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THESIS

ADSORPTION, LEACHING, AND DISSIPATION OF PYROXASULFONE AND TWO CHLOROACETAMIDE HERBICIDES

Submitted by

Eric P. Westra

Department of Soil and Crop Sciences

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Master's Committee:

Advisor: Ken Barbarick

Dale Shaner
Raj Khosla
Howard Schwartz

ABSTRACT

ADSORPTION, LEACHING, AND DISSIPATION OF PYROXASULFONE AND TWO CHLOROACETAMIDE HERBICIDES

Pyroxasulfone is a new pyrazole herbicide that controls weeds by inhibiting very long chain fatty acid synthesis. This mechanism of action places pyroxasulfone in the Weed Science Society of America (WSSA) group 15 or Herbicide Resistant Action Committee (HRAC) group K3 herbicides that include *s*-metolachlor and dimethenamid-*p*. Dimethenamid-*p* and *s*-metolachlor are referred to in literature as acetamide, acetanilide, chloroacetamide, or chloroacetanilide herbicides. In this thesis, these two herbicides are referred to as chloroacetamide herbicides based on the HRAC classification. The soil interactions of pyroxasulfone were evaluated and compared to s-metolachlor and dimethenamid-p to better understand how pyroxasulfone will behave under various field conditions Pyroxasulfone was compared with these two standard herbicides because of their similar mechanisms of action, use patterns, potential for use in similar cropping systems, and similar weed control spectrums. Sorption coefficients were determined for 25 different soils to evaluate relative differences in binding among pyroxasulfone, dimethenamid-*p*, and *s*-metolachlor. Across all soil types, the relative order of binding was pyroxasulfone=dimethenamid-*p* < *s*-metolachlor. Pyroxasulfone and dimethenamid-*p* were not statistically different in terms of their binding; however, *s*-metolachlor binding was statistically greater than both dimethenamid-*p* and pyroxasulfone. For all three herbicide, organic matter was the only soil property which was highly and significantly correlated to herbicide adsorption; all other soil properties correlated with herbicide adsorption could be explained by the correlation of OM and those soil properties. Based on the water solubility of these three herbicides, we expected the order of binding to be dimethenamid-*p* < *s*-metolachlor < pyroxasulfone. This study displayed the unique characteristics of pyroxasulfone in that it has the lowest water solubility of the three herbicides, yet sorption coefficient values indicate that pyroxasulfone is only loosely adsorbed by soil. Reduced soil binding along with a higher unit of activity makes pyroxasulfone a potent herbicide that provides comparable weed control when applied as low as one-eighth of typical application rates for other chloroacetamide herbicides.

Field studies were conducted in 2009 and 2010 at two contrasting field sites to evaluate the dissipation and movement of pyroxasulfone and s-metolachlor in the top 30 cm of the soil profile. The site at the horticultural farm (HORT) has a Nunn clay loam soil (Argiustoll), whereas the site at the Limited Irrigation Farm (LIRF) has an Olney fine sandy loam soil (Haplargid). Dissipation half-lives (DT_{50}) were the shortest at the Hort farm site with the heavier textured clay loam soil and increased moisture content. The LIRF site with lighter textured sandy loam soil and decreased moisture resulted in extended DT_{50} values and more variation between replicates for both herbicides. Across both years and field sites, pyroxasulfone DT_{50}s were approximately twice as long as for s-metolachlor. The extended half-life of pyroxasulfone suggests that it would provide longer weed control compared to s-metolachlor. Herbicide movement in the top 30 cm of the soil profile was greater at the LIRF site which suggests that movement was influenced by soil type to a greater extent than irrigation amount, since the LIRF site received much less total irrigation yet had the most movement downward in the profile. In general, pyroxasulfone moved downward in the profile to a greater extent than s-metolachlor. Observed herbicide movement confirmed sorption coefficient data that shows that pyroxasulfone is bound less to the soil compared to metolachlor and, hence, is more available in the soil solution where the herbicide movement is influenced by mass flow. Extended observed half-lives, reduced soil binding, and increased unit activity indicate that pyroxasulfone is a potent inhibitor of very long chain fatty acid (VLCFA) biosynthesis that can provide comparable weed control for longer periods of time at reduced use rates when compared to commonly used chloroacetamide herbicides.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter 1: Introduction

Pyroxasulfone is a new, pyrazole based herbicide which has pre-emergence activity and inhibits shoot elongation of susceptible seedling plants by inhibiting the biosynthesis of very-long-chain fatty acids (Tanetani et al., 2009). Although pyroxasulfone is not structurally related to chloroacetamide herbicides, it shares the same mechanism of action. Pyroxasulfone is used preemergent to control a broad spectrum of grasses and small seeded broadleaves and is selective in corn, soybean, wheat and sunflower (Tanetani et al., 2011). The advantage of pyroxasulfone over the chloroacetamide herbicides is its low use rate, and high unit activity on important broadleaf weeds such as *Amaranthus* spp. (Zollinger and Ries, 2007). Pyroxasulfone recently received a registration to be used in combination with flumioxazin in corn in the U.S. (Valent U.S.A. Press Release, 2012).

Dimethenamid-*p* and *s*-metolachlor are both chloroacetamide herbicides that control plants via the inhibition of very long chain fatty acid biosynthesis. Dimethenamid-*p* was first registered in corn in 1993. *s*-Metolachlor has been available commercially since 1977, and was registered in the U.S. in 1997 (Weed Sci. Soc. Am, 2007). Tolerance to chloroacetamide herbicides such as s-metolachlor and dimethenamid-p appears to result from more rapid metabolism via glutathione conjugation(Breaux, 1987; Jaworski, 1969). Conjugation appears to happen rapidly and the half-life of chloroacetamides in plants may only be a few hours or less (Breaux, 1987; Carringer et al., 1978; Fuerst and Gronwald, 1986), which suggests that these herbicides may be active at very low concentrations within the plant (Fuerst, 1987).

Pyroxasulfone has been classified by the Weed Science Society of America (WSSA) as a group 15, or by the Herbicide Resistance Action Committee (HRAC) as a group K3 herbicide which control plants by inhibiting the biosynthesis of very long chain fatty acids (VLCFA's). This group of herbicides includes both chloroacetamide herbicides *s*-metolachlor and dimethenamid-*p*, whose characteristics are included along with pyroxasulfone in Table 1.

Pyroxasulfone has been under development as the code number KIH-485, (CAS# 44 7399-55-5). Pyroxasulfone was discovered by Kumiai Chemical Industry who have partnered with several companies to register pyroxasulfone for specific uses in certain crops as either a solo product or sold as a premix. BASF has the solo product Zidua© pending use on corn (Zea mays), soybean (Glycine max), wheat (Triticum aestivum) and sunflower (Helianthus annuus). Bayer CropScience has a solo product Sakura© that is registered in Australia for triticale and wheat. FMC has a product with pyroxasulfone and fluthiacet-methyl Anthem© pending use on corn and soybean, as well as a premix with pyroxasulfone, atrazine and fluthiacet-methyl Anthem ATZ© for pending use on corn. Valent U.S.A. Corp. has a premix of pyroxasulfone and flumioxazin Fierce© that has just been released for no-till and reduced-till corn with pending use on soybean. It is fairly unique that Kumiai Chemical Industry has entered agreements with several different companies to market and sell pyroxasulfone as both solo and premix products for certain cropping systems (Farm Chemicals International, 2012).

Pyroxasulfone has been shown to inhibit biosynthesis of very long chain fatty acids, specifically inhibition of the elongation steps from C18:0 to C20:0 inhibits elongation of stearic acid from both the endoplasmic reticulum and chloroplast , C20:0 to C22:0, C22:0 to C24:0, C24:0 to C26:0, and C26:0 to C28:0 catalyzed by VLCFA elongases (VLCFAEs) (Tanetani, 2011). The chloroacetamide herbicides only inhibit two elongation steps from C18:1 to C20:1, and C20:1 to C22:1 (Fierce Technical Bulletin, 2011). This increase in sites of action for pyroxasulfone would potentially reduce the development of resistance compared to chloroacetamide herbicides that only affect two points in the pathway. Even after extensive use of chloroacetamide herbicides, resistance has only been documented in five species against this mechanism of action (Heap, 2012). This relatively small number of species with documented resistance makes this mechanism of action valuable from a resistance management approach.

Dimethenamid-*p* is a root and shoot growth inhibitor that controls germinating seeds before or soon after they emerge from the soil. *s*-Metolachlor is mainly absorbed through shoot tissue of germinating seedlings with some uptake through root tissue. Pyroxasulfone is similar to both chloroacetamide herbicides, and preliminary data has shown that pyroxasulfone can be absorbed through both root and shoot tissue although it appears to be predominately adsorbed through shoot tissue (E. Westra, Unpublished data).

Pyroxasulfone provides control of grasses and small seeded broadleaves similar to *s*-metolachlor and dimethenamid-*p*. Although weed control spectrum is similar among these three herbicides, pyroxasulfone provides better control of important broadleaf weeds such as kochia (*Kochia scoparia*), velvetleaf (*Abutilon theophrasti*), and *Amaranthus spp*. Pyroxasulfone can control weeds resistant to other herbicides such as glyphosate, acetolactate synthase (ALS) and acetyl-CoA carboxylase (ACCase)inhibiting herbicides (Zidua© Technical Brochure, 2011).

Dimethenamid-*p* can be applied EPP (early preplant), PPI (preplant incorporated), PRE (Preemergence), or early POST (Postemergence) depending on the cropping system. Although early post application of dimethenamid-p have little to no activity on emerged weeds. *s*-Metolachlor can be applied as Fall (post harvest applications), PPI, PRE, and early POST or at layby depending on the cropping system. Pyroxasulfone can be applied EPP,PP/PPI, PRE, and early POST depending on the cropping system. All three herbicides have the option for similar methods of application, and all require moisture or mechanical incorporation for activation and maximum efficacy.

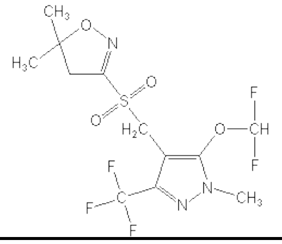
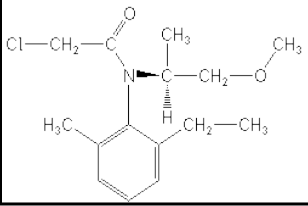
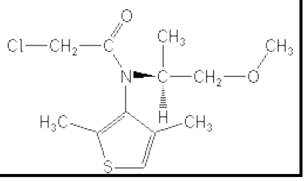
Similar to dimethenamid-*p* and *s*-metolachlor, pyroxasulfone use rates will depend on soil type, application timing, tank mix partner, and weed spectrum present. While it is not a new mode of action, pyroxasulfone is a potent inhibitor of VLCFA with a broad spectrum of weed control. Pyroxasulfone has been shown to control shattercane (*Sorghum bicolor*), Texas panicum (*Panicum texanum*), wild proso millet (*Panicum miliaceum*), and Italian ryegrass (*Lolium rigidum*) which have typically been difficult to control. Pyroxasulfone has provided weed control slightly to significantly longer than preemergent herbicides such as dimethenamid-*p* or *s*-metolachlor (Zidua© Herbicide Technical Brochure). Similar to other commercial pre-emergent herbicides, pyroxasulfone requires moisture for activation. Pyroxasulfone can be applied alone, or in combination with other herbicides, in order to increase the weed control spectrum. Pyroxasulfone has several types of formulations to meet farmers' needs. The 85% water dispersible granule (WG) is the typical formulation of pyroxasulfone when applied as a solo product, although there is also a suspension concentrate (SC) with 42.7% concentrate active ingredient (Global Technical Bulletin Pyroxasulfone). Projected use rates for pyroxasulfone are 90-250 g a.i. ha^{-1} for corn and soybean, and 60-120 g a.i. ha^{-1} for wheat, although it will not be labeled for use in durum wheat due to crop sensitivity.

Stahlman and Olson et al. (2010) stated that both the mechanism of action and probable use patterns for pyroxasulfone are similar to those of *s*-metolachlor. We compared pyroxasulfone with dimethenamid-*p* and *s*-metolachlor because of their similar mechanism of action, weed control spectrum, and potential weed control use in similar cropping systems.

Preliminary field testing with metolachlor and its isomer *s*-metolachlor showed comparable weed control between the two isomers even though *s*-metolachlor was applied at 65% the normal rate of metolachlor (O'Connell et al., 1998). Finding pre-emergent herbicides with increased weed control efficacy at lower use rates can replace older active ingredients and consequently reduce chemical loading imposed on the environment while maintaining a certain level of weed control efficacy. Shaner et al. (2006) showed that *s*-metolachlor was 1.4-1.6 fold more active than metolachlor on a gram for gram basis based on enrichment of the more active s-isomer. Due to increased weed control efficacy, in 1997 *s*-metolachlor displaced metolachlor and provided similar weed control at 35% less use rates, 2.1 kg ha^{-1}and 1.5 kg ha^{-1} for metolachlor and s-metolachlor, respectively.

Conversely, Mueller and Steckel (2011) showed that pyroxasulfone at 209 g ai ha^{-1} provided broadleaf signalgrass (Brachiaria platyphylla) control that was equal to or superior to acetochlor at 1,740 g ai ha^{-1}, dimethenamid-*p* at 1,500 g ai ha^{-1}, and *s*-metolachlor at 1,420 g ai ha^{-1}. These use rates and weed control efficacies show the potency of pyroxasulfone compared to other chloroacetamide herbicides, as well as the potential to reduce chemical loading of soil applied herbicides via lower field use rates. Having herbicides that control weeds at lower use rates helps reduce the chemical load to the environment. Metolachlor was replaced by *s*-metolachlor due to its increased weed control efficacy at lower use rates. When compared to *s*-metolachlor, pyroxasulfone provides comparable weed control at lower use rates which is favorable from an environmental and weed control standpoint.

Table 1.1) Herbicide characteristics for pyroxasulfone, *s*-metolachlor, and dimethenamid-*p*.

	pyroxasulfone	***s*-metolachlor**	**dimethenamid-*p***
Water solubility	3.49 mg L^{-1} @ 20°C	530 mg L^{-1} @ 20°C	1450 mg L^{-1} @ 20°C
Log K_{ow}	2.39	2.89	2.14
Vapor Pressure	$2x10^{-6}$ Pa @ 25°C	$3.7x10^{-3}$ Pa @ 25°C	$1.88x10^{-5}$ Pa @ 25°C
Formula	$C_{12}H_{14}F_5N_3O_4S$	$C_{12}H_{22}ClNO_2$	$C_{12}H_{18}CLNO_2S$
Molecular Mass	391.32 g mol^{-1}	283.79 g mol^{-1}	275.79 g mol^{-1}
Structure			

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Chapter 2: Evaluation of Sorption Coefficients for Pyroxasulfone, *s*-Metolachlor and Dimethenamid-*p*

We evaluated sorption coefficients for pyroxasulfone, s-metolachlor, and dimethenamid-p on 25 soil types with different chemical and physical properties to fully understand the influence of soil components on pyroxasulfone binding. Sorption coefficients were determined using a batch equilibrium method to evaluate relative differences in binding among herbicides. Based on water solubility values we would have expected the relative order of binding to be dimethenamid-p (1450 mg L^{-1} @ 20°C), s-metolachlor (530 mg L^{-1} @ 20°C), and pyroxasulfone (3.49 mg L^{-1} @ 20°C) in order of increasing binding. However, when sorption coefficients were calculated we observed the order of pyroxasulfone=dimethenamid-p < s-metolachlor in order of increasing binding. The average Kd (sorption coefficient) values were 1.7, 2.3, and 4.0 L Kg^{-1} for pyroxasulfone, dimethenamid-p, and s-metolachlor, respectively.

Although dimethenamid-*p* has water solubility values that are over 400 times greater than pyroxasulfone, there was no statistical difference in binding between pyroxasulfone and dimethenamid-*p*. *s*-Metolachlor was statistically greater than pyroxasulfone and dimethenamid-*p*.

Across all soil chemical and physical properties, sorption coefficients for all three herbicides were highly and statistically correlated to organic matter. Sand and silt were also statistically correlated to binding, although these correlations could be explained by the high correlation of organic matter to these components. Evaluation of sorption coefficients indicates that pyroxasulfone is most prevalent in the soil solution where herbicides are available for plant uptake. Reduced soil binding and greater activity at the target site could contribute to comparable weed control efficacies of pyroxasulfone even when applied at one-eighth of use rates of *s*-metolachlor and dimethenamid-*p*.

INTRODUCTION

Chloroacetamide herbicides for pre-emergence weed control in various crops were first introduced in the early 1950's and sixties. Although some of the first compounds were eventually replaced, the addition of safeners has extended the use of chloroacetamide herbicides for broadening the weed control spectrum when used in tank mixes (Böger et al., 2000). Acetanilide-derived herbicides are used for pre-emergence weed control in corn and soybean, as well as sorghum (*Sorghum bicolor*), sunflower (*Helianthus annuus*), peanut (*Arachis hypogaea*) and cotton (*Gossypium spp*.) (Stamper and Tuovinen, 1998).

Chloroacetamide herbicides are often used in tank-mixes with other herbicides to provide broad spectrum weed control. These herbicides play a vital role in managing herbicide resistant weeds, including those resistant to glyphosate, but their limited activity on many broadleaf weeds has increased the need for additional herbicide chemistries to achieve effective weed control. Evaluations of new herbicide compounds are crucial for the development of new types of chemistry for weed control, and for incorporation of these compounds into cropping systems to give farmers more diverse tools to manage weeds which are inherently difficult to control.

Pyroxasulfone is a new, pyrazole based herbicide with the same mechanism of action as chloroacetamides, e.g., the inhibition of very long chain fatty acid biosynthesis (Tanetani et al., 2009). This compound is used pre-emergent to control a broad spectrum of grasses and small seeded broadleaves, and is selective in corn, soybean, wheat and sunflower (Tanetani et al., 2011). The advantage of pyroxasulfone over the chloroacetamide herbicides is its low use rate and activity on important broadleaf weeds such as *Amaranthus* spp. (Zollinger and Ries, 2007). Pyroxasulfone recently received an EPA federal registration to be used in combination with flumioxazin in corn in the U.S. (Valent U.S.A. press release, 2011).

Herbicide sorption to soil influences a compound's environmental fate, persistence in the soil, and biological activity (Pusino et al., 1992). It is important to examine the affinity of pyroxasulfone to soil to provide insight into its interaction with soil when applied under field conditions. Soil texture and chemical properties influence herbicide binding, and understanding the influences of these properties on the binding of pyroxasulfone will help us predict behavior of the compound in different soils.

There have been numerous studies on how chloroacetamide herbicides bind to soil components. For example, soil organic matter is the predominant adsorbent for s-metolachlor (Obrigawitch et al., 1981; Pusino et al., 1992). This type of information does not exist for pyroxasulfone, so we cannot compare soil interactions to commonly used chloroacetamide herbicides. Measuring the soil-sorption coefficients for pyroxasulfone and comparing these values to commonly used chloroacetamide herbicides will give us a predictor of how this compound will act in the field and how it can be incorporated into current agricultural practices.

The objectives of this study were to (a) compare the relative soil binding between pyroxasulfone, *s*-metolachlor, and dimethenamid-*p* across 25 different soil types, and (b) evaluate the influence of different soil texture and chemical properties on soil binding of these three herbicides.

MATERIALS AND METHODS

Herbicide Soil Adsorption

A mixed herbicide stock solution was prepared by combining 1 mg mL^{-1} of pyroxasulfone, *s*-metolachlor and dimethenamid-*p* together in a 0.02M $CaCl_2$ solution. Pilot studies showed that combining the three herbicides together did not affect recovery or binding rates compared to each herbicide by itself. Batch equilibrium studies were conducted by combining 10 g of dry soil with 10 mL of herbicide stock solution in capped 50 mL glass centrifuge tubes which were shaken horizontally for 24 hours on a table shaker. Control herbicide solutions without soil were also included. After shaking, the samples were centrifuged at 1000 rcf (relative centrifugal force) for 10 minutes to separate the soil and herbicide solution. Three mL of the supernatant was combined with 3 mL of toluene, and shaken for two hours on a horizontal shaker. After being centrifuged at 1000 rcf for 10 minutes, 2 mL of the toluene supernatant was transferred to a volumetric flask and spiked with 500 ng L^{-1}butylate as an internal standard, and then injected in a GC/MS column to quantify herbicide concentrations in the solution. The herbicide concentrations in the toluene phase were analyzed using a gas chromatograph equipped with a mass spectrometer (Shimadzu GC-17A and GCMS QO 5050A, Shimadzu Scientific Instruments, Inc., Columbia, MD) which monitored the masses for butylate (m/z 146), *s*-metolachlor (m/z 162.15), dimethenamid-*p* (m/z 229.10) and pyroxasulfone (m/z 179.10). A RTX-5 30-m by 0.25-mm column (Restek, Bellefonte, PA) was used with a flow of helium at 1 mL/min.

Herbicide concentrations in the liquid solution were subtracted from initial total concentrations without soil to calculate the amount of herbicide bound to the soil. Ratios were then calculated by dividing the concentration of herbicide bound to the soil by the concentration in the soil solution as mathematically represented by equation [1].

$$Kd = [\text{herbicide sorbed to soil } (\mu g\ g^{-1})] / [\text{herbicide in solution } (\mu g\ mL^{-1})] \qquad [1]$$

K_{oc} for each herbicide was calculated as

$$K_{oc} = (K_d/f_{oc}) \times 100 \qquad [2]$$

F_{oc} is the soil organic C mass-fraction 100 g soil^{-1} that was measured for each soil

f_{oc} was calculated as

$$foc = som/1.72 \qquad [3]$$

Where som is the soil organic matter

Soil Analysis

Soils were air dried and passed through a 2.0 mm screen. Two replicates of each soil were sent to AgSource/Harris Laboratories (Lincoln, NE), and were analyzed for texture, pH, CEC, and organic matter. Soil samples and their replicate were randomized and blindly labeled to ensure the objectivity, quality and precision of analyses.

Statistical Analysis

Pearson correlations were calculated for sorption coefficients (K_d) vs. all soil textual and chemical properties with a significance level of $P< .05$. Fishers' LSD was calculated for the three herbicides. SAS version 9.2 statistical program was used for all analyses.

RESULTS

Herbicide sorption

Soil textural and chemical properties for all soils are listed in Table 1. The K_d values for all three herbicides in different soils are displayed in Table 2. The greatest amount of herbicide adsorption for all three compounds occurred in the Wisconsin 3&4 silt loam soil. For *s*-metolachlor and dimethenamid-*p*, the lowest adsorption occurred in the Pasco, Washington sand soil. For pyroxasulfone, the lowest amount of adsorption occurred in the 3-river sandy clay loam soil. Sorption coefficients ranged from 0.76 to 16.67 L Kg^{-1} for *s*-metolachlor, 0.32 to 9.57 L kg^{-1} for dimethenamid-*p*, and 0.49 to 5.91 L Kg^{-1} for pyroxasulfone. When combined across all soil types, the mean and median Kd values were 4.0 and 2.8 L Kg^{-1} for *s*-metolachlor, 2.3 and 1.7 L Kg^{-1} for dimethenamid-*p*, and 1.7 and 1.5 L Kg^{-1} for pyroxasulfone, respectively. Pearson correlations were calculated comparing K_d values to soil textural and chemical properties which are displayed in Table 3.

When comparing the K_d values for all three herbicides, we observed a significant relationship with organic matter, silt, and sand at r^2 = 0.91, 0.56, and -0.44 for *s*-metolachlor; r^2 = 0.91, 0.57, -0.44 for dimethenamid-*p*; and r^2 = 0.94, 0.59, -0.51 for pyroxasulfone (Table 3). Soil pH, cation exchange capacity, and clay content were not significantly correlated to K_d for all three herbicides (Table 3). Correlations between organic matter, sand and silt content resulted in significant linear relationships of -0.677 and 0.691, respectively (Table 6). High correlations among soil properties across all soils resulted in correlations between these soil properties and herbicide binding. Given that organic matter was highly correlated to herbicide binding (> 0.905 for all herbicides), and also highly correlated to sand and silt content, would explain the significant correlation with both sand and silt content and herbicide binding.

Fishers LSD for all three herbicides were run across all soil types. Fishers LSD = 0.6179, which resulted in statistical differences between *s*-metolachlor and both pyroxasulfone and dimethenamid-*p*, but there was no statistical difference between binding for pyroxasulfone and dimethenamid-*p* (Table 5). K_{oc} (organic carbon-water partitioning coefficient) is the distribution coefficient (Kd) normalized to total organic carbon content and is calculated from equation 2. K_{oc} values were calculated for all three herbicides across all soils. The average K_{oc} values ± standard error for *s*-metolachlor was 268 ± 20 L Kg^{-1} , dimethenamid-*p* 149 ± 11 L Kg^{-1}, and pyroxasulfone 113 ± 7 L Kg^{-1}.

DISCUSSION

Typically compounds with lower water solubility will have higher sorption coefficient values, and will result in higher amounts of herbicide bound to the soil (Bailey, 1968). Pyroxasulfone is a unique compound in that it has very low water solubility (3.49 mg L^{-1} @ 20°C) , and yet has reduced soil binding compared to *s*-metolachlor and dimethenamid-*p* which have higher water solubility's of 530 mg L^{-1} and 1450 mg L^{-1} @ 20°C, respectively. Based solely on water solubility values, we hypothesized that pyroxasulfone would have the greatest sorption coefficient (K_d) value followed by *s*-metolachlor and then dimethenamid-*p*. However, when sorption coefficient studies were measured across 25 different soil types we observe the trend of pyroxasulfone=dimethenamid-*p* < *s*-metolachlor in order of increasing soil binding. Average K_{oc} values listed in the WSSA Herbicide Handbook (9th Edition, 2007) for *s*-metolachlor (200 L Kg^{-1}) and dimethenamid-*p* (55 – 125 L Kg^{-1}) were similar to our average K_{oc} values of 268 and 149 L Kg^{-1} for *s*-metolachlor and dimethenamid-*p*, respectively. Although there is little sorption coefficient data for dimethenamid-*p* in the literature, our data shows relative differences in adsorption between *s*-metolachlor and dimethenamid-*p* were similar to listed K_{oc} values for these two compounds.

With all three herbicides, only organic matter resulted in a significant relationship with herbicide soil adsorption. Generally, compounds with lower water solubility are adsorbed to a greater extent by organic matter (Carringer et al., 1975; Rahman, 1976). This would explain why pyroxasulfone binding was highly correlated to OM, however, results for all three herbicides indicate that herbicide adsorption was highly correlated to organic matter (> 0.90 for all three herbicides) regardless of differences in their water solubility (Table 4). Generally adsorption of a herbicide is positively correlated with its ocatanol-water partition coefficient and negatively correlated with the compounds' water solubility (Singh et al., 2002). These herbicide characteristics appeared to predict the relative differences in soil binding between *s*-metolachlor and dimethenamid-*p*, but failed to predict the amount of soil binding for pyroxasulfone based on its water solubility and log K_{ow} (Table 4).

In general within a group of structurally related compounds, the phytotoxicity of the herbicides of higher water solubility was less influenced by organic matter than those materials of lower water solubility ((Carringer et al., 1975; Rahman, 1976; Weed and Webber, 1974). Bailey et al. (1968) also concluded that within a chemically homologous series, the extent of adsorption was directly related to or governed by the compounds' water solubility. This would explain relative differences in adsorption between dimethenamid-*p* and *s*-metolachlor. It also shows the impact of differences in chemical structure, and the influence of pyrazole and chloroacetamide based molecules on soil adsorption.

Weber et al. (2000) found that nonionizable organic herbicides generally bind to OM more readily than to other soil colloids such as clay minerals or metallic hydrous oxides. In their study, they showed that only two out of eight nonionizable herbicides K_d was correlated to clay minerals. Whereas all eight of the nonionizable herbicides tested were correlated to organic matter content (Weber et al., 2000). Previous work with *s*-metolachlor has shown soil retention was correlated to OM (Obrigawitch et al., 1981; Singh et al., 2001; Patakioutas and Albanis, 2002). Others have shown that herbicide retention is correlated to both OM and clay content (Weber and Peter, 1982; Wood et al. 1987; Weber and Swain, 1993). Weber et al. (2003)showed that K_d values were highly correlated with soil OM (r = 0.97), clay content (r = > 0.79), and CEC (r = > 0.94), although they did show a high correlation between percent clay and CEC (r = 0.93) which would explain their high correlation between K_d values and CEC. However, they did not list correlations between clay and OM for soils tested which could explain the correlation between sorption and clay content. Clay content and OM are typically correlated to each other since soils with higher clay content are more productive and return more carbon into the system annually, which contributes to increased OM content over time (Burke et al., 1988). In our study we observed a low correlation between OM and clay content (r = 0.208), and OM and CEC (r = 0.25) across all 25 different soil types (Table 6).

Although we did not have significant correlations to clay content or CEC, it is hard to say if correlations from previous literature were due to correlation between soil properties, or if binding was actually correlated to these soil properties. For the 25 soil types used in our experiment, organic matter appeared to be the only soil property that was highly correlated to binding. Other soil properties and their correlation to binding could be explained by that properties correlation to organic matter. Our results are in agreement with previous authors that found that OM was the main constituent for predicting binding. Results also differ from other previous reports that both OM and clay content were highly related to binding. Since we did not have co-correlation between OM and both CEC and clay content, we can conclude that OM was the dominant soil characteristic in terms of predicting herbicide binding.

Given that pyroxasulfone applied at lower use rates shows comparable weed control when compared to chloroacetamide herbicides (Mueller and Steckel, 2011), led us to examine if this increased activity per gram of active ingredient was due to reduced soil adsorption, or inherent activity of the compound. Previous work has shown that pyroxasulfone has I_{50} (molar concentration required for 50% plant inhibition) values that range from 0.13 to 4.20 µM for rice and wheat, respectively (Tanetani et al., 2011). Schmalfuβ et al. (2000) showed that metolachlor I_{50} values = 5 µM for leek seedlings. These five-fold differences in I_{50} values indicate enhanced activity of pyroxasulfone compared to *s*-metolachlor in the absence of soil adsorption. I_{50} values indicate that pyroxasulfone is more active than *s*-metolachlor which would contribute to comparative weed control efficacies, even though pyroxasulfone is applied at approximately one seventh the rate of *s*-metolachlor. We would expect that enhanced inherent activity of pyroxasulfone, as well as reduced soil binding, would allow for these lower application rates without compromising weed control

CONCLUSIONS

- Across all 25 soils evaluated, sorption coefficients indicate that pyroxasulfone had a lower degree of soil binding than dimethenamid-*p* and *s*-metolachlor, although pyroxasulfone behaved more similar to dimethenamid-*p*.

- Averaged across all soils evaluated, pyroxasulfone had the lowest average k_d value of 1.725 mg ml^{-1} while dimethenamid-*p* and *s*-metolachlor had higher average values of 2.278 mg $ml^{-1}$and 4.009 mg ml^{-1}, respectively.

- Results suggest that pyroxasulfone should be more available in the soil water solution than dimethenamid-*p* and *s*-metolachlor.

- Using a broad range of soils with diverse physical and chemical properties, statistical analysis suggests that organic matter correlates the best with herbicide binding for all three herbicides.

- Pearson correlations between sorption coefficient values and soil characteristics would support previous claims that pyroxasulfone activity under field conditions is inversely related to organic matter content (Knezevic et al., 2009).

Table 2.1.) Soil physical and chemical properties for the 25 soils which were evaluated in order of increasing organic matter.

	pH	OM %	CEC	% Sand	% Silt	% Clay	Texture
Pasco, WA	7.40	0.80	7.9	88.0	11.2	0.8	Sand
3River, MT	6.40	1.10	4.8	62.0	37.2	0.8	Sandy Loam
LIRF, CO	8.00	1.10	19.8	70.0	19.2	10.8	Sandy Loam
Yuma, CO	8.00	1.10	20.3	62.0	31.2	6.8	Sandy Loam
FL	6.90	1.30	4.3	84.0	15.2	0.8	Loamy Sand
Ephrata, WA	6.35	1.35	10.9	82.2	16.6	1.2	Loamy Sand
Gilcrest, CO	7.50	1.50	10.2	84.0	15.2	0.8	Loamy Sand
NC	4.90	1.50	3.8	90.0	9.2	0.8	Sand
Holtville, CA	7.90	1.80	36.6	30.0	31.2	38.8	Clay Loam
Ardec, CO	8.20	1.90	23.6	55.2	17.6	27.2	Sandy Clay Loam
Mt King, MT	7.80	2.00	26.8	34.0	33.2	32.8	Clay Loam
IN	5.80	2.10	7.4	72.8	22.0	5.2	Sandy Loam
Cutbank, MT	7.85	2.15	18.3	52.2	28.6	19.2	Sandy Loam
Hort Farm, CO	8.00	2.20	32.0	34.0	25.2	40.8	Clay
Moscow, ID	6.50	2.25	14.4	24.2	59.6	16.2	Silt Loam
Pendelton, OR	5.80	2.25	11.4	27.2	65.6	7.2	Silt Loam
Bozeman, MT	7.20	2.30	22.0	27.8	51.0	21.2	Silty Loam
Mt Jossette, MT	7.90	2.60	27.7	48.0	23.2	28.8	Sandy Clay Loam
Chesterfield, MO	5.20	3.05	12.5	24.2	56.6	19.2	Silt Loam
Huntley, MT	7.85	3.20	30.2	10.2	39.6	50.2	Clay
Columbia County, WI	6.70	3.45	12.4	34.8	58.0	7.2	Silt Loam
Columbia County, WI	6.60	3.65	12.5	38.8	57.0	4.2	Silt Loam
Green Lake County, WI	7.10	3.85	13.8	17.8	75.0	7.2	Silt Loam
Saskatoon, CA	6.75	4.70	27.9	31.2	37.6	31.2	Clay Loam
Dodge County, WI	5.55	6.25	18.9	21.8	69.0	9.2	Silt Loam

Table 2.2.) Sorption coefficients for *s*-metolachlor, dimethenamid-*p* and pyroxasulfone in order of increasing organic matter.

			***s*-metolachlor**		**dimethenamid-*p***		**pyroxasulfone**	
			Kd	**Std. Error**	**Kd**	**Std. Error**	**Kd**	**Std. Error**
	Texture	**OM %**	-------------------------(L/kg)-------------------------					
Pasco, WA	Sand	0.80	0.76	0.25	0.32	0.02	0.53	0.09
3River, MT	Sandy Loam	1.10	1.64	0.18	0.82	0.07	0.49	0.05
LIRF, CO	Sandy Loam	1.10	1.37	0.08	0.71	0.01	0.55	0.06
Yuma, CO	Sandy Loam	1.10	1.40	1.29	0.72	0.61	0.64	0.16
FL	Loamy Sand	1.30	2.65	0.25	1.42	0.04	0.68	0.16
Ephrata, WA	Loamy Sand	1.35	1.26	0.09	0.64	0.06	0.54	0.03
Gilcrest, CO	Loamy Sand	1.50	2.37	0.08	1.06	0.05	0.62	0.02
NC	Sand	1.50	2.60	0.04	1.32	0.03	0.83	0.03
Holtville, CA	Clay Loam	1.80	5.01	0.12	2.84	0.25	1.98	0.02
Ardec, CO	Sandy Clay Loam	1.90	2.48	0.08	1.48	0.05	1.09	0.03
Mt King, MT	Clay Loam	2.00	2.30	0.19	1.32	0.03	1.40	0.08
IN	Sandy Loam	2.10	5.00	0.03	2.50	0.01	1.72	0.04
Cutbank, MT	Sandy Loam	2.15	3.77	0.11	1.94	0.04	1.90	0.04
Hort Farm, CO	Clay	2.20	2.25	0.12	1.38	0.05	0.84	0.12
Moscow, ID	Silt Loam	2.25	3.89	0.12	2.26	0.03	1.53	0.03
Pendelton, OR	Silt Loam	2.25	2.72	0.08	1.42	0.04	1.46	0.02
Bozeman, MT	Silty Loam	2.30	3.93	0.04	1.94	0.05	1.89	0.01
Mt Jossette, MT	Sandy Clay Loam	2.60	2.83	0.05	1.71	0.06	1.92	0.03
Chesterfield, MO	Silt Loam	3.05	7.32	0.05	3.97	0.23	3.28	0.05
Huntley, MT	Clay	3.20	3.19	1.37	1.98	0.15	2.20	0.39
Columbia County, WI	Silt Loam	3.45	4.58	0.25	3.89	0.08	2.16	0.09
Columbia County, WI	Silt Loam	3.65	4.85	0.03	2.72	0.03	1.97	0.04
Green Lake County, WI	Silt Loam	3.85	8.24	0.09	4.60	0.19	3.26	0.04
Saskatoon, CA	Clay Loam	4.70	7.13	0.32	4.43	0.77	3.72	0.11
Dodge County, WI	Silt Loam	6.25	16.67	1.17	9.57	0.01	5.91	0.38

Table 2.3.) Pearson correlations were evaluated for s-metolachlor, dimethenamid-p, and pyroxasulfone K_d values vs. soil chemical and physical properties. (*signifies significance at α=0.05)

Soil Properties	***s*-Metolachlor**	**Dimethenamid-*p***	**Pyroxasulfone**
OM	0.905*	0.906*	0.942*
pH	-0.336	-0.312	-0.307
CEC	0.022	0.013	0.085
Sand	-0.437*	-0.443*	-0.512*
Silt	0.557*	0.574*	0.594*
Clay	-0.057	-0.072	0.012

Table 2.4.) Water solubility, and Log K_{ow} values for pyroxasulfone, dimethenamid-p, and s-metolachlor.

	pyroxasulfone	***s*-metolachlor**	**dimethenamid-*p***
Water solubility	3.49 mg L^{-1} @ 20°C	530 mg L^{-1} @ 20°C	1450 mg L^{-1} @ 20°C
Log K_{ow}	2.39	2.89	2.14

Table 2.5.) Fishers LSD grouping for all three herbicides across all soil types (α=.05) LSD=0.6179. Groups with the same letter are not significantly different. Mean is the average k_d for each herbicide across all soils tested, and N is the number of soils tested for each herbicide.

Means with the same letter are not significantly different.			
Grouping	**Mean**	**N**	**Herbicide**
A	4.0091	25	*s*-metolachlor
B	2.2781	25	dimethenamid-*p*
B	1.7248	25	pyroxasulfone

Table 2.6.) Pearson correlations between soil textural and chemical properties. The top value in each box is the linear relationship between soil components, and the bottom value is the p-value for the Null hypothesis that there is no correlation between soil components.

Pearson Correlation Coefficients, N = 25
Prob > |r| under H0: Rho=0

	OM	**pH**	**CEC**	**Sand**	**Silt**	**Clay**
OM	1.00000	-0.28843 0.1620	0.24909 0.2299	-0.67661 0.0002	0.69092 0.0001	0.20791 0.3186
pH	-0.28843 0.1620	1.00000	0.63134 0.0007	-0.03586 0.8649	-0.32468 0.1133	0.49548 0.0118
CEC	0.24909 0.2299	0.63134 0.0007	1.00000	-0.56305 0.0034	0.03728 0.8596	0.90764 <.0001
Sand	-0.67661 0.0002	-0.03586 0.8649	-0.56305 0.0034	1.00000	-0.80886 <.0001	-0.59508 0.0017
Silt	0.69092 0.0001	-0.32468 0.1133	0.03728 0.8596	-0.80886 <.0001	1.00000	0.01065 0.9597
Clay	0.20791 0.3186	0.49548 0.0118	0.90764 <.0001	-0.59508 0.0017	0.01065 0.9597	1.00000

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Chapter 3: Dissipation and Leaching of Pyroxasulfone and *s*-Metolachlor

Field studies were conducted in 2009 and 2010 at two contrasting field sites to evaluate the dissipation and movement of pyroxasulfone and *s*-metolachlor in the top 30 cm of the soil profile. Dissipation half-lives (DT_{50}) were the lowest under the heavier textured clay loam soil and increased moisture content at the Hort Farm site. The LIRF site with lighter textured sandy loam, soil and decreased moisture resulted in extended DT_{50} values and more variation between replicates for both herbicides. In general across both years and field sites, pyroxasulfone DT_{50} values were approximately twice as long compared to *s*-metolachlor. The extended half-life of pyroxasulfone suggests that it would provide longer weed control throughout the growing season compared to *s*-metolachlor. Herbicide movement in the top 30 cm of the soil profile was greatest at the LIRF site which suggests that movement was influenced by soil type to a greater extent than irrigation amount, since the LIRF site received much less total irrigation compared to the Hort Farm site yet had the most movement downward in the profile. In general, pyroxasulfone moved downward in the profile to a greater extent than *s*-metolachlor. Observed herbicide movement would confirm sorption coefficient data which indicates that pyroxasulfone is bound less to the soil and is more available in the soil solution where the herbicide is more vulnerable to movement through mass flow. Extended observed half-lives, reduced soil binding, and increased unit activity indicate that pyroxasulfone is a potent inhibitor of VLCFA biosynthesis that can provide comparable weed control efficacies for longer periods of time at reduced use rates when compared to commonly used chloroacetamide herbicides.

INTRODUCTION

Herbicide dissipation half-life (DT_{50}) and mobility of herbicides in the soil profile will affect weed control duration and efficacy of pre-emergent herbicides, and therefore should be evaluated for new herbicides such as pyroxasulfone. Comparisons of these traits of new herbicides to well known herbicides can provide insight on how new compounds will behave under field conditions. *s*-Metolachlor has low to moderate persistence in the soil with a DT_{50} of 15 to 70 d [Handbook 7th, U.S. EPA fact sheet 106 Metolachlor]. Of the current chloroacetamide herbicides, *s*-metolachlor appears to be the most persistent (Zimdahl and Clark 1982; Walker et al., 1983; LeBaron et al., 1988) and has the potential to leach to ground water because of its relatively high water solubility (530 mg L^{-1} at 20º C) and low Koc (200 mL g^{-1}). [Koc is a measure of the tendency of a compound to partition into soil organic carbon from aqueous solution, and is generally inversely related to movement to ground water (Sanyal and Kulshrestha, 1999)].

Pesticide mobility and fate in soil are influenced by sorption and degradation processes. The importance of these processes is determined in part by the physical, and chemical properties of the pesticide, such as organic-carbon and mineral-surface sorption coefficients, aqueous solubility, and soil DT_{50} (Savoca et al., 2000). Typically the adsorption of pesticides increases with increased soil organic matter and clay content, and increased adsorption can slow the herbicide's movement in soil (Rivard, 2003). Decreased herbicide movement usually occurs if the soil organic matter content is greater than 2.0%. In addition, leaching is inhibited in soils with high clay and/or silt content (Extoxnet, 2000b).

Besides the DT_{50}, the potential for an herbicide to move vertically in the soil profile in soil solution can affect weed control duration and efficacy based on the distribution and movement of residual herbicides in the soil profile. The degree of herbicide transport in the environment depends on several factors such as application rate, herbicide persistence and mobility, rainfall, topography, and climate (Wauchope, 1994). Wagenet and Hutson, (1990) state that pesticide movement is generally assumed to be a result of three processes: a) diffusion in the aqueous phase with a concentration gradient; b) if volatile, diffusion in the gas phase in response to a concentration gradient in the gas-phase; and c) convection or mass flow of the water or air where the herbicide is present. Volatilization of herbicides is most significant when residues remain on the surface of dry or moist soils, although Incorporation of herbicides into the soil profile can significantly reduce losses caused by volatilization (Carter, 1999).

Rainfall patterns and the timing/intensity of irrigation in relation to high rainfall intensities will influence herbicide movement in or from soil through mass flow. Carter et al. (1999) state that water movement in soil occurs in response to two main forces applied by gravity, or differences in soil porewater pressure. Herbicide movement can be influenced by the hydraulic influences of irrigation methods, and whether they promote greater downward distribution or vertical rise of applied irrigation.

Extensive leaching can occur in soils with low organic carbon content, and is greatest when soil texture is coarse (Extoxnet, 2000a). Precipitation and/or irrigation can move *s*-metolachlor very rapidly into ground water sources. Kalkhoff et al. (1998) showed that metolachlor metabolites were frequently present in ground and surface water in substantial concentrations in the Midwest where *s*-metolachlor is heavily used. Lin et al. (1999) showed that *s*-metolachlor may cause toxicity to aquatic organisms through non-point source pollution. Herbicides that are vulnerable to leaching can have negative environmental impacts on non-target organisms if herbicides move off-site via leaching or run-off.

Along with adverse environmental impacts, leaching of herbicides can result in reduced weed control efficacies. When residual herbicides leach below the zone where weeds emerge, the herbicides will not control weeds because they are not available for uptake. Even though an herbicide may be present in the soil profile, its location in the soil will determine whether or not it will control emerging weeds. Knowing the potential for herbicide movement of a new compound can result in usage restrictions to minimize undesirable impacts.

Besides soil movement, dissipation of herbicides in the soil is often due to microbial degradation. Herbicide degradation in the soil is affected by temperature, moisture, microbial activity, soil type, nitrification, oxygen concentration, and sunlight (Extoxnet, 2000a). Microbial degradation is a major component of field dissipation once herbicides have moved below the soil surface (Herbicide Handbook 9th edition). Zimdahl et al. (1982) showed that herbicide degradation rates for chloroacetamide herbicides increased as temperature and moisture content increased, which support the hypothesis that degradation of chloroacetamide herbicides is dominated by microbial degradation.

Chloroacetamide breakdown by photo degradation can be an important pathway for herbicide degradation if sufficient incorporation isn't achieved. According to the WSSA herbicide handbook about 50% of applied metolachlor degrades in eight days on sunlit soil, but is reduced to 6% of applied herbicide degraded by photolysis over 1 month when incorporated into the top 5 cm of the soil profile (Extonet, 2000a).

Predicting the DT_{50}, and mobility of a new compound like pyroxasulfone will help farmers make management decisions on how to use this herbicide to maintain weed control efficacy, as well as reduce leaching potential. The objectives of this study were to A) compare the dissipation of pyroxasulfone to *s*-metolachlor over two years, under two different field sites with contrasting soil types, and B) compare the vertical movement of pyroxasulfone to *s*-metolachlor in the top 30 cm of the soil profile under two different field conditions with contrasting soil types.

MATERIALS AND METHODS

Dissipation and Leaching

Field Design

Field sites in 2009 and 2010 were established at two locations in Northern Colorado:

A) **Hort Farm**: is a Colorado State University research site located just north of Fort Collins, CO. This site was irrigated via overhead linear for both initial herbicide incorporation, and in-season irrigation. The soil at the Hort Farm site is a Nunn fine clay loam (fine, smectitic, mesic aridic argiustoll) with 34% sand, 25.2% silt, 40.8% clay, 1.46% organic matter, and a pH of 8.0.

B.) **LIRF** (Limited irrigation research farm): is a USDA/ARS research station located northeast of Greeley, CO. This site was irrigated via sub-surface drip (buried 5-8 cm below soil surface) in 2009 and surface drip in 2010. For initial herbicide incorporation, sprinklers were set up to deliver one application of approximately 13mm of water before they were removed and drip tape installed. The soil at the LIRF is an Olney fine sandy loam, (fine-loamy, mixed, superactive, mesic ustic haplargids) with 70% sand, 19.2% silt, 10.8% clay, 1.1% organic matter, and a pH of 8.0.

Both field sites used conventional tillage practices and sunflowers were produced using standard management practices for this area. The sunflower variety used in both years was a Dekalb oil-seed type DK3845. Planting and herbicide application dates for each field site were June 23, June 25 in 2009 and June 2, June 5 in 2010 for the LIRF and Hort Farm sites, respectively. Field sites were set up in a randomized block design with 3 (2009) or 4 (2010) replications which included two soil applied herbicide treatments: pyroxasulfone (3-[[[5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl)-1*H*-pyrazol-4-yl]methyl]sulfonyl]-4,5-dihydro-5,5-dimethylisoxazole) or *s*-metolachlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-[(1*S*)-2-methoxy-1-methylethyl]acetamide)

Field Rate Structure

The rate structure for pyroxasulfone and *s*-metolachlor were the same at the two field sites: 280 g ai Ha^{-1} and 1680 g ai Ha^{-1} for pyroxasulfone and *s*-metolachlor respectively. In 2009 and 2010 sulfentrazone N-[2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1 ,2,4-triazol-1-yl]phenyl] methanesulfonamide was applied with both herbicides at a rate of 280 g ai Ha^{-1} to provide broadleaf weed control and to provide bare soil surfaces for soil sampling . Herbicide treatments were broadcast applied using a CO_2 backpack sprayer with a tee-jet 8002EVS sprayer nozzle calibrated to deliver 187 L ha^{-1}. Properties of pyroxasulfone and metolachlor are listed in table 1. Individual plots at both field sites both years were approximately 3 m wide by 12.2 m long and consisted of four rows of sunflower spaced 76 cm apart.

Soil Sampling

Soil samples were taken to a depth of 30 cm using a soil sampler containing a 2.5 cm-diameter zero contamination tube. Soil samples were split into four -7.5 cm long segments and analyzed separately. Three samples were randomly taken from each plot, combined by depth, and mixed thoroughly for analysis. The randomly selected soil samples were taken from bare surface crop rows which avoided removal of sunflower plants. Samples were selected from inner plot rows to ensure that the correct residual herbicides were sampled. Total dissipation rates were calculated by summing the concentrations in the four depth zones. Herbicide movement was evaluated based on four 7.5cm depth zones down to 30cm.

Sampling Dates

In 2009 soil samples were collected at 1, 7, 14, 28, 43, 57, 69, 87, and 140 days (+- 3 days between sites) after herbicide treatment from both field sites. In 2010 soil samples were collected at 1, 7, 14, 21, 28, 42, 56, 71, 85, and 148 days (+- 1 day between sites) after herbicide treatments from both field sites. Soil samples were immediately frozen until they could be processed and extracted.

Soil Properties

Soils were air dried and passed through a 2.0 mm screen. Two replicates of each soil were sent to AgSource/Harris Laboratories (Lincoln, NE) and were analyzed for texture, pH, CEC, and organic matter. Soil samples and their replicate were randomized and blindly labeled to ensure the quality and precision of analyses.

Chemical Extraction and Analysis

Ten and twenty grams of moist soil were used for the extraction of *s*-metolachlor and pyroxasulfone respectively. The differences in the amount of soil used for a single extraction between herbicides, was based on the difference in application rates of each herbicide, and detection limits on the GC/MS.

Soils were weighed and then combined with equal parts water to soil (10 or 20 mL of H_20), as well as with 10 mL of H_20 saturated toluene. Samples were shaken for 2 hours and then centrifuged at 1000 rcf for 10 minutes. Two mL of the toluene supernatant were transferred to a 2 mL volumetric vial spiked with 10.0 µL of butylate (0.1 mg mL^{-1}) to serve as an internal standard. Toluene was then transferred to a 2 mL GC vial and analyzed on the GC/MS. The herbicide concentrations in the toluene phase were analyzed using a gas chromatograph equipped with a mass spectrometer (Shimadzu GC-17A and GCMS QO 5050A, Shimadzu Scientific Instruments, Inc., Columbia, MD) and monitoring the masses for butylate (m/z 146), *s*-metolachlor (m/z 162.15), and pyroxasulfone (m/z 179.10), A RTX-5 30-m by 0.25-mm column (Restek, Bellefonte, PA) was used with a flow of helium at 1 mL/min.

Total sample weights were recorded to calculate soil bulk density from the sample tubes. For each extraction, a subsample of soil was oven dried to determine the soil water content in the sample. Bulk density and water content were then used to correct herbicide concentrations and calculate grams of herbicide recovered per hectare.

Statistical analysis

Model selections for dissipation data were performed in Sigmaplot (Version 11.0) based on maximum r^2 values.

DISSIPATION RESULTS

Hort Farm 2009

In 2009, the Hort Farm site received 452 mm of moisture from precipitation and over-head linear irrigation applied on a consistent basis (Figure 3.1). This irrigation type and total amount resulted in soil moisture levels maintained around field capacity, which resulted in data that was tightly fit by exponential decay curves. Data was analyzed and exponential decay models were used to fit the data based on maximum r^2 values during model selection. This resulted in an exponential decay curve for both pyroxasulfone (Figure 3.5-A) and s-metolachlor (Figure 3.7-A). The function that best described pyroxasulfone dissipation was:

$$f= a*\exp^{(-b*x)} \qquad [1]$$

Where, a is the herbicide concentration in the soil at time zero (g ha^{-1}); b is the first-order rate constant (d^{-1}); and f is time (d).

For pyroxasulfone, a=76.79 and b=0.0208 (Figure 5-A). *s*-Metolachlor data was best described by exponential decay model (Equation 1), where a= 1336.0 and b=-0.038 (Figure 7-A). Exponential decay models had r^2 values of 0.7320, and 0.8520 for pyroxasulfone and *s*-metolachlor, respectively at the Hort Farm field site in 2009. The DT_{50} for pyroxasulfone and *s*-metolachlor described by an exponential decay function was calculated using:

$$DT_{50}= \ln(2)/b \qquad [2]$$

Where b is the first-order rate constant (days), and DT_{50} is the time (days) needed for half of the herbicide to dissipate (Krutz et al. 2007).

This equation resulted in DT_{50}s of 33 and 18 days for pyroxasulfone and *s*-metolachlor, respectively. These results showed that under these field conditions, pyroxasulfone remained almost twice as long in the soil profile compared to *s*-metolachlor.

Hort Farm 2010

In 2010, the Hort Farm received 731 mm of moisture from precipitation and over-head linear irrigation (Figure 3.3). The increase in irrigation + precipitation from 2009 to 2010 did not change rates or curves for pyroxasulfone dissipation. Like the 2009 data, pyroxasulfone data from 2010 was best described by an exponential decay curve (Equation 1) where a= 56.5 and b = 0.0195(Figure 3.5-B). Exponential decay curve for pyroxasulfone resulted in an r^2=0.8085. The DT_{50} for pyroxasulfone under these conditions was 35.6 days which was similar to the calculated DT_{50} in 2009 (33 days). Similar to 2009, s-metolachlor data was best fit by an exponential decay curve (Equation 1) where a=737.5 and b=0.0269 (Figure 3.7-B). Exponential decay curve for s-metolachlor resulted in an r^2=0.7204. The DT_{50} for s-metolachlor was 25.8 days in 2010, which was longer than the DT_{50} in 2009 (18.1 days).

LIRF 2009

In 2009, the LIRF site received a total of 288 mm of moisture from precipitation and sub-surface drip tape (Figure 3.2). This field site was irrigated based on calculated evapotranspiration (E.T.) which explains the reduction in total irrigation and precipitation that this site received compared to the Hort Farm site (Figure 3.1 and 3.2). Irrigation application at this field site was also much less consistent throughout the growing season. Sub-surface drip tape was buried between 5 and 8 cm below the soil surface at the LIRF site in 2009. This type of irrigation would promote greater amounts of upward movement of moisture from soil capillarity and evaporative processes, as opposed to surface drip tape that applies irrigation on the soil surface which promotes greater downward distribution of moisture from gravitational forces (Carter, 1999).

At the LIRF site in 2009 pyroxasulfone data was best described by an exponential decay curve (Equation 1), where a= 102.78 and b=0.0078 (Figure 3.6-A). The exponential decay curve had an r^2=0.2760 (p-value=0.0187). Reduction in moisture at the LIRF field site extended half-lives of both herbicides compared to the Hort Farm field site. Pyroxasulfone DT_{50} was 33.3 days at the Hort Farm compared to 88.9 days at the LIRF field site in 2009. Reduced moisture also resulted in more variation between replicates as indicated by standard error bars (Figure 3.6-A). *s*-Metolachlor data were also best described by an exponential decay curve (Equation 1), where a= 714.0 and b=0.0147 (Figure 3.8-A). The exponential decay curve had an r^2=0.5234 (p-value = < 0.0001). Due to differences in moisture between the field sites (Figure 3.1 and 3.2), the DT_{50} of *s*-metolachlor was 47.2 days (Table 3.3) at the LIRF site, compared to 18.1 days (Table 3.2) at the Hort Farm site in 2009.

The LIRF field site received 164 mm less moisture compared to the Hort Farm site in 2009 (Figure 3.1 and 3.2). This reduction in total moisture applied throughout the growing season, as well as a less uniform irrigation application (Figure 3.2), resulted in drier field conditions which increased the DT_{50} values for both herbicides at the LIRF field site compared to the Hort Farm site in 2009. Drier soil conditions also resulted in greater variation between replicates.

LIRF 2010

In 2010, the LIRF site received a total of 447 mm of moisture from precipitation and surface-drip irrigation (Figure 4).Pyroxasulfone data was best described by the sigmoidal function:

$$f= a/(1+\exp(-(x-x_o)/b)) \qquad [3]$$

Where a represents the initial herbicide concentration in the soil at time zero (g ha^{-1}); b is the first-order rate constant ($days^{-1}$); x_o is the lag phase (days); and f is time (days).

For pyroxasulfone a=76.82, b=-2.79, and x_o=50.88 (Figure 3.6-B). The sigmoidal dissipation curve for pyroxasulfone had an r^2=0.7486. Herbicide dissipation displayed a lag phase around 50 days where herbicide concentration remained fairly constant before rapid dissipation occurred with a DT_{50}= 1.93 days (Table 4) which was calculated using:

$$DT_{50} = \ln(2)/ (-1/b) \qquad [4]$$

Where b is the first-order rate constant (d), and DT_{50} is the time (d) needed for half of the herbicide to dissipate.

s-Metolachlor data was also best described with a sigmoidal curve (Equation 3.3) where a= 477.30, b=3.319, and x_o= 50.26 (Figure 3.8-B). The sigmoidal dissipation curve had an r^2=0.5652 (p-value = < 0.0001). *s*-Metolachlor dissipation also appeared to have a lag phase around 50 days, where herbicide concentrations remained constant before rapid dissipation occurred with a DT_{50}=2.21 days (Table 3.3).

DISSIPATION DISCUSSION

Another route of herbicide degradation is from volatility or photolysis when herbicides remain on the soil surface for extended periods of time. Given that both pyroxasulfone (2.4 x 10^{-6} Pa @ 25°C) and *s*-metolachlor (3.7 x 10^{-3} Pa @ 25°C) have relatively low vapor pressures, and that incorporation occurred the day after treatment would lead us to predict that herbicide movement in our study was dominated by diffusion and mass flow in the aqueous phase. Incorporation of herbicides after application would minimize degradation from photolysis and volatility of herbicides.

Walker and Brown (1985) stated that soil moisture content influenced the degradation of chloroacetamide herbicides with slower rates of loss in drier soils. For the chloroacetamide herbicides propachlor, alachlor, dimethachlor, metazachlor, and *s*-metolachlor, they showed that the half-life in soil at 6% (w/w) moisture was between 2 and 4 times greater than at 15% (w/w) moisture. Out of the 5 chloroacetamide herbicides tested, *s*-metolachlor degradation was shown to be the most dependent on moisture content.

Zimdahl and Clark (1982) performed a bioassay to evaluate the degradation of alachlor, metolachlor, and propachlor in a clay and sandy loam soil at 20, 50, and 80% of field capacity maintained at 20°C. In the sandy loam soil type, the metolachlor DT_{50} was 100.3, 50.2, and 33.4 days for the 20, 50, and 80% of field capacity moisture levels, respectively. For the clay loam soil metolachlor DT_{50} was 37.6, 27.4, and 15.8 days at 20, 50, and 80% of field capacity moisture levels, respectively. For alachlor and propachlor the DT_{50} in soil at 20% of field capacity was between 2.26 and 7.0 times greater than the 80% of field capacity moisture level.

Ismail and Wei (1993) also showed that drier soil conditions extended half-lives for alachlor and *s*-metolachlor. Under a sandy loam soil, the DT_{50}s for alachlor and *s*-metolachlor were 8 and 12 days, respectively at 80% field capacity, compared to 20 and 22 days at 20% field capacity. The DT_{50}s were statistically different between the 80 and 20% field capacity moisture levels showing the increase in degradation rates as soil moisture increases.

There is not much literature evaluating the effects of drip tape versus sprinkler irrigation on the dissipation of chloroacetamide herbicides. But we can speculate that soils under sprinkler irrigation typically received more moisture compared to drip tape irrigation, which would increase the rate of dissipation. In our study the irrigation type determined how much total irrigation was applied throughout the growing season. Sprinkler irrigation resulted in 1.57 and 1.64 times more total water application compared to drip tape in 2009 and 2010, respectively. This increase in applied irrigation would result in an increased soil moisture content, which has been shown to increase the rate of herbicide dissipation.

Battam et al. (2003) conducted studies which evaluated the wetting fronts of sub-surface drip irrigation. They found that if the lowest available emitter rate is greater than the soil intake rate, water surfacing can result from irrigation. This study showed that irrigation from sub-surface drip tape is prone to upward movement in the soil profile. They also stated that wetting fronts from sub-surface drip emitters are approximately elliptical, which when buried would promote more vertical as opposed to horizontal distribution of herbicides. Sadler et al. (1995) discussed errors in the determination of emitter discharge rate and uniformity when soil-limiting flow causes a vertical water column between the emitter and the soil surface. Zimmer et al. (1988) also observed upward free water movement from buried emitters in soils. This suggests that sub-surface drip tape would promote more vertical rise of irrigation water compared to surface drip tape or sprinkler irrigation where irrigation is applied on the soil surface and water moves downward in the profile regulated by the soil infiltration rate. When comparing surface and sub-surface drip tape to sprinkler irrigation, the main difference is that sprinkler irrigation will wet the entire soil profile from top down, where drip tape is applying irrigation only in crop rows with wetting fronts extending into but not saturating furrows.

When the precipitation and irrigation schedule are compared for the LIRF site in 2010 (Figure 4), with dissipation rates, there appears to be a relationship between moisture applied and herbicide dissipation. Bowman (1988) stated that timing between herbicide application and precipitation affected metolachlor soil mobility.

The LIRF site in 2010 received a significant rainfall event which delivered approximately 70 mm of water between 7 and 14 days after treatment (DAT). Based on herbicide mobility results, we observed that the herbicides were pushed downward in the soil profile by the rainfall event, but were maintained in the top 30 cm where dissipation was evaluated, and therefore did not affect dissipation rates up until 42 DAT. However between the sampling dates of 42 and 56 DAT we observed that herbicide concentrations were significantly reduced. Between 42 and 56 DAT, LIRF received approximately 110 mm of moisture. If the herbicide was pushed downward in the soil profile with the rainfall event 10 DAT, when irrigation was applied we hypothesize that we potentially moved the herbicides below the 30 cm sampling depth zone which could explain the rapid dissipation DT_{50} that was only observed at the LIRF site in 2010.

In 2010, moisture at the LIRF site increased by 159 mm, compared to the 2009 total moisture (Figure 2 and 4). In 2010, the majority of irrigation was applied between 40 and 80 days after treatment. This is the time period where the lag phase ended and rapid dissipation occurred for both pyroxasulfone and *s*-metolachlor. In 2009, irrigation was distributed from 0 to 100 days after treatment which resulted in herbicide dissipation without a lag phase and longer DT_{50} values compared to 2010, which displayed a lag phase then rapid dissipation. Drier soil conditions prior to 40 days after treatment in 2010 appeared to play a role in the lag phase which was observed for both pyroxasulfone and s-metolachlor.

Burgard et al. (1993) also observed a lag phase of around 40 days where soil metolachlor levels did not decline. They did show that the average daily mean air temperature was 5° C, which has been shown to extend DT_{50} values for metolachlor. Walker and Zimdahl (1981) also observed a lag phase in dissipation of *s*-metolachlor under dryland conditions in Colorado, however, they did not report climatic conditions.

The calculated half-lives for *s*-metolachlor in our study are consistent with other results (Zimdahl and Clark, 1982; Walker and Brown, 1985; Braverman et al., 1986; Mersie et al., 2004; Shaner et al., 2006) that showed ranges of DT_{50}s from 10 to 142 days. Given that we observed *s*-metolachlor DT_{50} similar to previous authors, suggests that these methods should be sufficient for evaluation of pyroxasulfone DT_{50} under similar conditions. Although there is little literature available for pyroxasulfone DT_{50}'s,the values from our study were consistent with previously cited literature that reported DT_{50}s of 8 to 71 days for pyroxasulfone (Mueller, 2011), and slightly longer than DT_{50} of 10.5 to 35 days found in Australia (Australian Government Public Release Summary, 2011).

Dissipation data for both herbicides also supports the claim by Zimbdahl et al. (1982) that degradation was two times faster in a argiustoll clay loam soil compared to a haplargid sandy loam soil, which previous authors suggest was due to a) greater amounts of water given the field capacity in the clay loam, or b) a higher level of microbial activity in the clay loam soil. Given that our clay loam soil field site received more consistent irrigation compared to the sandy loam field site, would support this hypothesis that greater amounts of moisture accelerated degradation rates.

Herbicide Movement

Hort Farm Herbicide Movement

Movement data from the Hort Farm site in 2009 showed that the majority (>90%) of pyroxasulfone and s-metolachlor remained in the top 7.5 cm of the soil profile over the growing season (Table 4) (Figure 13), even though this field site received 453 mm of total precipitation. In 2010 greater amounts of pyroxasulfone were detected in the 7.5-15 and 15-22.5 cm depth zones, compared to 2009 (Table 5). The >90% of *s*-metolachlor remained in the top 0-7.5 cm (Figure 14), whereas 83, 12, and 4.5 % of total recovered pyroxasulfone was detected in the 0-7.5, 7.5-15, and 15-22.5 cm depth zones respectively (Table 4) (Figure 10).

LIRF Herbicide Movement

Similar to the Hort Farm in 2009, LIRF site data showed that the majority (>90%) of pyroxasulfone and *s*-metolachlor remained in the top 0-7.5 cm of the soil profile (Table 6) (Figure 11 and 15). The combination of lighter textured sandy loam soil with reduced irrigation applied via drip tape resulted in similar mobility of both herbicides when compared to the Hort Farm site in 2009. However, the LIRF site in 2010 received a significant rainfall event (~65mm) around 10 days after treatment which resulted in greater amounts of herbicide movement downward in the soil profile. Pyroxasulfone was detected at 54, 25, 15, and 6% of total recovered herbicide in the 0-7.5, 7.5-15, 15-22.5, and 22.5-30 cm depth zones, respectively (Table 6;Figure 12). *s*-Metolachlor was detected at 78, 16, 5, and 1% of total recovered herbicide in the 0-7.5, 7.5-15, 15-22.5 and 22.5-30 cm depth zones, respectively (Table 6) (Figure 16).

Between the sampling dates 7 and 14 days after treatment, the amount of the herbicides in the 7.5-15 cm depth zone increased dramatically, which would suggest that the rainfall event potentially moved both herbicides lower into the soil profile. Between the sampling dates at 42 and 56 days after treatment herbicide concentrations were reduced significantly in soil profile. Evaluating herbicide concentrations 56 days after treatment, although concentrations were reduced from 42 DAT, we observed herbicide concentrations that increased lower in the soil profile (eg concentrations in the 22.5 – 30 cm depth zone were greater than those observed in the three depth zones closer to the soil surface). We hypothesize that the initial rainfall event pushed the herbicide downward in the profile, but still maintained the majority of the herbicide in the top 30 cm which was sampled. Between 42 and 56 DAT we applied approximately 100 mm of irrigation which we hypothesize may have pushed the herbicide below our 30 cm sampling depth zone. If the herbicides were moved below our sampling depth, this would explain why our concentrations dropped off significantly between 42 and 56 DAT.

The main factors which increased herbicide movement at LIRF in 2010 compared to 2009 was the total amount of irrigation and precipitations that was received, the initial rainfall event that moved the herbicides downward in the profile, and that irrigation in 2010 was applied via surface drip which would promote greater downward movement compared to sub-surface drip tape in 2009.

Sorption coefficients for pyroxasulfone and *s*-metolachlor were evaluated across 25 different soils (Chapter 2). There was a high correlation between sorption coefficients and OM for pyroxasulfone and *s*-metolachlor, which has been previously documented (Kozak et al., 1983). The Hort Farm soil had twice as much OM compared to LIRF, which would explain why mobility of both herbicides was reduced under this soil.

Movement of *s*-metolachlor was evaluated in three soil types using soil thin-layer plates. The R_f values calculated from soil thin-layer plates showed that *s*-metolachlor move approximately 2.4 times greater distance in both the Amarillo fine sandy loam and Patrica fine sandy loam soils, compared to the Pullman clay loam (Obrigawitch et al., 1981). They state that the lower R_f values for the clay loam soil was attributed to higher organic matter and clay content compared with the two sandy loam soils. These results are similar to our findings that pyroxasulfone, and *s*-metolachlor were less mobile in a clay loam soil with increased organic matter, when compared to the sandy loam soil.

CONCLUSIONS

- Dissipation occurred more rapidly at the Hort Farm field site under heavier textured soil with over-head linear applied irrigation compared to the LIRF farm.

- The LIRF site with lighter textured soil and drip tape irrigation displayed extended half-lives as well as more variation between replicates due to drier soil conditions.

- Half-life times for pyroxasulfone were approximately twice as long compared to *s*-metolachlor regardless of field site in 2009.

- Herbicide movement was the greatest under lighter textured soils at the LIRF site, even though the Hort Farm field site received 57 and 64% more total irrigation in 2009 and 2010, respectively.

- Herbicide movement appeared to be impacted by soil type to a greater extent than moisture content or irrigation type.

- Across all site years pyroxasulfone moved further downward in the soil profile compared to *s*-metolachlor as supported by sorption coefficient values for these two compounds (Westra, unpublished).

Table 3.1) Chemical properties of *s*-metolachlor and pyroxasulfone.

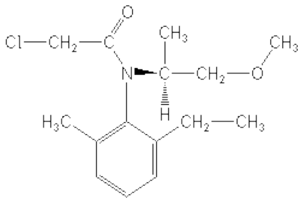
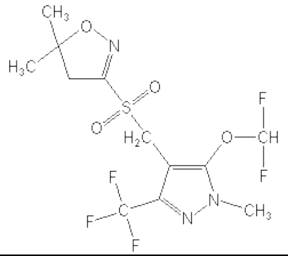
	***s*-metolachlor**	**Pyroxasulfone**
Molecular formula	$C_{15}H_{22}ClNO_2$	$C_{12}H_{14}F_5N_3O_4S$
Molecular Mass	283.79 g mol^{-1}	391.32 g mol^{-1}
Water Solubility	530 mg L^{-1} @ 20 °C	3.48 mg L^{-1} @ 20 °C
Vapor Pressure	$3.7x10^{-3}$ Pa @ 25 °C	$2.4x10^{-6}$ Pa @ 25 °C
Structure		

Table 3.2) Dissipation half-life (DT_{50}) and lag phase for *s*-metolachlor and pyroxasulfone at the Hort Farm site in both 2009 and 2010. N/A represents data where no lag phase was observed.

	2009		**2010**	
Hort Farm	**pyroxasulfone**	***s*-metolachlor**	**pyroxasulfone**	***s*-metolachlor**
DT_{50} (d)	33.3	18.1	35.6	26

Table 3.3) Dissipation half-life (DT_{50}) and lag phase for *s*-metolachlor and pyroxasulfone at the LIRF site in both 2009 and 2010. N/A represents data where no lag phase was observed.

	2009		**2010**	
LIRF	**pyroxasulfone**	**s-metolachlor**	**pyroxasulfone**	**s-metolachlor**
Lag phase (d)	N/A	N/A	50.1	50.3
DT_{50} (d)	88.9	47.2	1.93	2.21

Table 3.4) Percent of total recovered herbicide distributed in the top 30 cm of the soil profile over the growing season for the Hort Farm site in 2009 and 2010.

	2009		**2010**	
Depth Zone (cm)	**pyroxasulfone**	***s*-metolachlor**	**pyroxasulfone**	***s*-metolachlor**
0-7.5	91.09	93.82	82.48	94.24
7.5-15	6.29	3.02	11.71	3.42
15-22.5	1.41	1.43	4.47	1.2
22.5-30	1.2	1.73	1.35	1.14

Table 3.5) Percent of total recovered herbicide distributed in the top 30 cm of the soil profile over the growing season for the LIRF site in 2009 and 2010.

	2009		**2010**	
Depth Zone (cm)	**pyroxasulfone**	***s*-metolachlor**	**pyroxasulfone**	***s*-metolachlor**
0-7.5	92.23	93.6	54.31	77.46
7.5-15	5.51	3.3	25.23	16.33
15-22.5	1.35	1.78	14.6	4.87
22.5-30	0.92	1.32	5.86	1.34

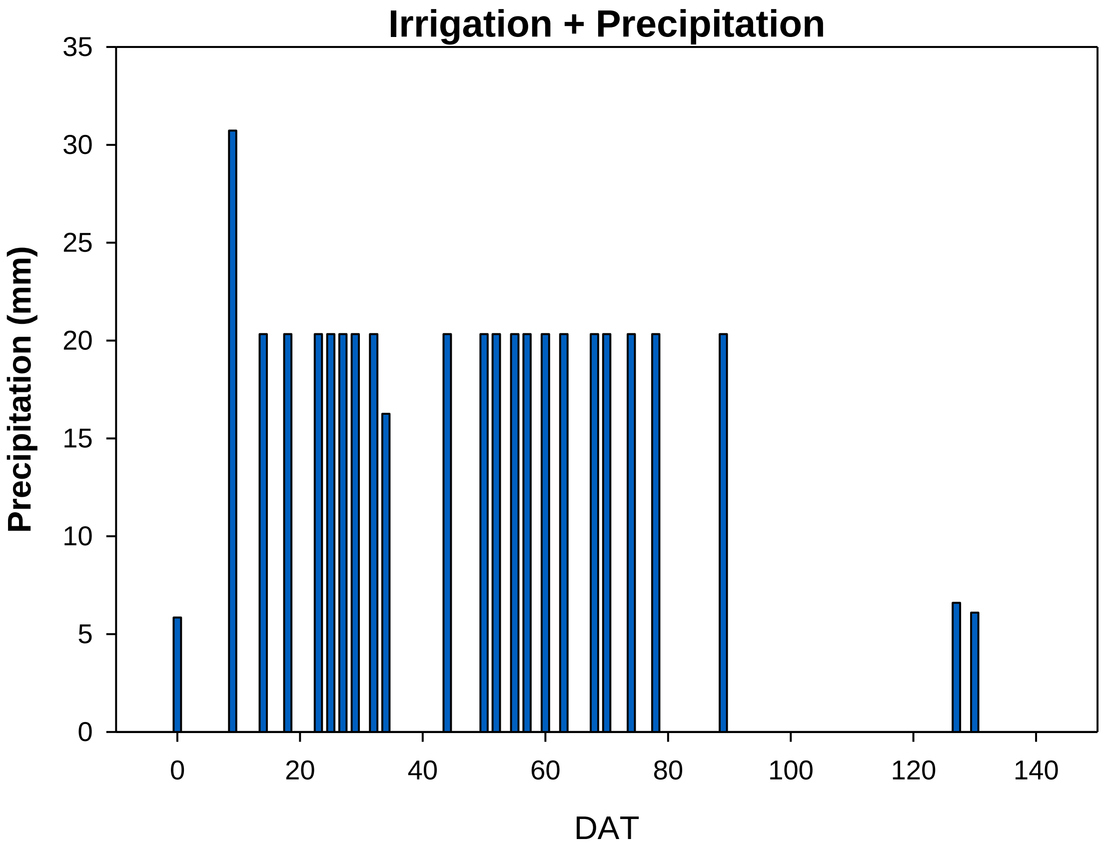


Figure 3.1) 2009 Hort Farm (Precipitation + Irrigation) (452 mm total) received during the growing season.

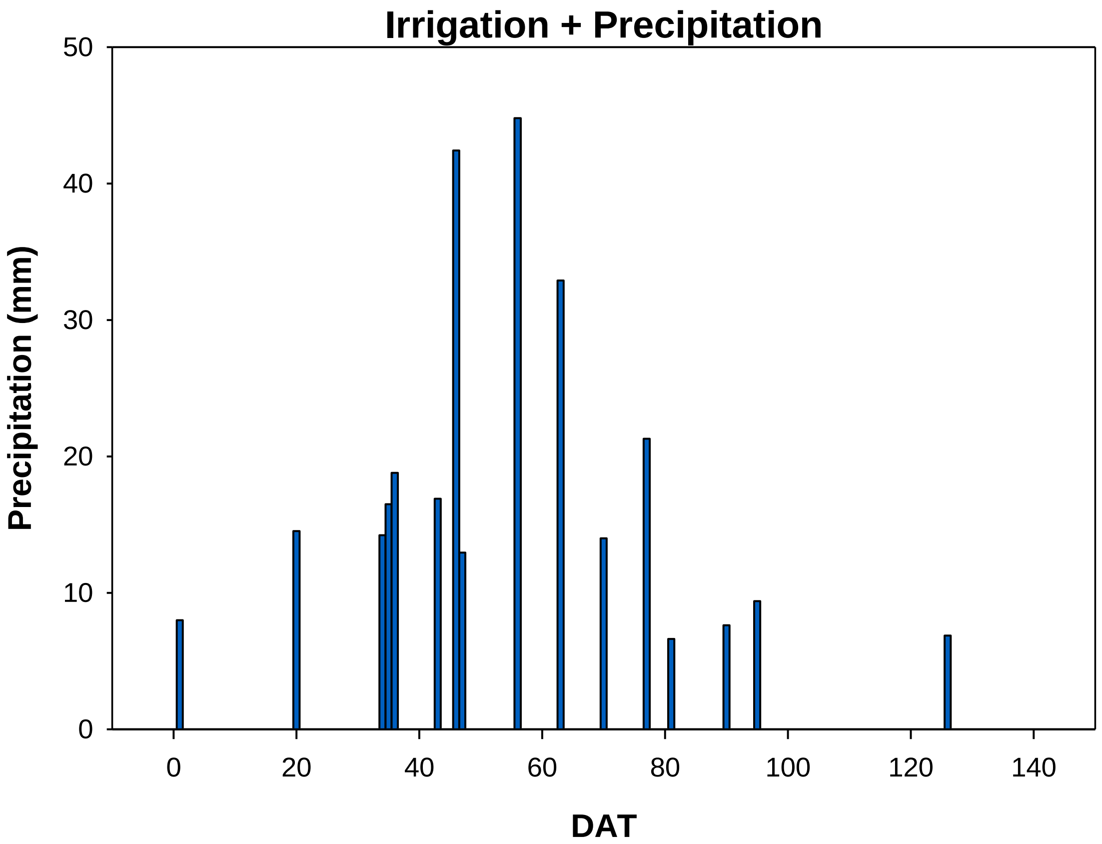


Figure 3.2) 2009 LIRF (Precipitation + Irrigation) (288mm total) received during the growing season.

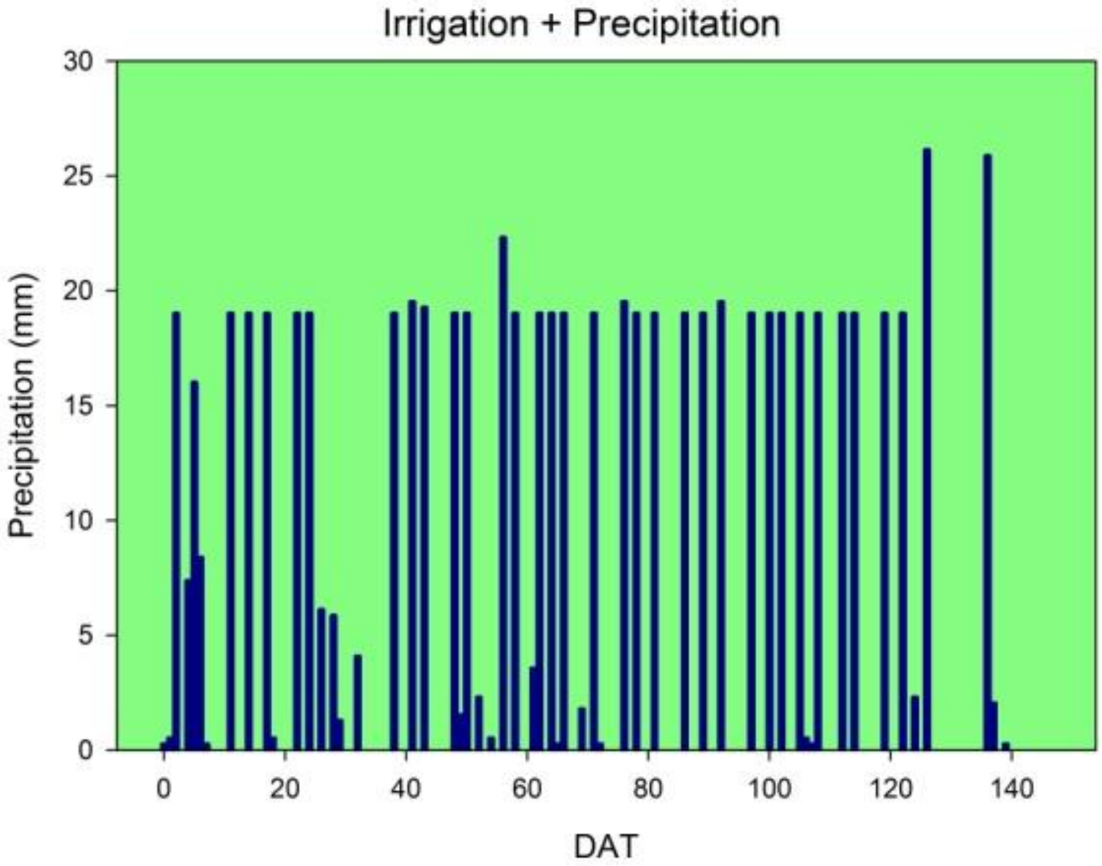


Figure 3.3) 2010 Hort Farm (Precipitation + Irrigation) (731mm total) received during the growing season.

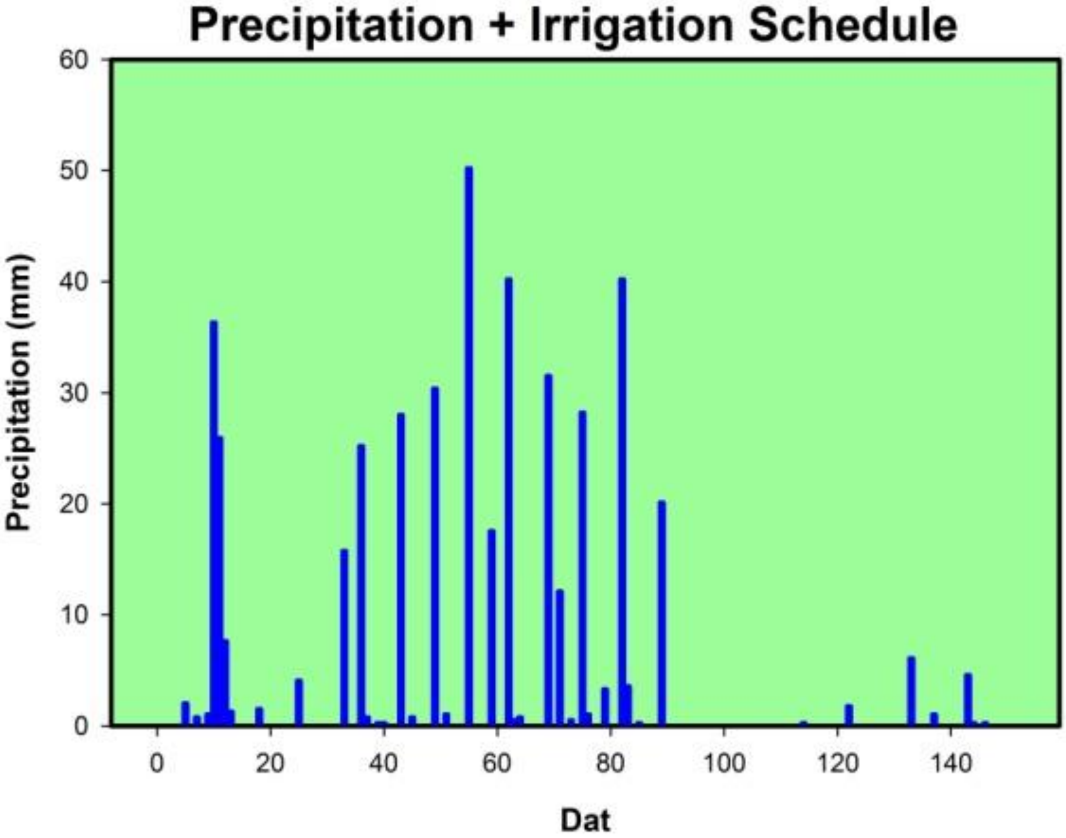


Figure 3.4) 2010 LIRF (Precipitation + Irrigation) (447mm total) received during the growing season.

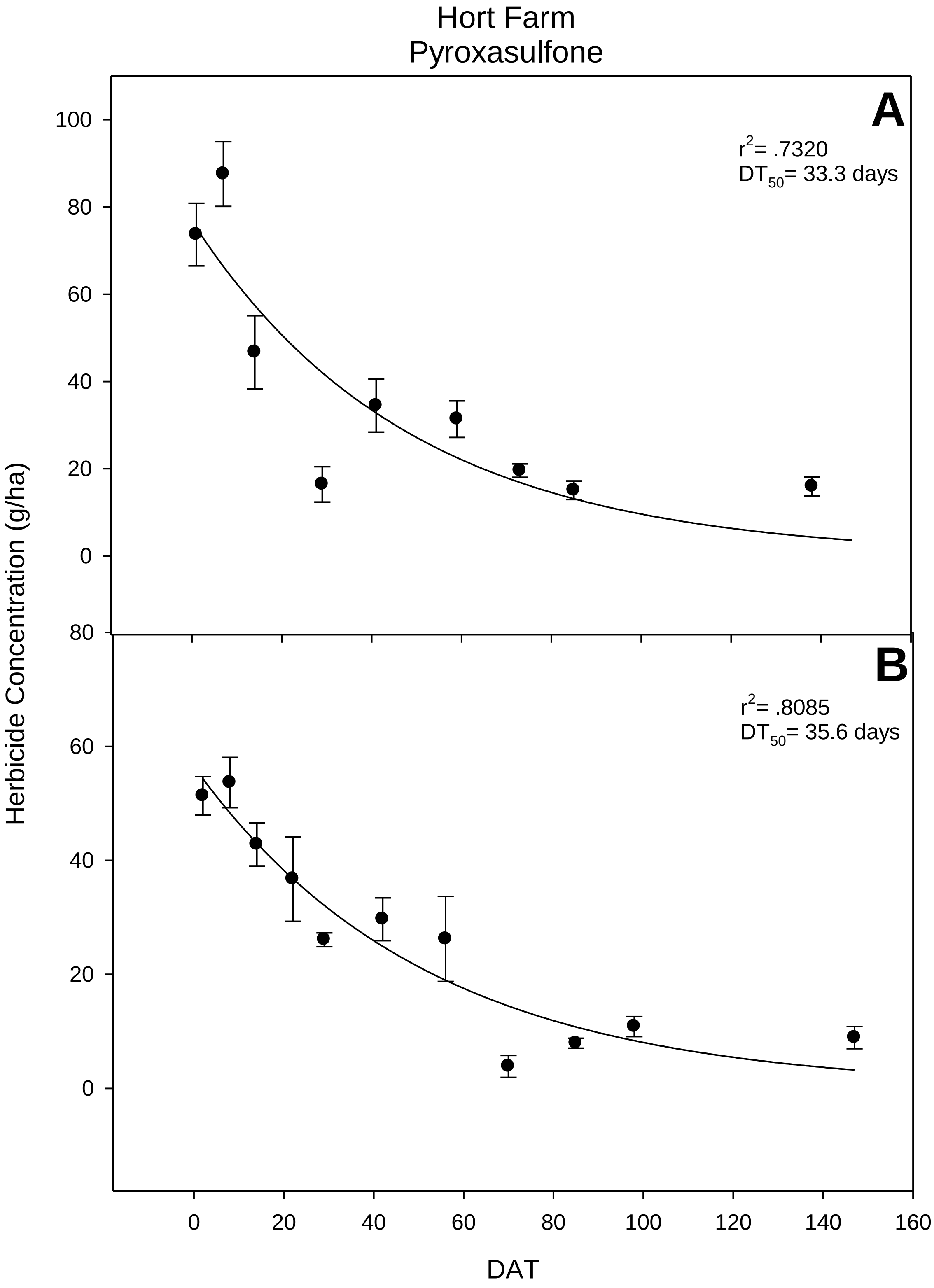


Figure 3.5) Dissipation of pyroxasulfone in the top 30cm of soil over time for the Hort Farm in A) 2009 B) 2010. Error bars represent standard error for dissipation averages.

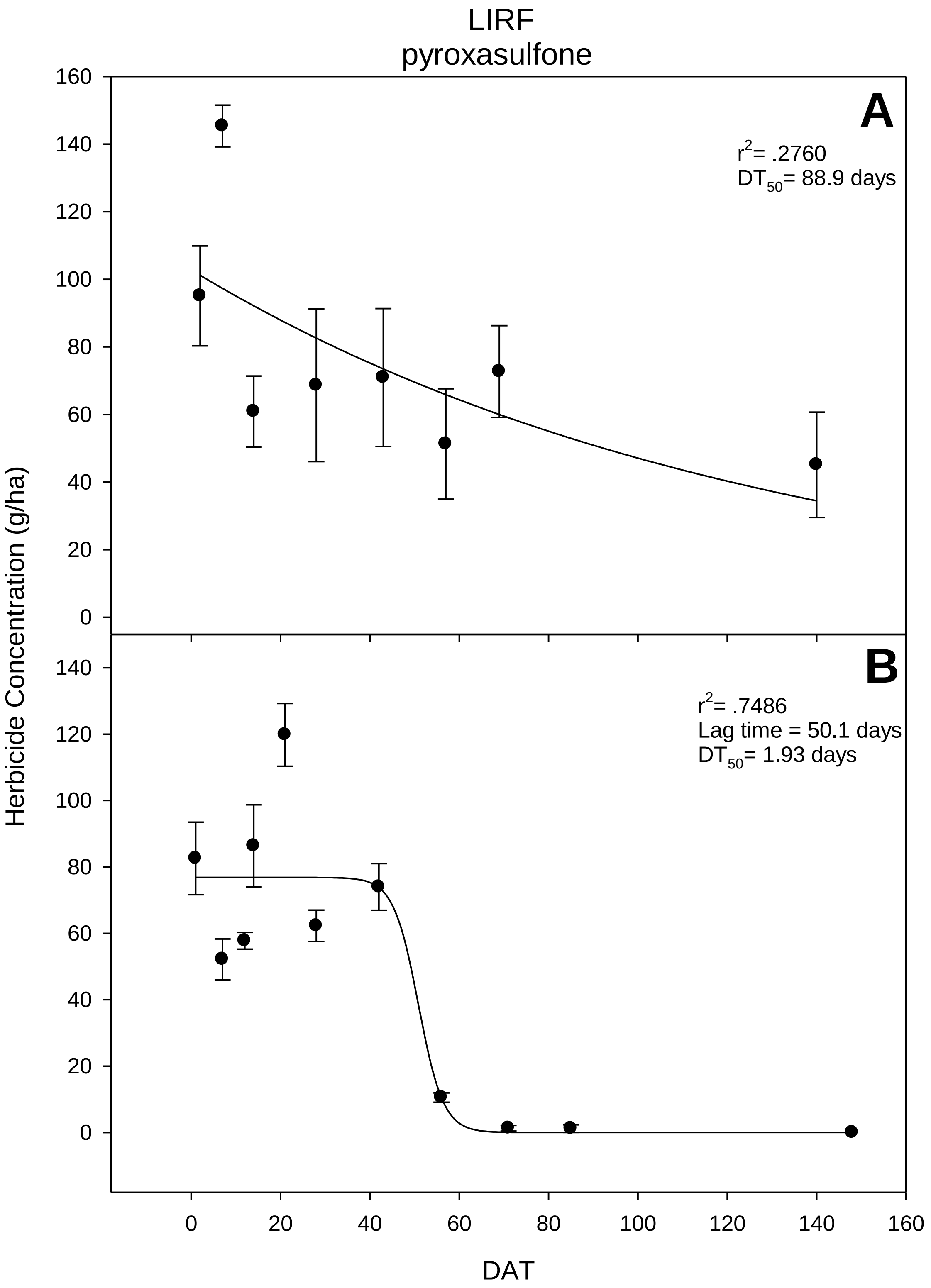


Figure 3.6) Dissipation of pyroxasulfone in the top 30cm of soil over time for LIRF in A) 2009 B) 2010. Error bars represent standard error for dissipation averages.

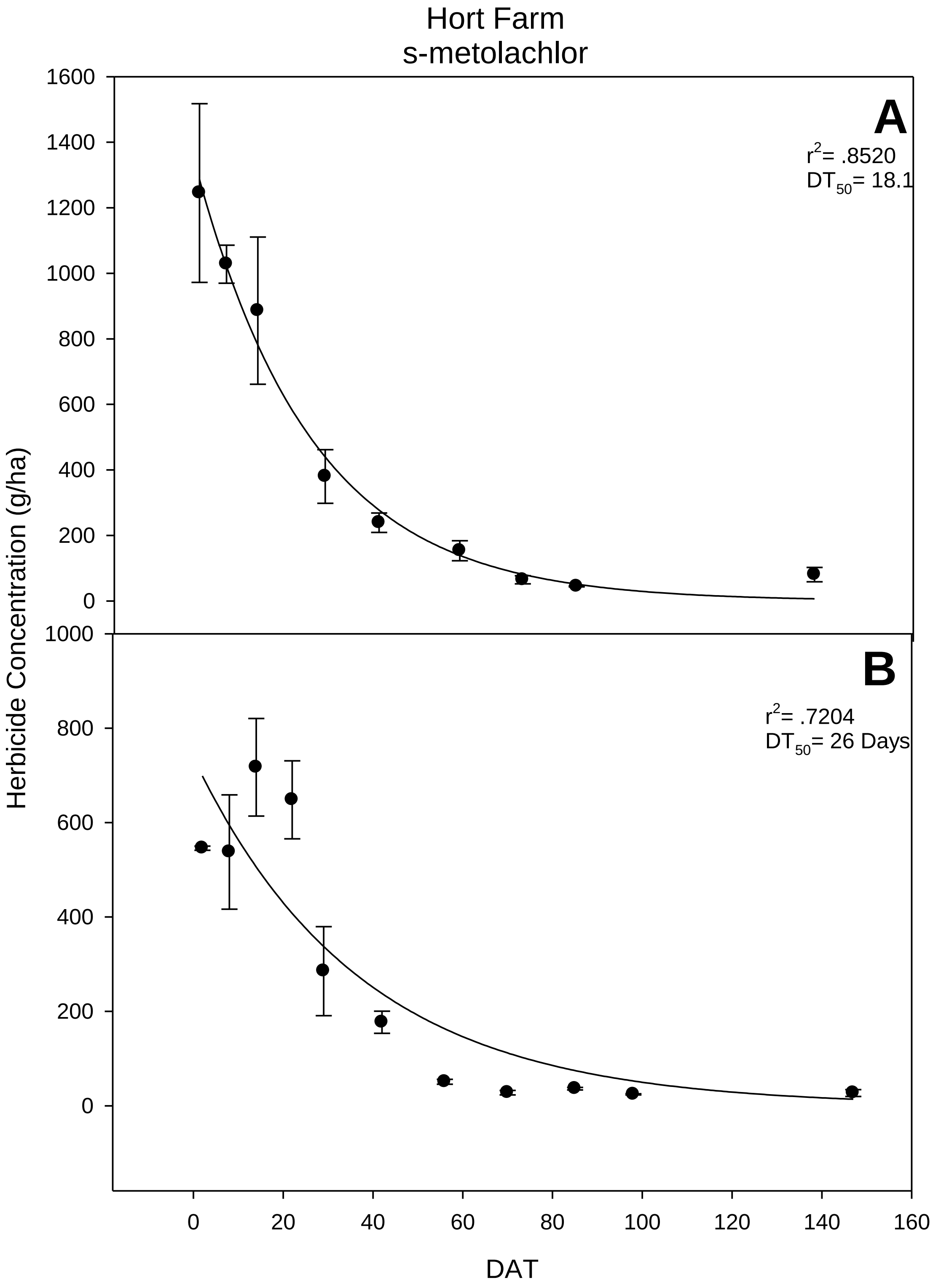


Figure 3.7) Dissipation of *s*-metolachlor in the top 30cm of soil over time for the Hort Farm in A) 2009 B) 2010. Error bars represent standard error for dissipation averages.

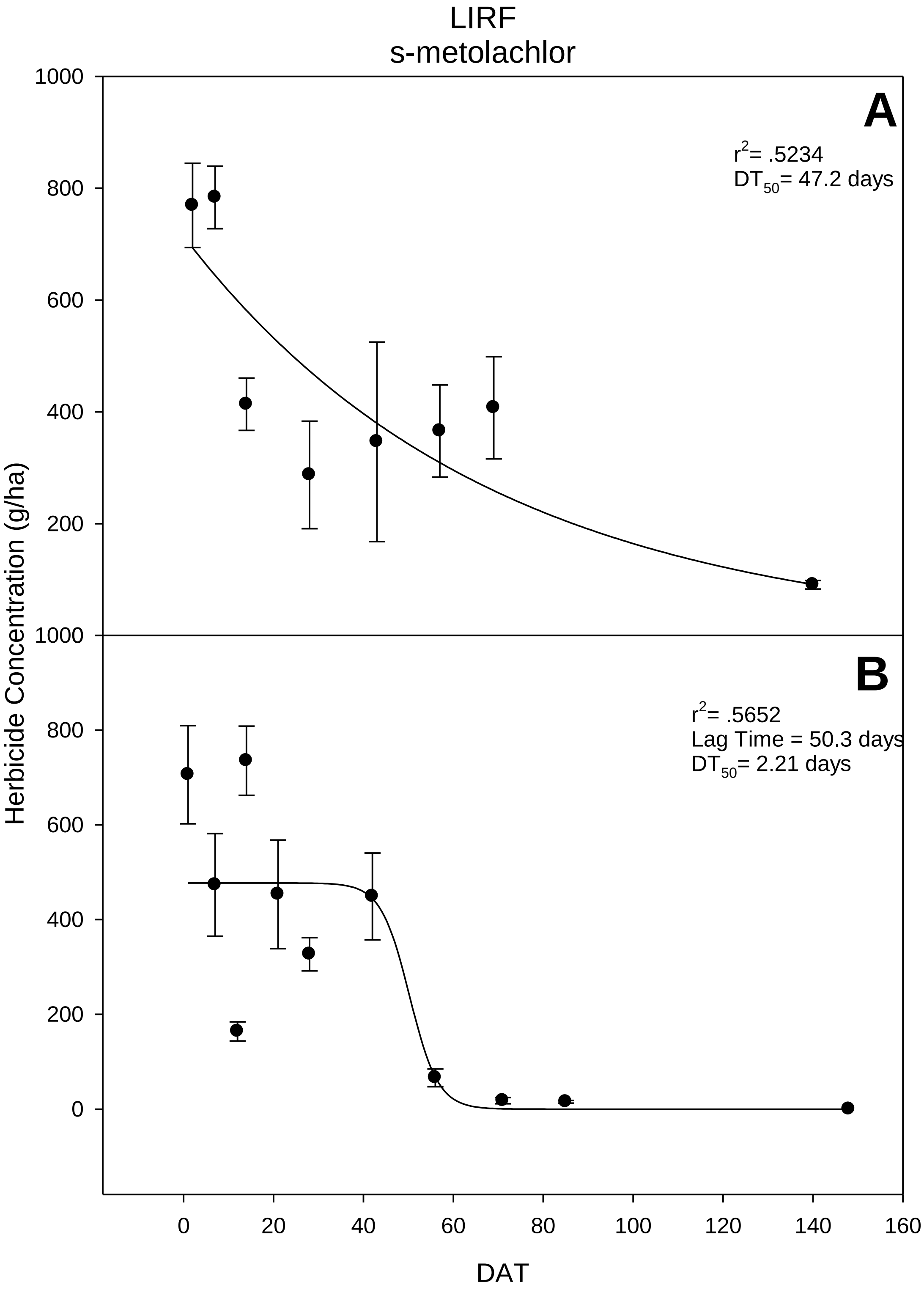


Figure 3.8) Dissipation of *s*-metolachlor in the top 30cm of soil over time for LIRF in A) 2009 B) 2010. Error bars represent standard error for dissipation averages.

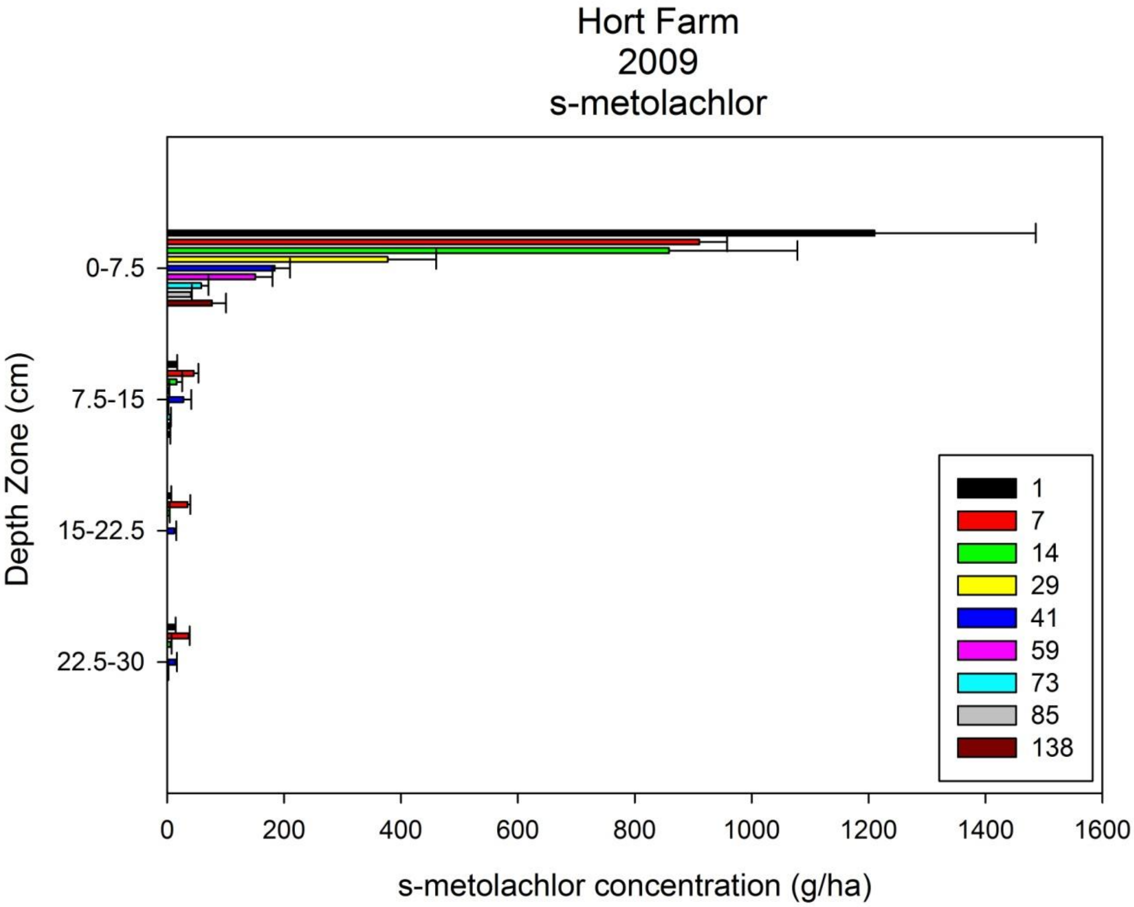


Figure 3.9. Distribution of *s*-metolachlor in the top 30cm of the soil profile over time at the Hort Farm site in 2009

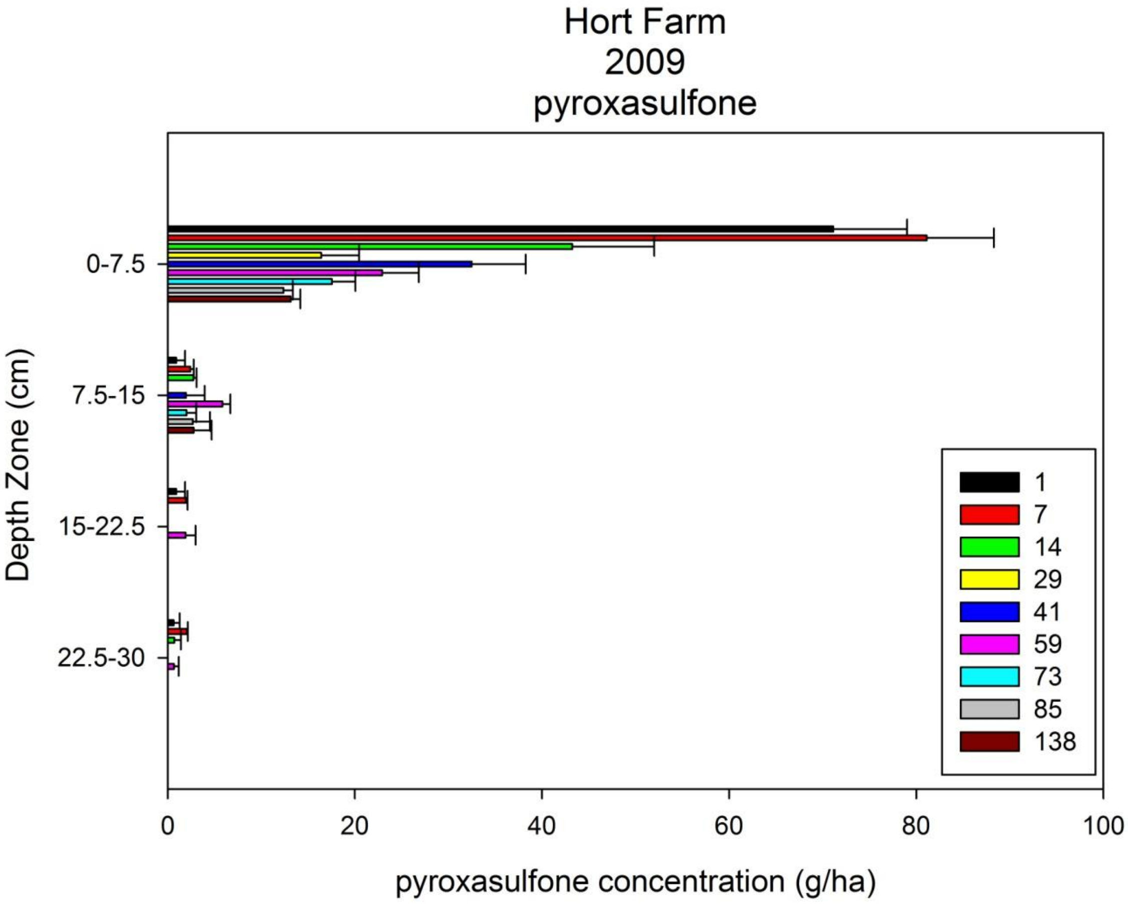


Figure 3.10. Distribution of pyroxasulfone in the top 30cm of the soil profile over time at the Hort Farm site in 2009

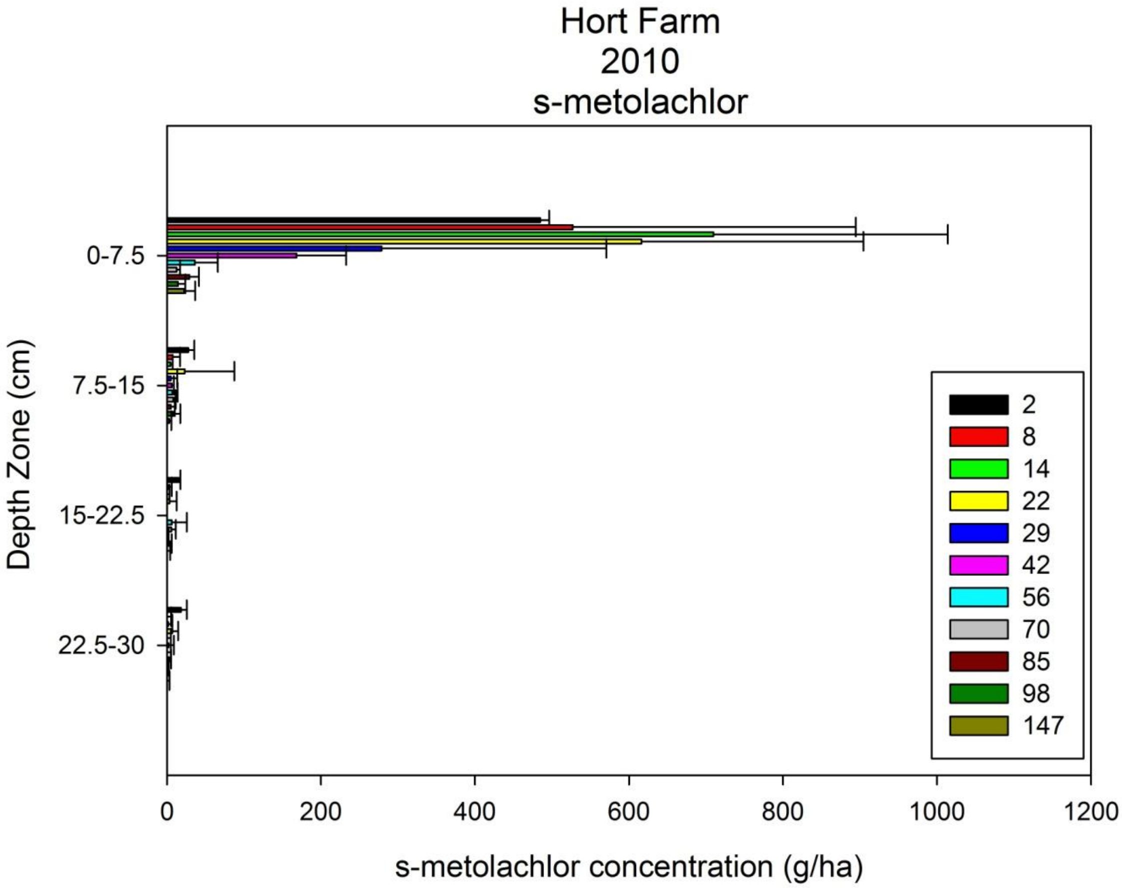


Figure 3.11. Distribution of *s*-metolachlor in the top 30cm of the soil profile over time at the Hort Farm site in 2010

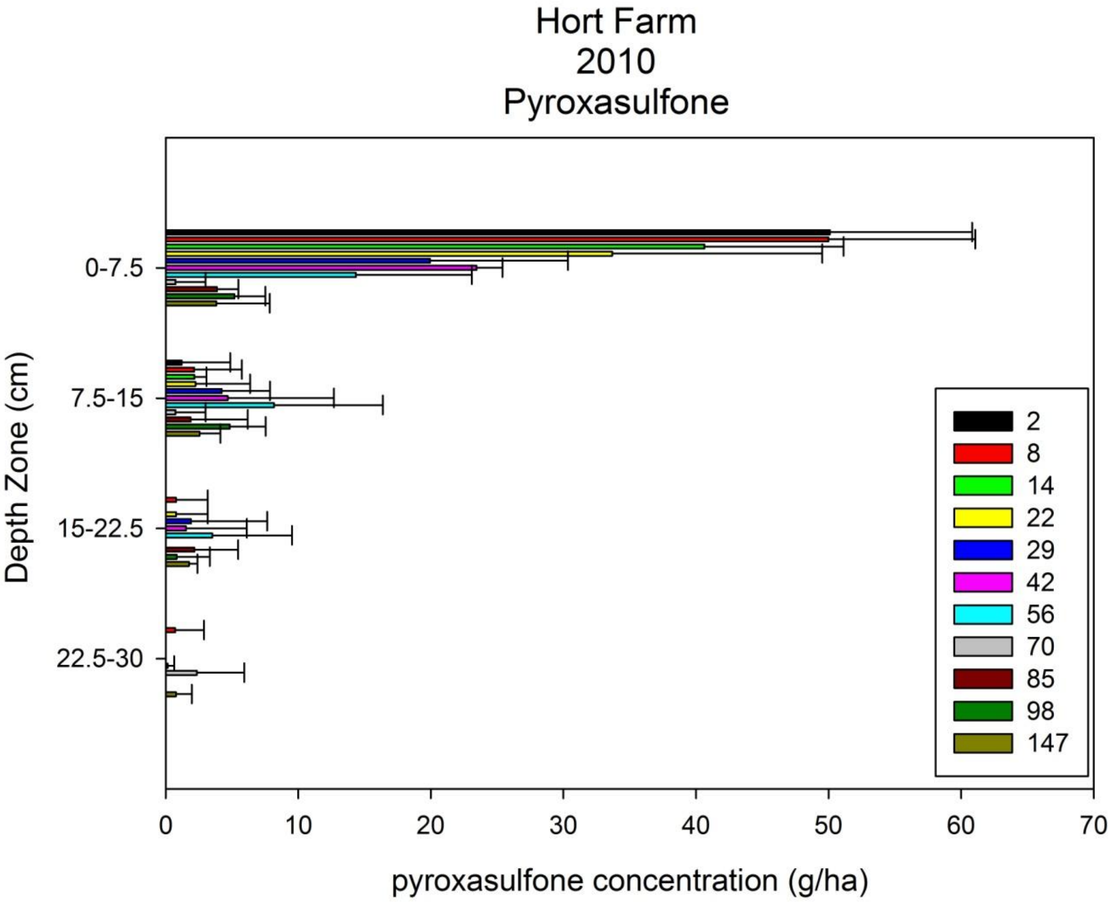


Figure 3.12. Distribution of pyroxasulfone in the top 30cm of the soil profile over time at the Hort Farm site in 2010

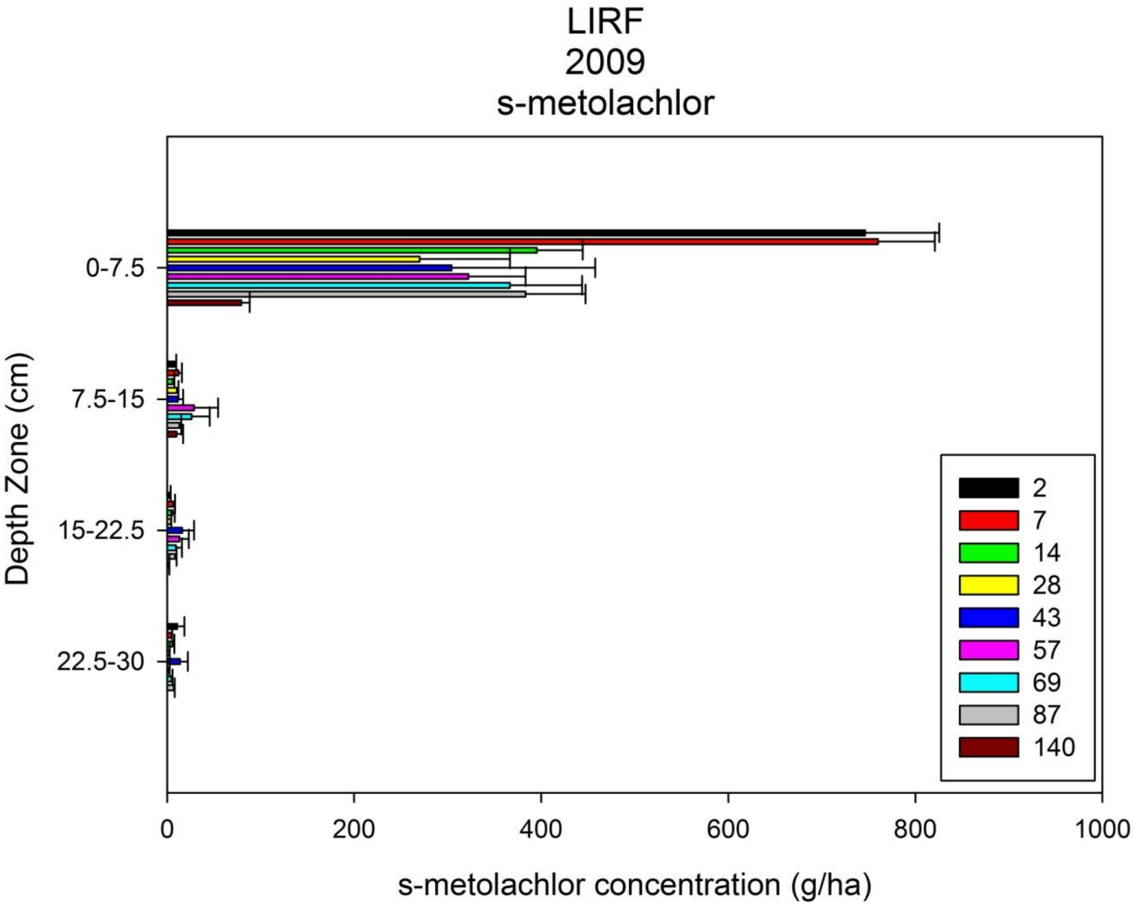


Figure 3.13. Distribution of *s*-metolachlor in the 30cm inches of the soil profile over time at the LIRF site in 2009

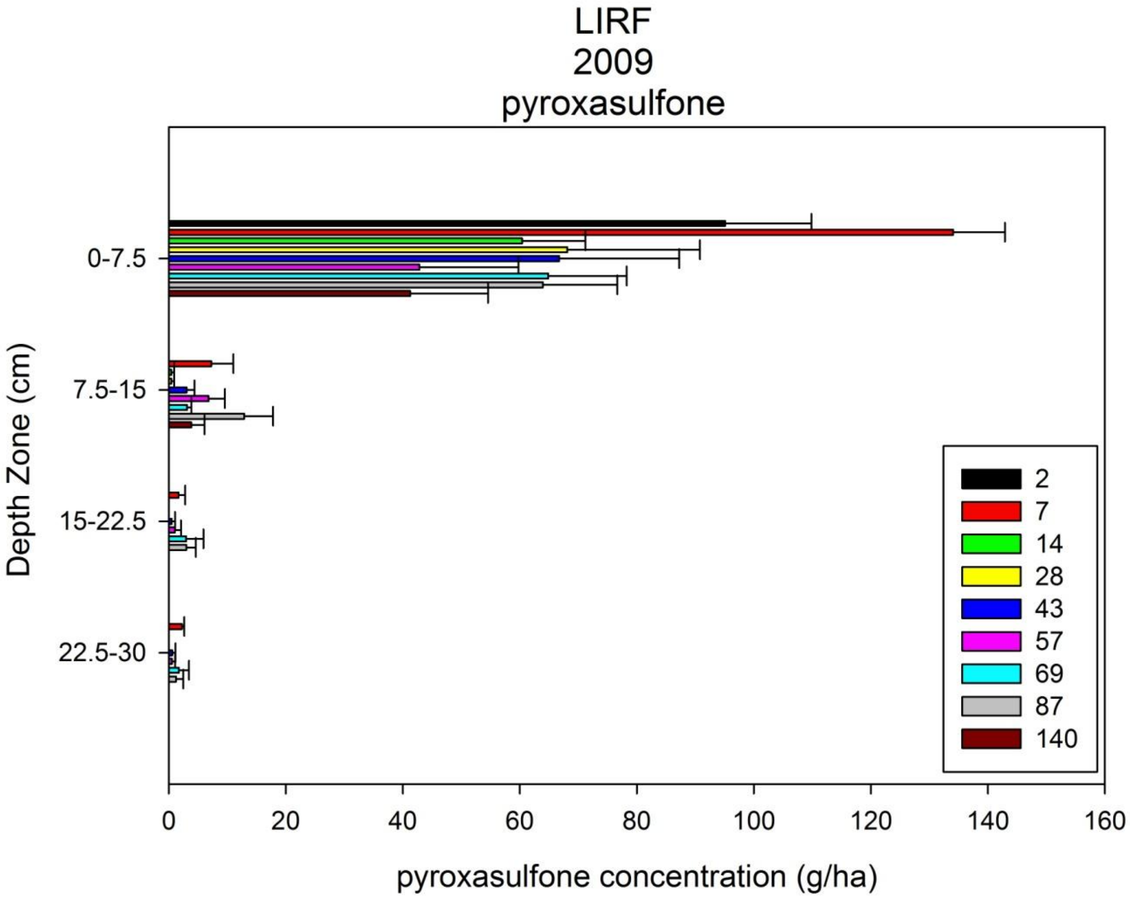


Figure 3.14. Distribution of pyroxasulfone in the top 30cm of the soil profile over time at the LIRF site in 2009

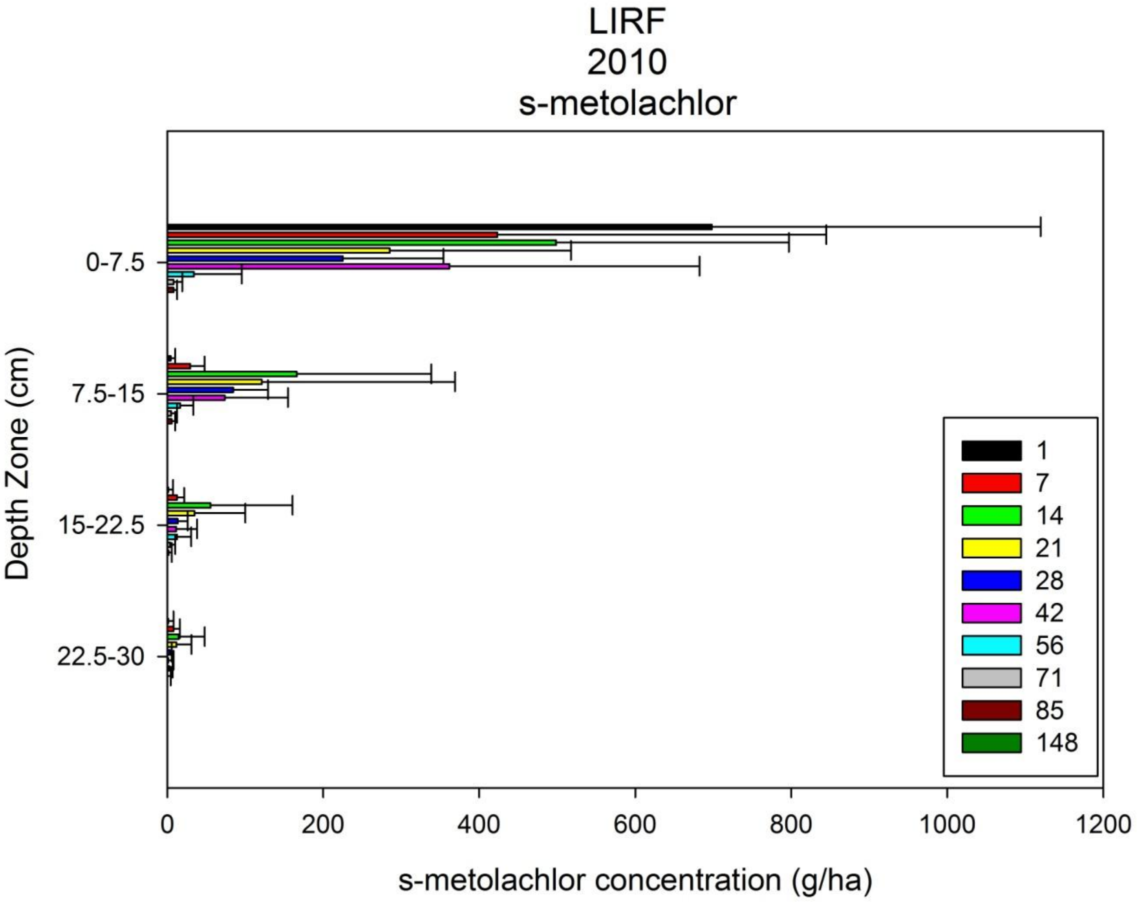


Figure 3.15. Distribution of *s*-metolachlor in the 30cm inches of the soil profile over time at the LIRF site in 2010

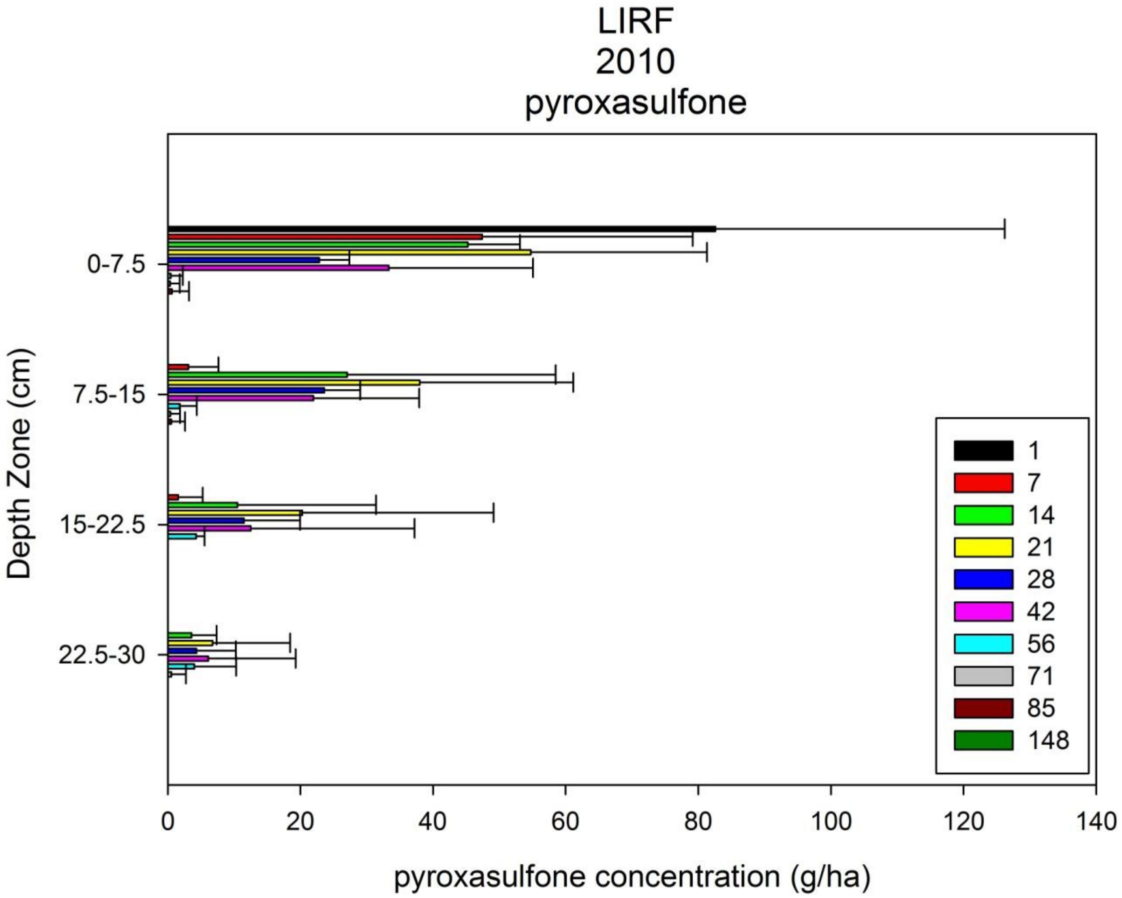


Figure 3.16. Distribution of pyroxasulfone in the top 30cm of the soil profile over time at the LIRF site in 2010

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