 d prior to planting, and placed in the greenhouse. Alfalfa 'DK 44-16RR' (Bayer CropScience, St. Louis, MO) (10 seeds pot^{-1}), 'National' pickling cucumber (National Pickle Packers Association) (two seeds pot^{-1}), 'Zorro' black bean (Michigan Agricultural Experiment Station) (two seeds pot^{-1}), 'Red Hawk' dark red kidney bean (Michigan Agricultural Experiment Station) (two seeds pot^{-1}), and sugarbeet 'Hilleshog 9616' (Hilleshog Seeds LLC, Longmont, CO) (three seeds pot^{-1}) were planted in separate pots filled with the three different soil types.

Immediately after planting, bicyclopyrone and mesotrione treatments were applied using a single nozzle (8001E, TeeJet Technologies, Wheaton, IL) track sprayer calibrated to deliver

187 L ha^{-1} at 193 kPa of pressure. The bicyclopyrone (Anonymous 2016a; Anonymous 2016b; Anonymous 2018a) rate of 50 g ha^{-1} and the mesotrione (Anonymous 2018b) rate of 210 g ha^{-1} were used as the 1X rates for each herbicide. Six bicyclopyrone and mesotrione rates ranging from 1/16 to 2X were applied to pots planted with alfalfa and rates ranging from 1/8 to 4X were applied to pots planted to cucumber, black bean, and kidney bean. Eight bicyclopyrone and mesotrione rates ranging from 1/64 to 2X and 1/128 to 1X, respectively, were applied to pots planted with sugarbeet. A no herbicide control was included for all crops. All treatments were replicated five times and repeated twice.

Shortly after application all pots were moved to the greenhouse and received approximately 1 cm of water for herbicide incorporation after application. Overhead watering of 1 cm was repeated the following day and then sub-irrigation using individual felt capillary mats below each pot (Hummert International, Earth City, MO) for the remainder of the experiment. Greenhouse conditions were set at 25 ± 5 C and sunlight was supplemented to provide a total midday light intensity of 1,000 µmol m^{-2} s^{-1} photosynthetic photon flux at plant height in a 16 h day.

Crops emerged within 3 to 5 d and crop injury was assessed 7, 14, and 21 d after emergence (DAE) for cucumber and dry bean and 7, 14, 21 and 28 DAE for alfalfa and sugarbeet on a scale of 0-100%, with 0 indicating no crop injury and 100 representing complete plant death. Aboveground biomass was harvested on the last day of evaluation for each crop. Biomass was dried at 60 C for 7 days and weighed.

Field Experiment. Herbicide carryover field experiments were conducted during the 2015-2016 and 2016-2017 field seasons at the Michigan State University Agronomy Farm in East Lansing, Michigan (42.6868 N, -84.4906 W) and the MSU Saginaw Valley Research and Extension Center near Richville, Michigan (43.3963 N, -83.6828 W). Soil at East Lansing was a Colwood-Brookston loam (fine-loamy, mixed, mesic typic haplaquolls) with pH of 6.0 and 4.5% organic matter in 2015-2016 and pH 6.2 and 4.2% organic matter in 2016-2017. Soil at Richville was Tappen-Londo clay loam (fine-loamy, mixed, active calcareous, mesic typic epiaquolls) with pH 7.8 and 2.6% organic matter in 2015-2016, and a pH 7.8 and 2.7% organic matter in 2016-2017. The experimental design was a split-plot design with rotational crop as the main plot factor and herbicide treatment as the sub-plot factor, with a plot size of 3 m wide by 10.7 m long. Each combination was replicated four times.

During the establishment year, glyphosate-resistant corn 'Dekalb 49-72' (Bayer CropScience, St. Louis, MO) and 'Stine 9417' (Stine Seed Company, Adel, IA) was planted at East Lansing and Richville locations, respectively, in conventionally tilled soils on May 1, 2015 and May 10, 2016 at both locations. Herbicide treatments were applied to V4 corn on May 28, 2015 and June 1, 2016. Herbicide treatments consisted of 50 and 100 g ha^{-1} of bicyclopyrone, 210 g ha^{-1} of mesotrione, and a no herbicide control. Bicyclopyrone rates were equivalent to 1 and 2X the labeled rate for corn. All herbicide treatments were applied with a crop oil concentrate (COC) at 1.0% v v^{-1} + granular ammonium sulfate (AMS) at 2.5% w w^{-1}. Herbicide treatments were applied using a custom-built tractor-mounted compressed air sprayer calibrated to deliver 178 L ha^{-1} at 207 kPa using TeeJet AIXR 11003 nozzles (TeeJet Technologies, Wheaton, IL). Glyphosate (0.84 kg ha^{-1}) + AMS (2.5% w w^{-1}) was applied POST twice to the entire experiment during the growing season to maintain a weed-free area. At the end of the season, corn was harvested as silage to remove aboveground biomass.

The following spring, soil at each location was shallow tilled (<5 cm depth) for seedbed preparation. The tillage implements used were a Triple K soil finisher (Kongskilde Agriculture, Albertslund, Denmark) and a John Deere S-tine soil finisher (John Deere, Moline, IL) at East Lansing and Richville, respectively. Tillage passes were made in the direction of the herbicide treatments to minimize cross contamination of treatments. Rotational crops were planted at times standard for each crop type.

Sugarbeet and alfalfa were planted in mid-April to early May (Table 2.2). Glyphosate-resistant sugarbeet 'Crystal 059' (ACH Seeds, Eden Prairie, MN) and 'Hilleshog 9616' were planted in 76 cm rows at a population of 118,000 seeds ha^{-1} in 2016 and 2017, respectively, using a John Deere MaxEmerge XP planter (John Deere, Moline, IL). 'DK 44-16RR'glyphosate-resistant alfalfa was seeded at 658,000 seeds ha^{-1} in 19 cm rows using a John Deere 1560 no-till drill (John Deere, Moline, IL). Field sites were maintained weed-free throughout the growing season with two POST applications of glyphosate at 0.84 kg ha^{-1} + AMS at 2.5% w w^{-1}.

During the first week of June cucumber and two classes of dry edible bean were planted (Table 2.2). 'National' pickling cucumber was planted in 76 cm rows at a population of 195,000 seeds ha^{-1}. 'Zorro' black bean and 'Red Hawk' dark red kidney bean were each planted at a population of 259,000 seeds ha^{-1} in 76 cm rows. Both cucumber and dry bean were maintained weed-free throughout the growing season with a preplant application of glyphosate and supplemental hand-weeding as needed.

Data collection. Stand counts for cucumber, black bean, kidney bean, and sugarbeet were taken 7 and 14 DAE from the center two rows of each plot. Stand counts were not recorded for alfalfa. Rotational crop injury was evaluated every two weeks starting 14 DAE on a scale of 0-100%, with 0 indicating no crop injury and 100 representing complete plant death. Each crop was harvested at maturity from the two center rows for 3 m of plot length, except for alfalfa. Alfalfa was harvested from two-0.25 m^2 sub-samples, when plants reached approximately 50% bloom (early August). Sub-samples were oven dried, weighed, and dry matter was recorded.

Cucumber was harvested by hand in early August and fresh weights were recorded. Due to issues with overall stand establishment and honeybee (*Apis mellifera* L.) pollination, cucumber was not harvested in 2016. Dry bean and sugarbeet were harvested between mid-September and mid-October. Black bean plots were direct harvested using a small-plot research combine (Massey-Ferguson 8XP, AGCO, Duluth, GA) with a 1.5 m header. Kidney bean were harvested by hand pulling and separating dry bean seed from pods, stems, and leaves by using a stationary thresher (Almaco LPR, Almaco, Nevada, IA). Black and kidney bean yields were adjusted to 18% moisture. Sugarbeet were topped, harvested by hand, and weighed. Sub-samples of sugarbeet roots were taken from each plot and analyzed for quality by the Michigan Sugar Company laboratory (Michigan Sugar Company, Bay City, MI). Sugarbeet quality is expressed as kg of recoverable white sucrose per Mg of root (RSWMg). Total sugar production is expressed as kg of recoverable white sucrose ha^{-1} (RWSH).

Statistical analysis. Dose-response greenhouse experiments were analyzed using the drc package in R (R version 3.6.2, R Development Core Team 2019), and the appropriate model was determined using the mselect function. The four-parameter log logistic model was selected to determine I_{50} and GR_{50} values (doses required to cause 50% crop injury or 50% growth reduction) from the crop injury and dry weight data, respectively. The lack of fit for the four-parameter log logistic model was determined by the drc modelFit function.

$$y = 0 + \frac{d-0}{1+exp[(b(log(x)-log(e))]} \qquad \text{[Eq. 1]}$$

$$y = c + \frac{d-c}{1+exp[(b(log(x)-log(e))]} \qquad \text{[Eq. 1]}$$

For this equation, *y* is the biomass response (percent of non-treated control), *x* is the dose, *c* and *d* are the lower and upper limits, respectively, *b* is the relative slope around *e*, and *e* is the ED_{50} (Streibig 1988). For each crop, plant injury and plant biomass reduction, *c* and *d* were set to 0% and 100%, respectively. Plant injury and reduction of plant biomass differences in ED_{50} values (based on a t-statistic with $P \leq 0.05$) were compared using the EDcomp function and selectivity indices (R/S ratio; Ritz et al. 2015), which are the ratios between two ED_{50} values from dose-response curves. Herbicide response differences in I_{50} and GR_{50} values were compared using the selectivity indices based on a t-statistics with $P \leq 0.05$ (Knezevic et al. 2007).

Field experiment data was analyzed conducted using SAS® 9.4 (SAS Institute Inc., Cary, NC). Normality assumptions were examined by normal probability plots of the residual and a checking a histogram. Unequal variance assumption was tested by a visual inspection of side-by-side box plots of the residuals followed by the Levene's test for unequal variances. Analysis of variance for the field experiments was conducted using PROC MIXED. Each rotational crop was analyzed separately. The statistical model consisted of site-year (individual year and location) and herbicide treatment as fixed effects, and replication nested within site-year as the random effects. Replications were used as an error term for testing the effects of site-year. When an interaction of site-year by herbicide treatment was significant, data was separated by location and year interactions were tested. Data were combined over years when the interaction of year and herbicide treatment were not significant. Treatment means were separated using Fisher's Protected LSD at $\alpha \leq 0.05$.

Results and Discussion

Greenhouse Experiment. Injury symptoms from bicyclopyrone and mesotrione to the various crops in the greenhouse consisted of bleaching, stand reduction, and stunting.

Alfalfa. Alfalfa was sensitive to both bicyclopyrone and mesotrione when tested on the three soil types in the greenhouse (*Figure 2.1*). The I_{50} values of bicyclopyrone indicated that alfalfa was injured less when MSUGH soil (I_{50} = 31 (0.62X)) was treated compared with soil collected from the East Lansing (I_{50} = 15.5 (0.31X)) location (*Table 2.3*). Alfalfa was injured most when the Richville soil was treated with bicyclopyrone (I_{50} = 11.5 g ha^{-1} (0.23X)). I_{50} values for mesotrione were also similar for the three soil types and ranged from 30 (0.14X) to 77 g ha^{-1} (0.37X). While there was no difference in I_{50} values across soil types, the GR_{50} values for both bicyclopyrone and mesotrione were approximately 50% lower for alfalfa grown in the clay loam soil collected from Richville compared with East Lansing and MSUGH soils (*Table 2.3*).

Cucumber. Cucumber injury in the greenhouse from bicyclopyrone and mesotrione consisted of delayed emergence, reduced vigor, and bleaching on the edges of the leaves. Cucumber was less sensitive to bicyclopyrone when compared with mesotrione (*Figure 2.2*). I_{50} and GR_{50} values for cucumber were greater than 200 g ha^{-1} or 4-times the field use of bicyclopyrone grown in soil collected from East Lansing and MSUGH soil, suggesting that cucumber was tolerant to bicyclopyrone in loam and sandy loam soils. However, cucumber sensitivity to bicyclopyrone was greater when cucumber was grown in the clay loam soil collected from Richville. I_{50}values for cucumber on clay loam soils were similar to loam and sandy loam soils. This is likely a factor of limiting the greenhouse rate to 200 g ha^{-1} and not testing higher bicyclopyrone rates for increased I_{50} accuracy, due to the extreme level of tolerance cucumber expresses toward bicyclopyrone applications (*Figure 2.2*). However, GR_{50} values were significantly affected by applications of bicyclopyrone 26 (1/2X) g ha^{-1} (*Table 2.3*), this plant growth response to bicyclopyrone was not noticed until analyzing the data and looking at the weigh of each cucumber plant. The difference in crop response to bicyclopyrone between the Richville soil and the East Lansing and MSUGH soils is likely due to lower organic matter and a higher pH value in the Richville soil. Higher soil organic matter could lead to less herbicide availability for plant uptake and the East Lansing and MSUGH soils are higher in organic matter. Cucumber was sensitive to mesotrione in all three soils with I_{50} and GR_{50} values less than the 115.5 g ha^{-1} (0.56X) and 42 g ha^{-1} (0.19X), respectively. Our results of cucumber sensitivity to mesotrione in the greenhouse were similar to a field study conducted by Felix et al. (2007), where they reported 19 to 35% cucumber injury 42 DAT, at two locations when mesotrione was applied PRE at 210 and 420 g ha^{-1}. Felix et al. (2007) also reported reductions in cucumber yield at one of those locations.

Dry Edible bean. Injury was less when dry bean was treated with bicyclopyrone and planted in the Richville clay loam soil compared with the other two soil types in the greenhouse (*Figure 2.3, Figure 2.4, and Table 2.3*). The Richville soil had the highest pH of 7.8, which has shown to shorten the half-life of mesotrione (Dyson et al. 2002). Also, as soil pH increases herbicide generally cause a tighter bond with soil particles making them less available for plant uptake (Loux and Reese 1993). Black and kidney bean tolerance was higher for bicyclopyrone compared with mesotrione in the greenhouse (*Figures 2.3 and 2.4*). In general, I_{50} and GR_{50} values were greater than the 1X rate of bicyclopyrone (50 g ha^{-1}), showing similar tolerances to both varieties of dry bean. Kidney bean was tolerant to a 1X or greater rate of mesotrione (210 g ha^{-1}), whereas black bean was more sensitive to mesotrione, with I_{50} and GR_{50} values of approximately 1/2X rate of mesotrione (105 g ha^{-1}). Soltani et al. (2007) reported differences in dry bean market class tolerance to mesotrione; researchers reported minimal injury in black and white beans one year following field application while cranberry and kidney beans had significant injury and growth reductions at labeled and twice the labeled rates of mesotrione.

Sugarbeet. Sugarbeet was injured by bicyclopyrone and mesotrione in the greenhouse; injury was slightly lower in the Richville soil compared with the soil from East Lansing and MSUGH (*Figure 2.5*). GR_{50} values revealed that sugarbeet was 4-times more sensitive to mesotrione compared with bicyclopyrone (*Table 2.3*). Also, sugarbeet were more sensitive to herbicide applications when grown in the East Lansing soil versus the Richville and MSUGH. This was noticeable for most bicyclopyrone and mesotrione applications.

Field Experiment. Injury symptoms from bicyclopyrone and mesotrione to the various crops in the field consisted of bleaching, stand reduction, and stunting.

Alfalfa. Alfalfa seeded the 10 to 11 months following bicyclopyrone (50 and 100 g ha^{-1}) or mesotrione (210 g ha^{-1}) application was not injured in any of the four site-years of this research (*Tables 2.2 and 2.4*). Alfalfa harvested at 50% bloom yielded 1,450 to 1,580 and 1,620 to 1,790 kg ha^{-1} of dry matter at East Lansing and Richville, respectively, and was not reduced from bicyclopyrone or mesotrione compared with the no herbicide control (*Table 2.5*). In 2015, rainfall was 23.6 and 15.7 cm within the first 30 d after bicyclopyrone and mesotrione applications in East Lansing and Richville, respectively (*Table 2.4*). However, in 2016 rainfall was only 3.6 and 6 cm after application in East Lansing and Richville, respectively. Neither bicyclopyrone nor mesotrione, regardless of rainfall amounts during the 11 months following the herbicide application injured alfalfa. This would suggest that 25% or less of bicyclopyrone or mesotrione remained in the soil 11 months after application, based on alfalfa crop sensitivity studies conducted in the greenhouse.

Cucumber. Due to poor cucumber germination in 2016, cucumber data is only presented from the 2016-2017 field season. Cucumber stands, injury, and yield were not affected by bicyclopyrone or mesotrione applications made the previous year at East Lansing or Richville (*Table 2.6*). Cucumber yields were almost 3-times greater at East Lansing than Richville. Cucumber yields in East Lansing may have been higher due to the lower established populations reducing competition for limited micronutrient resources (i.e., iron, manganese, boron, copper, and zinc) due to higher soil pH levels (7.8) at Richville. In a two-year Canadian study, Riddles et al. (2013) found that cucumber dry weight and yields were not affected by mesotrione at rates up to 560 g ha^{-1}, even though some initial visual injury was reported.

Dry Edible Bean. Bicyclopyrone at 50 and 100 g ha^{-1} and mesotrione at 210 g ha^{-1} did not affect dry bean emergence or reduce plant stands compared with the untreated control in any of the four site-years (*Table 2.2 and 2.7*). Minor crop injury consisted of bleaching of the leaf margins was observed 28 days after emergence at the East Lansing location. In black bean, minor bleaching (3%) was evident where mesotrione was applied. Injury to kidney bean was more noticeable at 11% in the mesotrione treatment. While there were no differences in black or kidney yield due to carryover from bicyclopyrone or mesotrione, there were major differences in yield between the East Lansing and Richville locations. Black bean yields averaged 4,360 kg ha^{-1} at East Lansing and only 1,720 kg ha^{-1} at the Richville and kidney bean yields averaged 3,350 and 1,620 kg ha^{-1} at East Lansing and Richville, respectively (*Table 2.7*). Differences in dry bean yield between locations may have been due to differences in soil pH leading to possible micronutrient deficiencies since no micronutrients were applied during the growing season. Another theory to explain the increased yield at East Lansing, is dry edible bean have not been grown in the location of this study in past years. This can cause a large yield boost when a new crop is introduced to the field. During the dry edible bean growing season, growing degree days and precipitation during the growing seasons were similar at both locations (*Table 2.4*).

Sugarbeet. Due to a significant year by treatment interaction, sugarbeet data is presented separately for 2016 and 2017 at both East Lansing and Richville. There was considerable variation in sugarbeet stand and yield between the four site-years. Yield in 2016 at the Richville location were approximately half of the yields at the East Lansing location and in 2017 at the Richville location yields were approximately a third of the yields at the East Lansing location. Differences between these site years were likely due to environmental conditions and soil fertility. The field conditions at planting were favorable for good seed germination and emergence at the East Lansing and Richville locations. In 2016, after planting 29 and 15 mm of rain fell over a period of 10 days at the East Lansing and Richville locations, respectively (*Table 2.4*). In 2017, after planting there was 41.5 and 28 mm of in the first 10 days at these locations. This trend of increased rainfall early in the growing season is shown in the difference between PD1 (planting date) and PD2 for 2016 and 2017 (*Table 2.4*). Also, the difference in growing degree days (GDD) between PD1 and PD2 for each season indicate that 2017 was a warmer spring with more rainfall than 2016. This could have caused environmental stand and early season vigor differences. Yields in 2016 were higher than yields in 2017 and higher at the East Lansing location than the Richville location in both years. Rainfall was vastly different from the first of July to the 31st of August when comparing 2016 and 2017. At the East Lansing location in 2016 received 25.9 cm of rain and in 2017 only 10.2 cm of rain. At the Richville location in 2016 this location received 21.9 cm of rain and in 2017 only 8.5 cm of rain was recorded. The period of July 1st through mid-August is an important period because this when sugar beet is putting most of its resources towards root size before sugar production. Without moisture during this time period the sugar beet tuber size would be reduced. Bicyclopyrone did not affect stand or yield of sugarbeet that were planted 10.5 to 11.5 months after treatment in all 4 site-years (*Tables 2.2 and 2.8*). However, sugarbeet were affected by mesotrione carryover in 2 of the 4 site-years. Sugarbeet stands were reduced by 20 and 97% in 2016 and 2017, respectively, at East Lansing. These reductions in stand also equated to similar responses for sugarbeet injury. While mesotrione affected sugarbeet stand and injury in both years at East Lansing, sugarbeet yield and recoverable white sucrose per hectare (RWSHa) was only impacted in 2017. The extreme nature of stand loss and injury early in the growing season of 2017 resulted in no harvestable crop by the end of the growing season. Dyson et al. (2002) found lower soil pH resulted in higher mesotrione sorption and increased half-life, resulting in more herbicide carryover at lower soil pH values. Though sugarbeet stand counts, crop injury, and yield differences were notice in 2017 and not 2016, this understanding of mesotrione and soil pH can easily explain why sugarbeet responded differently between the East Lansing and Richville locations.

Based on the results from this research, sugarbeet are the most sensitive crop to both bicyclopyrone and mesotrione, followed by alfalfa and black bean. Cucumber and kidney bean were most tolerant to both herbicides, with cucumber being the most tolerant crop to bicyclopyrone, while kidney bean was most tolerant to mesotrione. All crops tested showed equal to greater crop tolerance to bicyclopyrone than mesotrione. During the course of the field research, crop response due to herbicide carryover was only present at the East Lansing location. At East Lansing, sugarbeet and kidney bean were injured from the 2X rate of bicyclopyrone and mesotrione. Sugarbeet stand was affected when mesotrione was applied the previous season during both years at East Lansing. However, yields were only affected during the 2016-2017 season. Sugarbeet response at the East Lansing location may have been due to the soil properties at this location. Bicyclopyrone and mesotrione are both weak acids, soil acidity less than 6.0, can cause weak acidic herbicides to persist longer in the soil. Soil organic matter was 4.5% at this location. The higher soil organic matter can increase the potential binding sites for bicyclopyrone and mesotrione, potentially slowing down herbicide degradation (Chen et al. 2018; Dunne 2012; Dyson et al. 2002). Soil organic matter can also affect the carrying capacity of soil microorganisms. Microorganisms are the primary way bicyclopyrone and mesotrione are degraded in the soil. In order for microorganisms to breakdown herbicides in the soil, the environmental conditions must be appropriate to support microbial communities (Dumas et al. 2017). Soil temperatures above 17 C and adequate soil moisture are two requirements for microbial degradation (Batisson et al. 2009). Though, adequate soil moisture is required for microbial degradation, it is also important to remember that mesotrione adsorbs tighter to soil particles making mesotrione less available for microbial breakdown but also that bicyclopyrone is more water soluble than mesotrione. Lindley et al. (2020) noticed that in season’s with more than 2.5 cm of rainfall shorty after application caused more injury to sweet potatoes, likely because bicyclopyrone was moved into the root zone of young tender sweet potato clones. These characteristics of bicyclopyrone could promote microbial degradation and the potential for herbicide runoff. Bicyclopyrone has exhibited a half-life of 4-13 day depending on soil and environmental conditions, while mesotrione has a longer half-life of 5-62 days (*Table 2.1*). Based on the results of this research, alfalfa, black bean, cucumber, kidney bean, and sugarbeet are all more sensitive to mesotrione than bicyclopyrone. Sugarbeet was the most sensitive to both herbicides on all three soils compared in the greenhouse and was the only crop where significant stand loss, crop injury, and yield losses occurred in the field. Alfalfa was the next most sensitive crop grown in the greenhouse on all three soils. However, there was no crop response from either field season at the East Lansing and Richville location. Cucumber, black bean, and kidney bean was all about equal in their tolerance to bicyclopyrone, whether planted in the field or in the greenhouse. Due to the tolerance of bicyclopyrone to the crops tested in this study, a 10-month rotational restriction is likely for alfalfa, cucumber, and dry bean, but a longer rotation restriction would be required for sugarbeet. However, since soils with a pH of less than 6 were not tested during this study, the rotation restrictions may have to be adjusted is soils are more acidic. Based on the crop sensitivity data and field research, it can be determined that bicyclopyrone is likely to have shorter rotation restrictions than mesotrione, but not because there is less herbicide residue in the soil but because the crops tested in this study seem to be less sensitive to bicyclopyrone.

APPENDIX

APPENDIX

CHAPTER 2 TABLES AND FIGURES

Table 2.1. Herbicide properties for bicyclopyrone and mesotrione that affect the persistence of these herbicides once applied.

Herbicide	pKa	Water Solubility	Kow	Koc	Microbial Degradation	Half-Life
		— mg L^{-1} —				— Days —
Bicyclopyrone	3.06	138.7	1.58	13.11	Yes	4 - 13
Mesotrione	3.1	157.5	1.49	141.7	Yes	5 - 62

Table 2.2. Planting dates and the number of months between herbicide application (MAA) in previous corn crop and planting rotational crops in East Lansing and Richville, MI.

	East Lansing				Richville			
	2016		2017		2016		2017	
Rotational crops	Planting date	MAA[a]	Planting date	MAA	Planting date	MAA	Planting date	MAA
Sugarbeet	May 6	11.3	May 16	11.5	April 18	10.75	April 17	10.5
Alfalfa	May 6	11.3	April 19	10.6	April 18	10.75	April 17	10.5
Cucumber	June 7	12.4	June 5	12.2	June 9	12.5	June 5	12.1
Black bean	June 7	12.4	June 5	12.2	June 9	12.5	June 5	12.1
Kidney bean	June 7	12.4	June 5	12.2	June 9	12.5	June 5	12.1

[a]POST herbicides were applied to V4 corn on May 28, 2015 and June 1, 2016 in East Lansing and May 28, 2015 and June 3, 2016 in Richville.

Table 2.3. I_{50} and GR_{50} values, with standard errors (± S.E.) for alfalfa, cucumber, black bean, kidney bean, and sugarbeet planted in soils collected from field locations and from MSUGH and treated with various rates bicyclopyrone and mesotrione in the greenhouse.

		I_{50} values[a]		GR_{50} values	
		Bicyclopyrone[b]	Mesotrione	Bicyclopyrone	Mesotrione
Crop	Soils[c]	X rate (± S.E.)	X rate (± S.E.)	X rate (± S.E.)	X rate (± S.E.)
Alfalfa	E. Lansing	0.31 (±0.05)[d]	0.22 (±0.04)	0.73 (±0.76)	1.17 (±2.79)
	Richville	0.23 (±0.04)	0.14 (±0.02)	0.27 (±0.04)	0.05 (±0.5)
	MSUGH	0.62 (±0.17)	0.37 (±0.07)	0.82 (±2.05)	0.75 (±0.81)
Cucumber	E. Lansing	>4.0 (NA)[e]	0.30 (±0.11)	>4.0 (±28.7)	0.22 (±0.16)
	Richville	>4.0 (±3.35)	0.19 (±0.07)	0.52 (±0.33)	0.16 (±0.03)
	MSUGH	>4.0 (NA)[e]	0.56 (±0.11)	>4.0 (±4.62)	0.20 (±0.14)
Black bean	E. Lansing	1.15 (±0.43)	0.67 (±0.13)	0.99 (±2.9)	0.21 (±2.24)
	Richville	>4.0 (NA)[e]	>4.0 (±177)	>4.0 (±413.7)	2.80 (NA)[e]
	MSUGH	1.64 (±0.37)	0.61 (±0.04)	2.51 (±5.1)	0.69 (±0.11)
Kidney bean	E. Lansing	3.56 (±2.16)	2.21 (±0.97)	>4.0 (NA)	1.66 (±10.45)
	Richville	>4.0 (±11.1)	1.80 (±1.05)	2.80 (NA)	3.75 (NA)
	MSUGH	3.33 (±2.35)	0.98 (±0.16)	>4.0 (±24.46)	1.21 (±0.55)

Table 2.3 (cont'd)

Sugarbeet	E. Lansing	0.08 (±0.01)	0.02 (NA)	0.17 (±0.03)	0.01 (±0.003)
	Richville	0.11 (±0.07)	0.03 (±0.004)	0.32 (±0.07)	0.06 (±0.21)
	MSUGH	0.1 (±0.01)	0.003 (±0.02)	0.32 (±0.07)	0.03 (±0.001)

[a]I_{50} and GR_{50} values are the required herbicide doses to reduce cause 50% injury and reduce plant biomass 50%.
[b] The field use rates of bicyclopyrone is 50 g ha^{-1} and mesotrione is 210 g ha^{-1}.
[c]Soil information for the East Lansing was a Colwood-Brookston loam (fine-loamy, mixed, mesic typic haplaquolls) with pH of 6.0 and 4.5% organic matter, Richville was a Tappen-Londo clay loam (fine-loamy, mixed, active calcareous, mesic typic epiaquolls) with pH 7.8 and 2.6% organic matter, and MSUGH was a sandy loam sterilized field soil with a pH of 7.4 and 3% organic matter.
[d] Means followed by the same letter within a column are not significantly different using paired t-test between soil types.
[e]NA = not available

Table 2.4. Precipitation, growing degree days (GDD), and the number of days where soil temperatures were below freezing (0°C) at various intervals between POST herbicide application[a] in corn the previous year and rotational crop planting in East Lansing and Richville, MI.

	East Lansing						Richville					
	2015-2016			2016-2017			2015-2016			2016-2017		
Interval	Precip.	GDD	Soil temp. ≤0 C	Precip.	GDD	Soil temp. ≤0 C	Precip.	GDD	Soil temp. ≤0C	Precip.	GDD	Soil temp. ≤0 C
	– cm –	base 0 C	— d —	– cm –	base 0C	— d —	– cm –	base 0 C	— d —	– cm –	base 0 C	— d —
0-14 d	7.2	247	0	2.5	266	0	11.2	220	0	5.3	256	0
15-30 d	16.4	323	0	1.1	342	0	4.5	310	0	0.7	328	0
0-90 d	43.3	1809	0	28.5	1986	0	30.7	1746	0	27.2	1945	0
Total PD1[b]	87.6	3728	11	79.9	3469	20	62.2	3321	65	70.2	3438	56
Total PD2	91.8	4253	11	92.5	4112	20	70.0	4040	65	81.2	4104	56

[a]POST herbicides were applied to V4 corn on May 28, 2015 and June 1, 2016 in East Lansing and May 28, 2015 and June 3, 2016 in Richville.

[b]Total precipitation, GDDs, and days with freezing soil temperatures between herbicide application and the first planting date (PD1), sugarbeet and alfalfa, and the second planting date (PD2) cucumber, black bean and kidney bean.

Table 2.5. Response of alfalfa planted 10.5 to 11.3 months after bicyclopyrone and mesotrione applications in herbicide carryover experiments conducted in East Lansing and Richville, MI. Data were combined over years 2015-2016 and 2017-2018 for each location.

		East Lansing		Richville	
Herbicide	Rate	Injury[a]	Yield	Injury	Yield
	– g ha^{-1} –	— % —	— kg ha^{-1} —	— % —	— kg ha^{-1} —
Bicyclopyrone	50	0[b]	1,460	0	1,720
Bicyclopyrone	100	0	1,550	0	1,750
Mesotrione	210	0	1,580	0	1,620
Control	—	0	1,450	0	1,790

[a]Injury was evaluated 28 d after alfalfa emergence.
[b]Treatment means were not significantly different at $\alpha \leq 0.05$.

Table 2.6. Response of cucumber planted 12 months after bicyclopyrone and mesotrione applications in herbicide carryover experiments conducted in East Lansing and Richville, MI.[a]

		East Lansing			Richville		
Herbicide	Rate	Stand[b]	Injury[c]	Yield	Stand	Injury	Yield
	– g ha^{-1} –	– plants ha^{-1} –	— % —	— kg ha^{-1} —	– plants ha^{-1} –	— % —	— kg ha^{-1} —
Bicyclopyrone	50	148,500[d]	0	36,100	171,800	0	12,400
Bicyclopyrone	100	136,100	0	31,900	166,800	0	9,700
Mesotrione	210	141,300	0	31,400	188,400	0	10,000
Control	—	114,800	0	31,100	173,000	0	12,300

[a]Data is presented only from the 2016-2017 experiment, due to poor cucumber establishment in the 2015-2016 experiment.
[b]Cucumber stand was determined 14 d after emergence.
[c]Injury was evaluated 28 d after cucumber emergence.
[d]Treatment means were not significantly different at $\alpha \leq 0.05$.

Table 2.7. Response of black and kidney bean planted 12 months after bicyclopyrone and mesotrione applications in herbicide carryover experiments conducted in East Lansing and Richville, MI. Data were combined over years 2015-2016 and 2017-2018 for each location.

Black bean		East Lansing			Richville		
Herbicide	Rate	Stand[a]	Injury[b]	Yield	Stand	Injury	Yield
	– g ha^{-1} –	– plants ha^{-1} –	— % —	— kg ha^{-1} —	– plants ha^{-1} –	— % —	— kg ha^{-1} —
Bicyclopyrone	50	225,900	0 A[c]	4,460	213,000	0	1,460
Bicyclopyrone	100	226,290	0 A	4,370	213,200	0	1,840
Mesotrione	210	228,250	3 B	4,270	202,100	0	1,740
Control	—	226,800	0 A	4,350	220,000	0	1,790
Kidney bean							
Bicyclopyrone	50	121,300	1 A	3,370	108,400	0	1,620
Bicyclopyrone	100	132,500	5 B	3,150	105,800	0	1,530
Mesotrione	210	123,200	11 C	3,490	119,800	0	1,630
Control	—	124,100	0 A	3,380	126,700	0	1,680

[a]Dry bean stand was determined 14 d after emergence.
[b]Injury was evaluated 28 d after dry bean emergence.
[c]Means followed by the same letter within a column for each class of dry bean significantly different at $\alpha \leq 0.05$.

Table 2.8. Response of sugarbeet planted 10.5 to 11.5 months after bicyclopyrone and mesotrione applications in herbicide carryover experiments conducted in East Lansing and Richville, MI.

East Lansing		2015-2016				2016-2017			
Herbicide	c	Stand[a]	Injury[b]	Yield	RWSH[c]	Stand	Injury	Yield	RWSH
	– g ha^{-1} –	– plants ha^{-1} –	— % —	— kg ha^{-1} —	— kg ha^{-1} —	– plants ha^{-1} –	— % —	— kg ha^{-1} —	— kg ha^{-1} —
Bicyclopyrone	50	107,600 A[c]	0 A	81,800	24,400	84,700 A	0 A	53,500 A	17,100 A
Bicyclopyrone	100	100,100 A	1 A	72,500	21,700	70,100 A	15 A	44,300 A	14,300 A
Mesotrione	210	81,500 B	20 B	75,100	22,400	2,600 B	97 B	0 B	0 B
Control	—	101,800 A	0 A	79,800	23,400	83,300 A	0 A	47,200 A	14,900 A
Richville									
Bicyclopyrone	50	109,700	0	36,300	10,700	61,800	0	17,200	5,500
Bicyclopyrone	100	116,000	0	40,900	12,100	61,300	0	20,000	6,500
Mesotrione	210	111,400	0	37,700	10,900	63,600	0	16,500	5,400
Control	—	112,800	0	38,900	10,800	55,200	0	22,000	7,000

[a]Sugarbeet stand was determined 14 d after emergence.
[b]Injury was evaluated 28 d after sugarbeet emergence.
[c]RWSH = Recoverable white sucrose per hectare
[d]Means followed by the same letter within a column for each location are not significantly different at $\alpha \leq 0.05$.

Figure 2.1. Effect of preemergence applications of bicyclopyrone (a) and mesotrione (b) on alfalfa. Alfalfa was planted is soils collected from East Lansing (loam ■), Richville (clay loam ▲), and the Michigan State greenhouse complex (MSUGH) (sandy loam ●). The left column is crop injury 14 DAE and the right column is dry plant biomass 28 DAE.

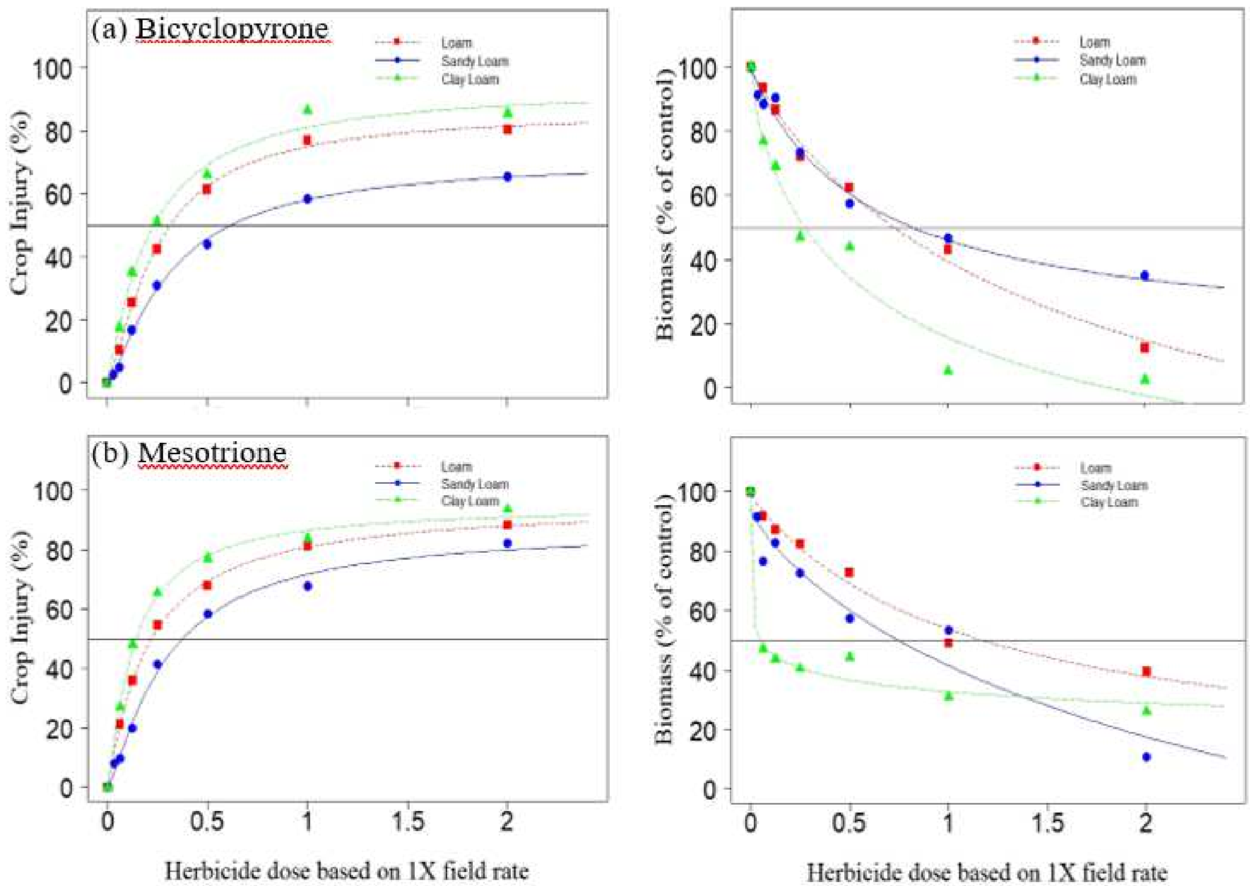


Figure 2.2. Effect of preemergence applications of bicyclopyrone (a) and mesotrione (b) on cucumber. Cucumber was planted in soils collected from East Lansing (loam ■), Richville (clay loam ▲), and the Michigan State greenhouse complex (MSUGH) (sandy loam ●). The left column is crop injury 14 DAE and the right column is dry plant biomass 21 DAE.

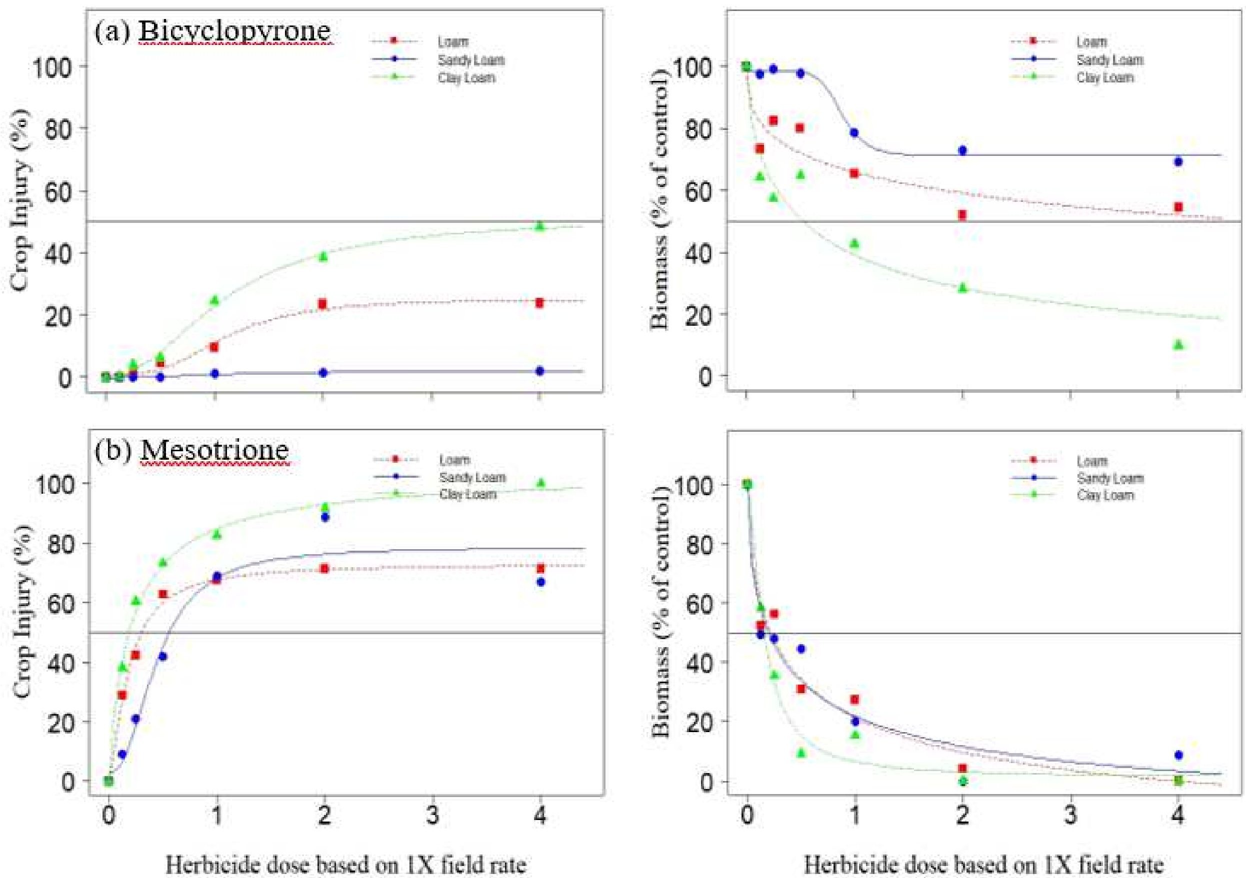


Figure 2.3. Effect of preemergence applications of bicyclopyrone (a) and mesotrione (b) on black bean. Black bean was planted in soils collected from East Lansing (loam ■), Richville (clay loam ▲), and the Michigan State greenhouse complex (MSUGH) (sandy loam ●). The left column is crop injury 14 DAE and the right column is dry plant biomass 21 DAE.

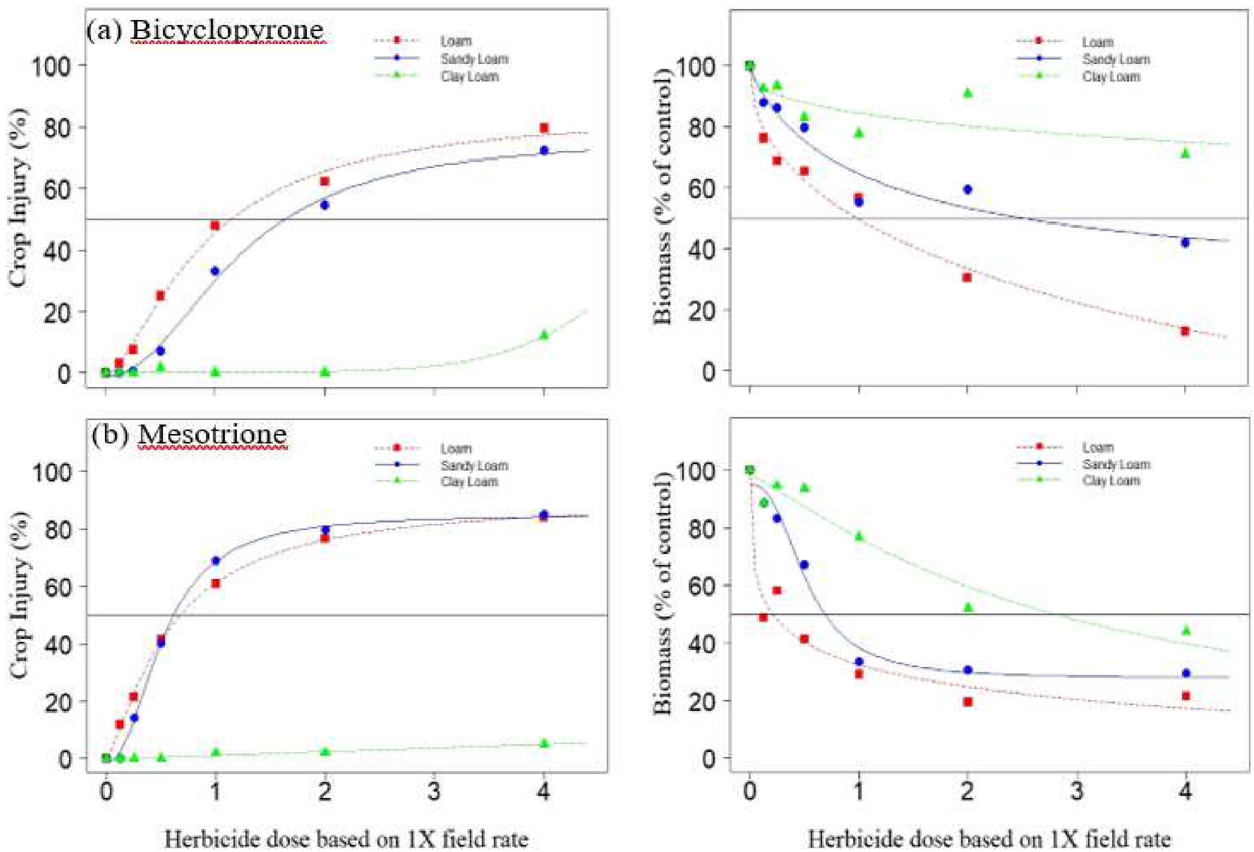


Figure 2.4. Effect of preemergence applications of bicyclopyrone (a) and mesotrione (b) on kidney bean. Kidney bean was planted in soils collected from East Lansing (loam ■), Richville (clay loam ▲), and the Michigan State greenhouse complex (MSUGH) (sandy loam ●). The left column is crop injury 14 DAE and the right column is dry plant biomass 21 DAE.

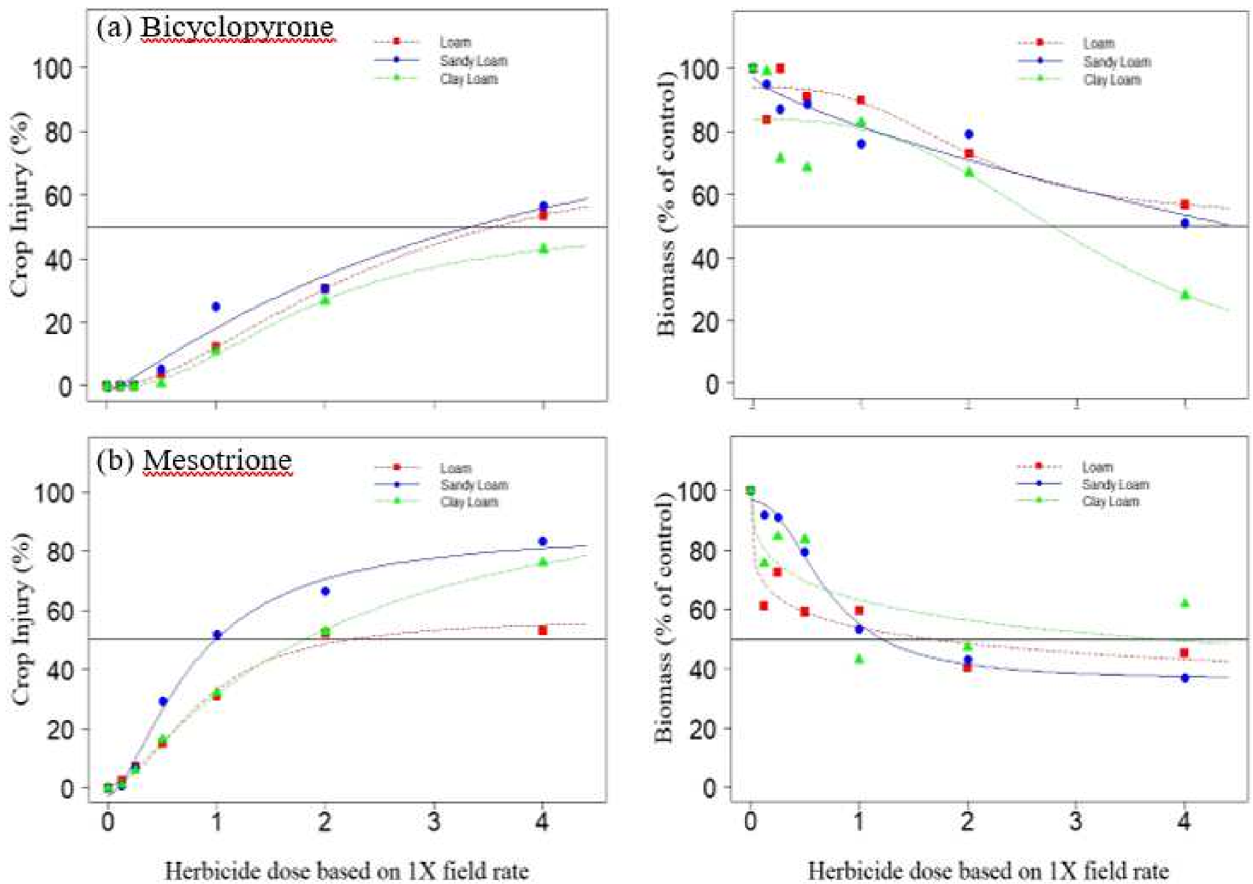
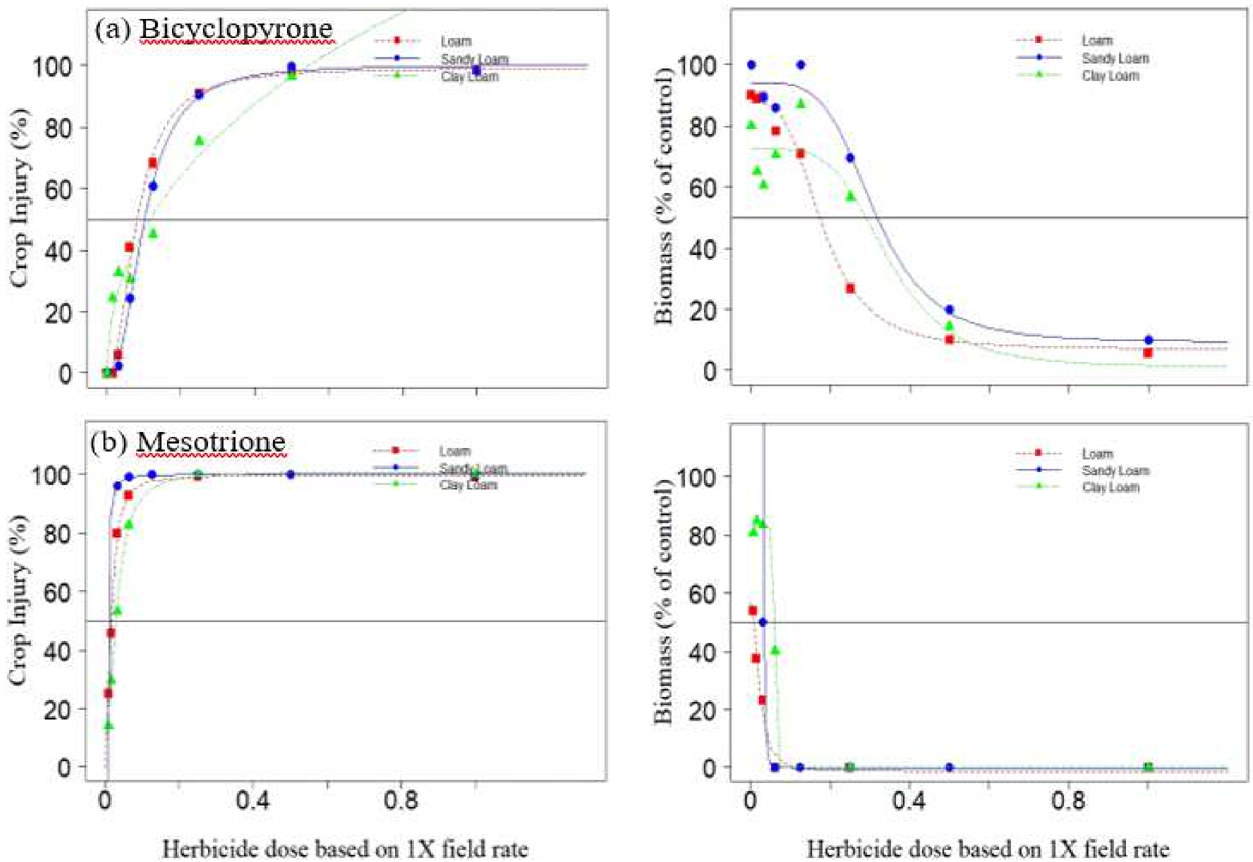


Figure 2.5. Effect of preemergence application of bicyclopyrone (a) and mesotrione (b) on sugarbeet. Sugarbeet was planted in soils collected from the East Lansing (loam ■), Richville (clay loam ▲), and Michigan State greenhouse complex (MSUGH) (sandy loam ●). The left column is crop injury 14 DAE and the right column is dry plant biomass 28 DAE.



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