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Soil Residual Herbicides: Science and Management

Topics in Canadian Weed Science Volume 3

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Science and Management

Edited by Rene C. Van Acker

Canadian Weed Science Society
Société canadienne de malherbologie

Topics in Canadian Weed Science **Volume 3**

Soil Residual Herbicides:
Science and Management

Edited by

Rene C. Van Acker

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Canadian Weed Science Society – Société canadienne de malherbologie
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Foreword

The discipline of weed science in Canada has come a long way since the first formal Canadian weed committee, the Associate Committee on Weed Control, held its inaugural meeting in Edmonton, Alberta in 1929. Eighteen committee members discussed the ever increasing problem of weeds on Canadian farms. Since then, similar committees including the Canada Weed Committee, the National Weed Committee and the Expert Committee on Weeds, have met regularly to address the challenges associated with weed management in Canada. Weed science as a scientific discipline blossomed after the introduction of 2, 4-D in the 1940s. The numerous synthetic herbicides that followed 2, 4-D heralded a new and exciting era for weed control, and herbicides became the dominant control strategy for the next forty years. In the 1980s, however, it became apparent that more integrated approaches to weed management were required. The prolonged use of some herbicide classes resulted in the selection of resistant weed populations while other herbicides had a propensity to persist in soil and groundwater for long periods resulting in both production and environmental problems. These issues and others stimulated a renewed interest in topics such as integrated weed management, weed biology and ecology, biological weed control, application technology, and the environmental impact of herbicides. In response to these challenges, a vibrant, new weed science society emerged in Canada in 2002.

Today, the Canadian Weed Science Society - Société Canadienne de Malherbologie, includes a rich mixture of members involving federal, provincial and municipal government employees, multinational herbicide industry researchers and managers, university professors and graduate students, contract researchers, and consultants and industry agronomists. Our goals are (1) to establish and maintain a process for sharing and disseminating weed science knowledge in Canada; (2) to provide a forum for discussion of weed management issues in Canada; and (3) to take a proactive stand on behalf of all stakeholders on issues related to weed management at provincial and federal levels.

I am pleased to introduce the third volume in the series - "Topics in Canadian Weed Science". It is our intention to utilize this publication format to more consistently publish and distribute the relevant proceedings of our annual workshops and symposia. I encourage you to visit our website for further information regarding our society (www.cwss-scm.ca).

John O'Donovan
President, 2003-2004
CWSS-SCM

Preface

Welcome to the third volume of *Topics in Canadian Weed Science,* which is published periodically by the Canadian Weed Science Society – Société canadienne de malherbologie (CWSS-SCM). The series provides current information, reviews, research results and viewpoints on weed-related topics and issues. It is intended to advance the knowledge of weed science and increase awareness of the consequences of weeds in agroecosystems, forestry, and natural habitats. The topics addressed are diverse and exemplify the challenges facing the various stakeholder groups that make up CWSS-SCM.

This volume is a compilation of peer-reviewed papers based on oral presentations made at the plenary session of the 2004 CWSS-SCM annual meeting held in Winnipeg, Manitoba. The Local Arrangements Committee for the Annual Meeting chose the "Science of Soil Residual Herbicides" as the theme with national and international speakers addressing the subject. The topic generated much interest amongst society members, and resulted in the formation of a CWSS-SCM Herbicide Residue Working Group.

The CWSS-SCM Board of Directors expresses their gratitude to Gary Turnbull and the Winnipeg Local Arrangements Committee, the contributing authors, reviewers, and the editors who have made this publication possible. We also ask the readers of this volume to publicize this series to a more global audience. Other volumes include *Field Boundary Habitats: Implications for Weed, Insect, and Disease Management* and *Weed Management in Transition*.

Eric Johnson
Publications Director
CWSS-SCM

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Cover

Photograph: Group 2 herbicide soil residue affecting seedling canola. Photo courtesy of Richard Lussier, Agricore United, Grande Prairie, Alberta.

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SYMPOSIUM

Soil residual herbicides: Science and management.

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Introduction

The papers in this volume of *Topics in Canadian Weed Science* were presented at a symposium held during the Canadian Weed Science Society – Société canadienne de malherbologie (CWSS-SCM) meeting held in Winnipeg, Manitoba in November 2004. The science and management of soil residual herbicides was chosen as the symposium theme because it had become very topical. In farming operations across Canada, pressures of time and scale, and the need for cropping flexibility have heightened interest in the nature and management of soil residual herbicides. Residual weed control, landscape and weather effects on herbicide persistence, crop sensitivity to herbicide residues, recropping intervals, bioassays and residual herbicide stacking are all issues weed scientists, agronomists and farmers have to deal with in regard to soil residual herbicides. The agriculture industry in Canada needed more information and discussion on the topic of soil residual herbicides and CWSS-SCM responded by organizing a practical symposium. The symposium hosted international, national and regional experts from government, industry and universities to present the current state of science and management knowledge on this topical issue.

Herbicides that persist in the soil are of benefit to farmers seeking to control late emerging summer annual weeds in spring sown crops, and to managers looking for long-term vegetation control on rights-of-way and industrial sites. Herbicides that persist in the soil can also create problems for farmers who want to diversify their rotation into subsequent crops which may be sensitive to certain herbicide residues. Understanding the nature of herbicide residues in soil and the factors which contribute to rapid dissipation or extended persistence can help farmers and managers to exploit the opportunities such herbicides bring, while avoiding their challenges (Helling et al. 1971). Dr. Charles Helling from the Agricultural Research Service of the United States Department of Agriculture (USDA) in Beltsville, Maryland was keynote speaker at the conference and his paper provides a comprehensive overview of the scientific nature of herbicide persistence and availability in the soil. Dr. Dale Shaner from the ARS-USDA in Fort Collins, Colorado and Dr. Harry Strek from Dupont Crop Protection in New Jersey provided overviews similar to that provided by Dr. Helling but specific to the herbicide products offered by BASF and Dupont, respectively, for use in Canada. Dr. Jeff Schoenau (University of Saskatchewan) presented the results of recent field-based research on the impact that landscape position can have on herbicide persistence in the soil, particularly in regard to relative soil moisture levels, organic matter and pH. Eric Johnson (Agriculture and Agri-Food Canada, Scott, SK) presented the results of ongoing research into the potentially damaging effects to certain crops of having a history of various soil residual herbicides over-time on the same field. This problem has come to be known colloquially as herbicide residue “stacking” and has been a major concern to farmers and agronomists using and recommending the use of Group 2 herbicides (i.e. imidazolinones and sulfonylureas). Farmers and extension agronomists who have to deal with crop damage problems which may or may not be related to the presence of soil persistent herbicides will benefit from the diagnostic advice offered by Richard Lussier (Agricore United, Grand Prairie, Alberta), and the practical agronomic and management advice offered by Peter Sikkema (Ridgetown College, University of Guelph) and Denise Maurice (Agricore United, Calgary, Alberta). Predicting whether herbicide residues in the soil will be a problem for subsequent crops in rotation can be very difficult. One tool that farmers and agronomists can use is the bioassay. Paul Watson (Alberta Research Council) and John O’Sullivan (Simcoe Horticulture Experimental Station, University of Guelph) describe the methods and usefulness of these assays for field crops and vegetable crops, respectively.

The papers presented in this symposium provide an excellent basis for those wishing to gain an understanding of the scientific nature of the persistence of herbicides in the soil. They also offer sound and practical advice for farmers and agronomists who are charged with managing soil residual herbicides to both capture the opportunities they offer while avoiding the challenges they bring.

Literature cited

Helling, C. S., P. C. Kearney, and M. Alexander. 1971. Behavior of pesticides in soils. Advan. Agron. 23:147-240.

The science of soil residual herbicides

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Residual herbicides are those for which season-long weed control is expected due to their persistence in soil. The economic advantage of residual soil activity can be partially off-set by two problems: carryover of herbicide residue that may injure susceptible rotational crops, and increased risk of transport of herbicide to surface water or groundwater. Herbicide persistence is determined by complex interactions between the pesticide and the soil environment. Among the most important parameters and processes are (a) herbicide chemistry, (b) intrinsic soil properties (e.g., texture, organic matter content, pH), (c) extrinsic soil and meteorological factors (e.g., temperature, rainfall), and (d) other parameters (e.g., mode and rate of herbicide application, prior history of pesticide use, plant cover, topography). The major processes that reduce herbicide concentration in soil include transport (leaching, runoff, volatilization) and degradation, but adsorption to soil particles is extremely important in regulating herbicide concentration in the soil water, and therefore bioavailability. In general, low soil moisture, organic matter, and temperature are associated with slower microbial degradation; herbicide carryover is thus more likely in drier, seasonally cooler-climates, which characterize much of western Canada. Herbicide persistence is usually expressed as half-life, i.e., the time for dissipation of 50% (DT_{50}) of the applied herbicide from soil; the DT_{50} is inherently variable, due to the effects of climate and soil. Herbicides that have a $DT_{50} \geq 40$ d are considered to have moderate to long soil persistence; 50 such herbicides are listed within this review.

Additional Keywords: persistence in soils, dissipation half-life in soils, herbicide degradation in soils, herbicide leaching in soils, herbicide carryover in soils

Introduction

An overview of herbicide fate and behaviour in soils is appropriate when attempting to conceptualize soil persistence of herbicides. It also provides some historical and scientific structure for subsequent, detailed presentations in this monograph about current problems with residual herbicides and how to recognize and manage them.

Residual herbicides are those that control weeds throughout the growing season due to persistence of bioactive residues in the soil. Herbicide residue that remains in soil when the next crop is planted is termed carryover, or sometimes "bio-persistence." Depending on the amount of herbicide residue and the sensitivity of rotational plants grown later, carryover may or may not have an economic impact. Even if not injurious to weeds or rotational crops, carryover increases the potential for environmental concerns such as water contamination. For residual herbicides, this may be recognized formally by herbicide label restrictions on replanting or reuse of the product.

Expressions of soil persistence

Persistence refers to how long a pesticide [or its metabolite(s)] remains detectable in the environmental compartment of interest. One biologically-based definition (Vencill 2002) of a persistent herbicide is one "…that, when applied at the recommended rate, will harm susceptible crops planted in normal rotation, after harvesting the treated crop, or that interferes with regrowth of native vegetation in non-crop sites for an extended period of time." This practical description of persistence of course varies depending on plant sensitivity, and is influenced by chemical, soil, weather, and management factors.

To reemphasize the point, herbicide (or any pesticide) persistence is not a fixed property, but rather a highly complex result of many competing processes that affect the chemical's fate. Nevertheless, another common expression of herbicide persistence is the field dissipation half-life, or simply "half-life" ($t_{0.5}$, $t_{½}$, or DT_{50}). Although the DT_{50} is not strictly correct in a chemical kinetics sense, nevertheless it is a practical index of the time needed for the residual amount of herbicide to decline by 50% in soil or water. Mathematically, herbicide dissipation follows a first-order (or more correctly for field dissipation, pseudo first-order) decay process:

$$C = C_0 \exp[-k_d t] \qquad [1]$$

where C_0 is the initial concentration in soil, C is the concentration in the soil after t days, and k_d is the dissipation rate coefficient. The linearized Equation 1 is:

$$\log (C / C_0) = -0.4343\, k_d t \qquad [2]$$

Applying Equation 2 to an initial soil application of 1 kg ha^{-1}, and half-lives of 7 days (short persistence) or 60 days (moderately long persistence) for herbicides A and B, the dramatic faster decline in total residues (parent herbicide) for non-persistent chemicals is obvious (Fig. 1). Because so many extrinsic factors affect half-life, it is best represented as a mean or median value, with a range appropriate for the soil, climate, or regional conditions of interest. For example, although atrazine persistence is listed by Hornsby et al. (1996) as $t_{½} = 60$ d, their detailed summary reports field half-lives ranging from 18-120 d. Loss of 50% of chemical is a convenient, but arbitrary index of persistence; occasionally an additional value is provided, e.g., DT_{90}, or 90% loss of herbicide. This could be very helpful as a practical limit for residual phytotoxicity (pending confirmation by bioassay), and moreover would be valuable when dissipation is not well predicted by Equation 1.

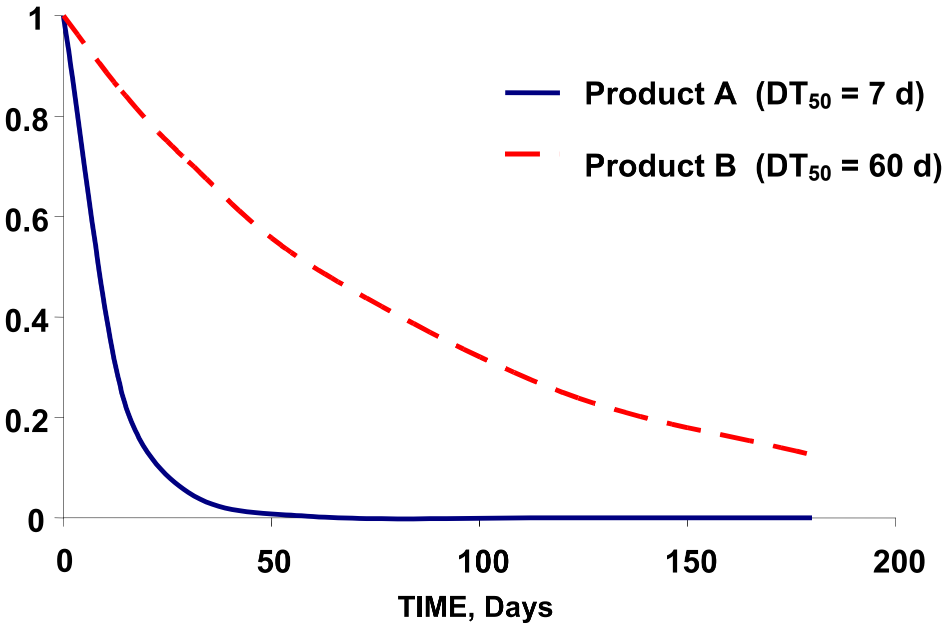

Figure 1. Hypothetical first-order dissipation of soil-applied herbicides "A" (DT_{50} = 7 d) and "B" (DT_{50} = 60 d).

More complex models exist that describe laboratory and field dissipation of herbicides and attempt to quantify the role of temperature, soil moisture, volatilization, and other factors on dissipation. Nash (1988) discussed some of these in a summary of published herbicide dissipation rates. His conclusion was that a lumped sum of the various dissipation pathways gave an appearance of pseudo first-order kinetics "with a high degree of statistical significance." Although in a practical sense this is true, a biphasic model of dissipation may more accurately depict the rapid, early loss of pesticide which is followed by much slower dissipation. This is particularly true when describing persistence, not only within the growing season, but also in the cold period of late fall, winter, and early spring. The two-compartment dissipation model (Equation 3) of Hill and Schaalje (1985)

$$C = C_0 \exp[-(k_s + k_r)t] + C_0\,(k_r \,/\, k_s + k_r - k_d) \times \{\exp[-k_d t] - \exp[-(k_s + k_r)t]\} \quad [3]$$

describes the loss of flucarbazone-sodium in five Western Canadian soils (Eliason et al. 2004). *C* is the concentration of the herbicide at time *t*. C_o is the initial concentration of the herbicide and k_s and k_r are surface loss and retention rate constants, respectively. Figure 2 shows a hypothetical biphasic dissipation curve.

There is no universally accepted classification of pesticide environmental persistence. However, Roberts (1996) used a classification based on the mean half-life of the pesticide in the soil: 1) Impersistent [or "nonpersistent"], DT_{50} <5 d; 2) Slightly persistent, DT_{50} = 5-21 d; 3) Moderately persistent, DT_{50} = 22-60 d; and 4) Very persistent, DT_{50} >60 d. For the purpose of identifying a set of "residual herbicides" for this review, however, this author has set $DT_{50} \geq 40$ d as indicating moderate to long persistence.

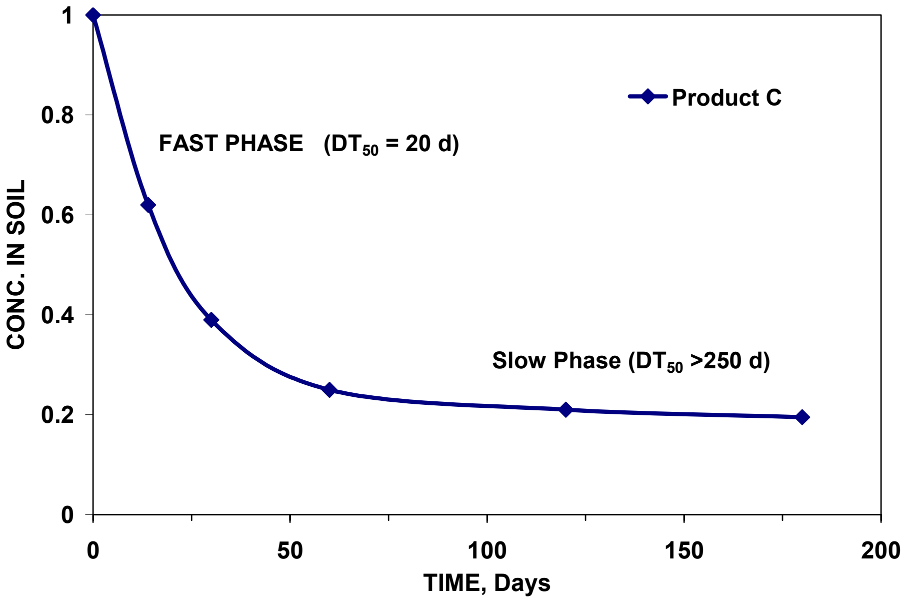

Figure 2. Hypothetical biphasic dissipation of soil-applied herbicide "C".

Processes affecting herbicide dissipation

Many reviews (Cessna et al. 2002; Cheng 1990; Grover 1988, 1991; Helling 1976; Helling and Gish 1985; Helling et al. 1971; Khan 1980; Koskinen and Clay 1997; and Mangels 1991) have described the environmental fate of herbicides or other types of pesticides. The fundamental principles affecting their fate and behaviour in the soil are the same.

Adsorption

Adsorption is defined as the accumulation of herbicide at the soil solution–soil colloid interface, or at the soil–air interface. “Sorption” is sometimes used instead of adsorption to describe the physical loss of chemical from the soil solution phase through contact with soil solids. The adsorption of a herbicide to the soil affects the transformation and transport of the herbicide, as well as its bioavailability. The bioavailability of a herbicide affects its performance by regulating the amount of residual chemical in the soil solution that is readily available for uptake. This, in turn, is directly related to persistence. As with much that is associated with soils, even the correlation between herbicide adsorption and bioavailability is not always clear (Hance 1988), especially with respect to availability of the herbicide to microorganisms. However, increased adsorption probably protects herbicides from biological degradation (Ogram et al. 1985).

Adsorption and desorption are complex dynamic processes, generally simplified for soil–pesticide research to the Freundlich adsorption isotherm model, Equation 4:

$$C_s = K_f C_{eq}^{1/n} \qquad [4]$$

where C_s is the sorbed concentration, C_{eq} is the equilibrium solution concentration, K_f is the Freundlich adsorption coefficient, and 1/n (sometimes written as “N”) is an empirical exponent. Units can be molar or by weight, but the latter is most common. If at equilibrium the adsorption–desorption processes are completely reversible, factor 1/n = 0, and the equation reduces to:

$$C_s = K_d C_{eq}, \text{ or } K_d = C_s/C_{eq} \qquad [5]$$

where K_d is the herbicide distribution coefficient, i.e., between solution and soil or sediment.

Soil organic matter (OM) or organic carbon (OC) content is usually the soil parameter most highly associated with herbicide adsorption. Adsorption coefficients of individual pesticides are often normalized for different soils by dividing the measured K_f or K_d by the fractional content of soil OM or OC. These K_{om} or K_{oc} values are theoretically more constant values. For example, the K_d values for nitrapyrin in eight different soils had a CV = 167% whereas the K_{oc} values had a CV = 20% (McCall et al. 1980). Normalizing K_d values to K_{oc} is most successful for relatively nonpolar chemicals because they are less sensitive to soil pH effects that might increase or decrease sorption. Published K_{oc} values (e.g., as in Hornsby et al. 1996) for individual herbicides can be used to estimate K_d for specific soils, with the caveat that the derived estimate might be relatively poor for ionizable chemicals or for soils with very low or very high OM content. All other things being equal, herbicide persistence is expected to be longest for the most strongly adsorbed chemicals and in the most strongly sorbing soils. The former tend to be compounds with low water solubility (e.g., trifluralin) or those that are cations (e.g., diquat and paraquat). Finer-textured mineral soils high in organic matter tend to have the highest capacity for adsorbing herbicides.

Herbicide chemical structure greatly influences soil adsorption strength and type. Cations such as diquat and paraquat are strongly and quickly sorbed, especially to soil clay. Glyphosate is also bound and largely inactivated in soil. The specific formulation of acidic herbicides can affect adsorption: the estimated K_{oc} values for triclopyr–triethylamine salt versus the butoxyethyl ester are 20 and 780 mL g^{-1} (Vencill 2002), respectively. Hydrolysis will quickly convert both to the free acid, but initially the low adsorption of the salt implies a much higher potential for some leaching into the soil; that, in turn, would protect the triclopyr from photodecomposition.

Degradation

Degradation of herbicides in soils occurs by abiotic and biotic processes. The transformation products usually are less phytotoxic than the parent. Complete mineralization of the herbicide to CO_2 rarely occurs, and often a significant fraction of the herbicide forms part of a bound residue (BR) pool. BRs are not easily characterized, but are likely to be high molecular weight polymers or metabolic fragments that become covalently bonded to soil OM. Khan (1991), in a review of bound residues, identified dinitroanilines, atrazine, and prometryn as residual herbicides that may produce large amounts of BRs. Although BRs may have some biological availability, they probably represent no inherent threat despite long persistence.

Abiotic loss is often inferred when half-lives are similar for nonsterile and sterilized soil in laboratory tests. However, microbial metabolism of the parent herbicide is the dominant mechanism of loss from the surface horizon. Atrazine is degraded by both chemical and biological mechanisms, although the latter seems to be the dominant pathway. At low pH, atrazine is chemically transformed to hydroxyatrazine in the soil. However, biological dehalogenation of atrazine to hydroxyatrazine has also been demonstrated (Mandelbaum et al. 1993). Although atrazine has been commercially available since 1958, only comparatively recently was a soil bacterium isolated that could mineralize the *s*-triazine ring (Radosevich et al. 1995).

Transformations within soil of the original herbicide normally—but not always—lead to reduced effectiveness. One of the few exceptions is isoxaflutole, which is hydrolyzed (largely abiotically) to the more biologically active diketonitrile–isoxaflutole (Taylor-Lovell et al. 2002). Because moisture is required to effect this transformation, application to dry soil of the strongly adsorbed parent

(Taylor-Lovell et al. 2000) will cause no loss nor show herbicidal activity until environmental conditions trigger the chemical conversion of the proherbicide to its active form.

Herbicide degradation, as for metribuzin (Moorman and Harper 1989), is generally slower in subsoil, where the microbial population is much less than in topsoil. Unless photodegradation is a significant process, degradation is slower in the surface organic debris than in soil. Atrazine loss, for example, was faster in the underlying mineral soil than in the organic layer of a Canadian grassland soil, and still faster (although still low relative to most other studies) in a coniferous forest soil (Entry and Emmingham 1996).

Microbial degradation is sensitive to many factors including soil temperature, aeration, moisture content, pH, soil organic matter, existence of an active rhizosphere (plant growth), and perhaps nutritional status. Today, most-probable-number enumeration methods are increasingly being used for herbicides such as 2,4-D and atrazine (Jayachandran et al. 1998) to better understand persistence. Also, molecular typing allows identification of bacterial strains that degrade specific pesticides. Spatial variability in the distribution of those microorganisms may also help explain field-scale variability in herbicide performance as well as understanding processes at the soil aggregate scale.

Transport

Leaching

Herbicide movement into soils following rainfall or irrigation is often beneficial when root uptake is necessary for weed control. Depending on the product’s chemical characteristics, leaching from the soil surface reduces losses by volatilization and photodegradation. Thus, limited leaching may extend soil persistence. Deeper migration reduces the residual herbicide in the upper vadose zone (region below the water table), and so could lessen persistence in the zone most relevant to crop production. Such leached chemicals no longer contribute to weed control and may contaminate groundwater or surface water via lateral discharge. Since microbial activity is much lower in the subsurface horizons and in groundwater compared to the vadose zone, herbicide persistence generally is much longer once it moves below the vadose zone. However, when abiotic degradation is important—as with atrazine—increased persistence in subsoil may be slight (Radosevich et al. 1996). The persistence of atrazine in groundwater is quite long (Klint et al. 1993; Widmer et al. 1993), no doubt contributing to the observation that it has been the most commonly detected pesticide in U.S. (Public Health Service 2003) and Canadian water samples.

Leaching potential has long been predicted based on herbicide and soil characteristics, and on various laboratory methods such as adsorption, soil leaching column, and soil thin-layer chromatography tests. Rapid degradation greatly reduces the potential loss by leaching. For example, the relatively new herbicide florasulam has very high potential mobility—68-92% leached through a soil column. Because it also had DT_{50} values of 2-10 days and DT_{90} values of 16-34 days, it was judged unlikely to contaminate groundwater (Health Canada 2004; Vencill 2002). The principal metabolite, 5-hydroxyflorasulam, was equally mobile, but more persistent, and presents a higher potential for carryover, so leaching may occur under conditions of excessive rainfall or irrigation (Health Canada 2004).

Most herbicide leaching occurs during mass flow of water through the soil matrix, ensuring ample exposure of chemical to soil and soil biota surfaces. Preferential (or macropore) transport represents a condition whereby water and dissolved constituents rapidly percolate deeper into the soil profile by following larger pores formed from root channels, arthropod activity, or natural soil structure voids; by unstable wetting front flow; or by funnel flow in sloping layered soils (Kung 1990). It is increasingly likely that preferential movement explains much of the unexpectedly rapid leaching of herbicides to shallow groundwater in certain conditions such as substantial water input (irrigation, rainfall) on medium- to fine-textured soils that were already moist (Gish et al. 2004). Prediction of pesticide loss from the surface horizon by preferential transport is difficult because the size spectrum of conducting pores is not adequately defined. Furthermore, pesticide—soil interactions that may restrict leaching under normal conditions are less effective when time and surface area are diminished by rapid flow down larger pores. Preferential transport will only move a small fraction of applied herbicide below the rooting zone and may have a slight effect on extending the residues of the herbicide in the subsoil. The same process will also decrease the surface horizon concentration of herbicide, but probably by <5%. Near the soil surface, wetting and drying cycles will tend to sequester the herbicide within finer soil pores, where it is less susceptible to leaching and perhaps degradation.

Runoff

Runoff refers to the off-site surface transport of herbicides in solution, suspension, or while adsorbed to particulates. Comprehensive reviews on runoff have been written (Leonard 1988; Leonard 1990; Waucope 1978). There is a direct correlation between persistence and the potential for runoff loss, particularly when the chemical remains within the upper 1 cm of surface soil. Runoff is triggered by rainfall, and the highest pesticide loss occurs during the first major runoff-producing event. The losses are affected by many factors, including the timing of pesticide application relative to the timing, intensity and duration of rainfall, antecedent soil moisture, soil texture, surface crusting, compaction, topography, pesticide formulation, and management practices (e.g., no-till; buffer strips; controlled tile drainage). While herbicide transport by runoff represents an important mechanism for potential environmental contamination of surface waters, the process itself generally removes <5% of total applied chemical and for most pesticides, <0.3% (Waucope, 1978).

Volatilization

Volatilization of herbicides has been considered to be relatively small due to the inherently low vapour pressure of most such chemicals, or because loss is reduced through soil incorporation or formulations that minimize vapour phase loss. However, it is recognized today that many pesticides are transported far from their sites of application via volatilization and losses are likely to greatly exceed those from leaching or runoff (Taylor and Spencer 1990). Despite its relatively low vapour pressure, the consistent occurrence of atrazine in rainwater (Miller et al. 2000) is a strong indicator of some loss by volatilization, spray drift, and as material sorbed onto dust (wind erosion). Metolachlor is another herbicide for which vapour phase loss can be large during the first 48 h after application, depending on the climatic conditions. Volatilization peaks during and immediately after application, but sensitive methods for monitoring air also show vapour phase fluxes early in precipitation events, or even diurnal fluctuations, as soil water moves toward the soil surface. Maximum loss is expected when application occurs to moist soil followed by a long period of drying. Once the herbicide has moved into the soil (probably only a few centimetres) and adsorption occurs, loss by volatilization should greatly diminish.

Factors affecting soil persistence of herbicides

No single soil, meteorological, herbicide chemistry, or application method factor solely defines persistence. However, some of the most important predictors of herbicide dissipation are summarized below.

Soil (and related meteorological) characteristics

pH

Herbicide adsorption to soil can be strongly affected by soil pH, and this can affect persistence. In general, ionizable chemicals may protonate at low pH (e.g., weakly basic amines), or conversely, become anions at neutral or alkaline conditions, such as the weak acids 2,4-D or picloram. The solubility and hydrolytic stability of sulfonylureas, which are weak acids, increase in alkaline soil and result in a substantially increased potential for carryover. On the other hand, triazines and imidazolinones are more strongly adsorbed and more persistent, in acidic soils. Even if the pesticide itself does not become charged, soil pH may affect the soil surface characteristics, potentially strengthening or weakening binding of certain herbicides.

Soil pH has also been proposed as the underlying reason for in-field spatial variability in the degradation of phenylurea herbicide isoproturon (Bending et al. 2003). The bacterial strains found to degrade isoproturon had a very narrow optimum pH for metabolism of 7-7.5. Thus, liming, for example could easily affect localized differences in residual herbicide, whether the transformation is biotic or abiotic.

Organic matter content

In general, microbial activity is higher in soils with high soil OM content, so herbicide degradation is expected to be faster, and persistence shorter as soil OM increases. Counterbalancing this is the greater capacity of higher soil OM to sorb the herbicide, keeping less in soil solution and reducing transport by leaching. This was given as a possible explanation of the increasing DT_{50} of 2,4-D as soil OM increased (Bolan and Baskaran 1996), although in another study (Benoit et al. 1999), increased sorption seemed to enhance the rate of mineralization of 2,4-D and its polar phenolic metabolites to CO_2.

Texture, composition

Nash (1988), after evaluating numerous reports, was unable to conclude that soil type *per se* affected herbicide persistence. Contributing—but sometimes contradictory—factors include the relationships of soil type to moisture holding capacity, organic matter content, aeration status, soil temperature, pH, and microbial activity. Adsorption can be affected markedly by the composition of the soil's mineral fraction; for example, imazapyr is strongly bound to a Hawaiian oxisol soil that is dominated by amorphous iron and aluminum oxides (Helling and Doherty 1995; Helling 1997). This had the practical effects of reducing the herbicide's phytotoxicity and preventing its leaching, although not its degradation.

Moisture content

Prolonged drought not only reduces herbicide performance by reducing uptake by weeds, but also slows the rate of degradation in the soil. Higher soil moisture in aerobic soils is normally associated with enhanced microbial activity and decreased persistence. However, unless anaerobic degradation is important, saturated soil prolongs herbicide persistence. Soil moisture fluctuations impact microbial cell number, biomass, enzyme activities, etc. Genetic fingerprinting has been used to show which microbial communities are resistant or resilient to soil drying-rewetting in a study on the degradation of two pesticides (Pesaro et al. 2004). Drying the soil greatly lengthened the $t_{½}$ values for the pesticides and their metabolites. Mojašević et al. (1996) found a consistent, parallel increase in half-life for seven pesticides (including herbicides alachlor, atrazine, cyanazine, metolachlor, and metribuzin) as soil moisture content decreased from 35 to 25 to 12%, except that carbofuran dissipation was disproportionately reduced at 12% moisture content. Field persistence of these pesticides was more variable compared to laboratory studies, but the rankings were similar.

Temperature

Within the normal environmental range, higher soil temperature has been associated with faster dissipation of herbicides. The approximate effect is a 2.2-fold increase in rate per 10°C increase. While the longer term effect is likely to be accelerated degradation, volatilization also increases as temperature increases, especially during and soon after application. On a large scale, Nash (1988) used the data of Hamaker (1972) to demonstrate the greatly extended half-life of picloram going from latitude ~25° N to ~55° N. Similarly, the half-life of diphenamid ranges from 1-2 wk in the southern United States to 5-6 wk in northern U.S. (Vencill 2002). There are many reports of herbicides and other pesticides dissipating more rapidly in tropical than in temperate climates (Helling 1997; Laabs et al. 2002; Racke et al. 1997), most likely related to higher mean soil temperature in tropical and subtropical areas. In one study (Bailey 2003), reduced persistence of autumn-applied isoproturon was attributed to an apparent two-decade warming trend in Great Britain. If these observations are true, this would seem to have significant long-term implications for herbicide use and effectiveness as the global temperature increases.

Herbicide chemistry

Persistence of herbicides is affected by the ease of degradation, susceptibility to water-borne transport losses, and by volatilization of each chemical. To some extent, moderately volatile herbicides such as alachlor, butylate, clomazone, EPTC, and trifluralin can be protected by soil incorporation or controlled-release formulation, thus extending persistence and improving weed control. Similarly, the specific formulation of acidic herbicides such as 2,4-D will also affect volatility: low molecular weight esters (e.g., butyl) are more volatile than the “low volatile”, higher molecular weight isooctyl ester; salt formulations (e.g., the dimethylamine) reduce such potential loss even more.

The main impact of herbicide chemistry is on adsorption and degradation. The former is especially influenced by existence of a permanent positive charge (as in diquat and paraquat) or functional groups that can accept a proton, typically an amine or a carboxylic acid. Since most mineral soils have a significant cation-exchange capacity, adsorption of a protonated herbicide occurs in acidic soils. As pH increases, a smaller fraction remains protonated and the molecule becomes neutral or negatively charged and less strongly adsorbed. Except in strongly acidic soils, acidic herbicides such as dicamba, 2,4-D, and picloram exist almost solely in the ionized, anionic form and therefore are only weakly adsorbed to soil. In some cases such as glyphosate, unique bonding mechanisms may occur that lead to complexation, for example, with cations in soil solution or on soil colloid surfaces. Molecular modifications that affect biological stability are much harder to predict, although ester moieties are generally hydrolyzed quickly in soil.

Application (management) factors

Higher rates of herbicide application are associated with longer persistence of residues, even though the DT_{50} values are generally unaffected. At very high rates, simulating chemical spills, longer DT_{50} values have been shown (Gan et al. 1995), indicating that the first-order dissipation model for loss cannot be projected indiscriminately. The lower rates of many newer herbicides do not preclude carryover, however, as exemplified by chlorsulfuron, which is applied at ca. 5-50 g ha^{-1}, but may affect sensitive species such as sugar beets 3-4 y after application in an alkaline soil (Vencill 2002). It is likely that most cases of higher-than-label rates of herbicide will occur when unintentional application overlap occurs, and carryover damage to sensitive rotational crops may be limited to such isolated spots in the field.

Vegetated buffer strips are used to reduce soil and pesticide runoff. The higher soil organic C and microbial activity within the strip promote adsorption and degradation. For example, the DT_{50} for metolachlor is 23 d in a bare field soil versus 10 d within an adjacent buffer strip (Staddon et al. 2001).

Prior history of the use of certain herbicides and other pesticides may affect their soil persistence (Racke and Coats 1990). For example, thiocarbamate herbicides such as EPTC and butylate show accelerated degradation in fields previously treated with these compounds (Harvey 1987; Roeth 1986). More recently, there have been several reports of shorter persistence of atrazine in sites where this herbicide had been used for a number of years, and more atrazine-degrading microorganisms were isolated from the “history” soils, indicating that adaptation had occurred (Jayachandran et al. 1998; Koskinen and Clay 1997). The DT_{50} of isoproturon was related to the recency and frequency of prior use (Walker and Austin 2004). Failure of carbetamide to adequately control grasses following repeated annual application was associated with its enhanced degradation by adaptive soil bacteria (Hole et al. 2001); reapplication once, 14 months after the first dose, reduced its DT_{50} from 54 to 9 d. In these examples, enhanced microbial degradation with diminished soil persistence and weed control is distinguished from loss of efficacy that arises from herbicide-resistant weed biotypes (Heap 2004).

Cross-enhancement is enhanced degradation that may occur for a chemical applied to soil treated previously with a different—though usually structurally similar—pesticide. One such case is the use of the fumigant (and herbicide) metham sodium. This degrades to the biocide methyl isothiocyanate (MITC). Degradation of three other isothiocyanates was enhanced when incubated with a

MITC-history soil (Warton et al. 2003). With long-term use of individual products, or sometimes classes, some degree of enhanced herbicide degradation is likely.

Soil persistence of selected residual herbicides

Any estimate of field dissipation half-life or comparable index of persistence is dependent on a variety of factors. For example, DT_{50} values tend to be shorter in warm, moist climates compared to cooler, drier soils. Alkaline soils tend to prolong persistence for certain herbicide classes, notably sulfonylureas and triazines. Thus, although a single value may be reported for DT_{50}, for a herbicide, it usually represents a range, often very wide.

With that caveat, Table 1 lists estimates of the aerobic DT_{50} for 50 of the more persistent, or residual herbicides based primarily on values from Vencill (2002) and Hornsby et al. (1996). The 20 herbicides denoted as having carryover should not be assumed to always carryover, nor should the remainder be regarded as never having this potential. Among the 50 herbicides, diquat, glyphosate, and paraquat are unlikely to ever exhibit carryover phytotoxicity due to their very strong binding to soil. One herbicide, flucarbazone-sodium, is not listed in Table 1 because its DT_{50} generally seems to be <30 d (Health Canada 2000); however, its sulfonamide metabolite is highly persistent. Moreover, flucarbazone-sodium had a half-life of 110 d in a Udic Boroll soil from Manitoba, in a laboratory incubation (Eliason et al. 2004), suggesting the potential for residual carryover in other alkaline soils with high OM and clay content.

Table 1. Herbicides with moderate to long persistence in temperate-zone soils[a].

Herbicide	DT_{50}[b] d	K_{oc}[c] mL g^{-1}	Carryover potential[d]
Atrazine	60	100, 213*	●
Benefin	40	9000	
Bensulide	120	1000	
Bromacil	60-150	32, 72*	
Cacodylic acid	50	1000	
Chlorimuron	40	110 (pH 7)	
Chlorsulfuron	40	40 (pH 7)	●
Clopyralid	40 (12-70)	6-60	●
DCPA	100	5000	
Dichlobenil	60	400, 234*	
Diquat	1000	1×10^6	
Diuron	90	480	
Ethalfluralin	60	4000	
Ethofumesate	30	340	●

Table 1. Herbicides with moderate to long persistence in temperate-zone soils[a] (continued).

Herbicide	DT_{50}[b] d	K_{oc}[c] mL g^{-1}	Carryover potential[d]
Fluometuron	85	100	
Flumetsulam	60 (30-90)	700 (12–anion)	●
Fomesafen	100	60[e]	●
Glyphosate	47	24,000	
Halosulfuron	6-34	90-200	●
Hexazinone	90 (30-180)	54	
Imazapyr	90 (25-142)	100	●
Imazaquin	60	20 (pH 7)	●
Imazethapyr	60-90	10 (pH 7)	●
Isoproturon	40	80-230	
Linuron	60 (60-150)	400	
Metolachlor	30-50, 90	200	
Metribuzin	40 (30-60)	60, 95*	
Metsulfuron	30 (14-180)	35 (pH 7)	●
MSMA	180	7000 (250-2850)	
Napropamide	70	700	
Oxadiazon	60	3200	
Oxyfluorfen	30-40	1×10^5	
Paraquat	1000	1×10^6	
Pendimethalin	44	17,200	
Picloram	90 (20-300)	16 (17-160)[f]	●
Prodiamine	120	13,000	
Prometon	500	150 (51-213)	
Prometryn	60-70	400	
Quinclorac	35-50, 166	36 (13-54)	●
Quizalofop-P	60	510[g]	
Simazine	60	130, 214*	●
Sulfentrazone	32, 110-280	43	●
Sulfosulfuron	14-75	~90-800	●
Tebuthiuron	360-400	80 (22-91)	●
Terbacil	120 (150-180)	55	●
Triallate	82	2400	
Triasulfuron	10-95	65-190[h]	●
Triclopyr	36 (10-46)	20, 780[i]	
Trifluralin	60 (45-120)	7.5×10^3, 3.1×10^4*	●

[a] Values for DT_{50}, and K_{oc} are primarily from Hornsby et al. (1996) and Vencill (2002). Values marked by an asterisk were from Doucette (2000). All sources are secondary compilations, and original values (listed in Hornsby et al.) can vary

widely. In some cases, this is indicated through inclusion of a range of values in parentheses, together with the "best" estimate.

[b] Average field dissipation half-life (sometimes showing typical range of values).

[c] Experimental or mathematically-derived estimate of the sorption coefficient, normalized on soil or sediment organic carbon content.

[d] Symbol '●' indicates potential injury to rotational crops. This may occur only under certain conditions (soil, weather, application rate and timing, sensitive species, etc.). Designation (by ●) does not imply high probability; lack of designation does not preclude the possibility of carryover.

[e] K_{oc} value is for Na salt of fomesafen.

[f] Lowest K_{oc} values are for K salt of picloram.

[g] K_{oc} value for ethyl ester of quizalofop-P.

[h] At soil pHs of 7.1-7.8.

[i] Estimated $K_{oc} = 20$ for triethylamine salt, 780 for butoxyethyl ester of triclopyr.

The sorption index K_{oc} is also included in Table 1 since, along with DT_{50}, it provides some basis for judging leaching potential. Arnold (1995) suggested that DT_{50} and K_{OC} can be used as leaching criteria. Herbicides may have high leaching potential if they have the following properties: soil $DT_{50} > 21$ d; $K_{oc} < 500$; water solubility > 30 mg L^{-1}; hydrolysis $DT_{50} > 4$ d; photolysis $DT_{50} > 4$ d; and vapour pressure < 10^{-4} Pa. On that basis, triazines (atrazine, hexazinone, metribuzin, prometon, simazine), imidazolinones (imazapyr, imazaquin, imazethapyr), sulfonylureas (chlorimuron, chlorsulfuron, metsulfuron, triasulfuron), bromacil, fluometuron, fomesafen, metolachlor, picloram, quinclorac, tebuthiuron, and triclopyr would warrant study. However, soil pH strongly affects adsorption of triazines, imidazolinones, and sulfonylureas, and so leaching and risk would be greatest for neutral to alkaline soil, especially with low clay and organic matter. Some of these herbicides, e.g., atrazine and picloram, are Restricted Use Pesticides because of the risk of leaching to shallow groundwater. The extremely high K_{oc} of glyphosate guarantees that only in extreme cases (e.g., high-rate, multiple applications to essentially non-sorbing media) might leaching occur. Giesy et al. (2000) thoroughly examined the few cases where glyphosate leaching to groundwater was reported and concluded that only one was valid. That (Smith et al. 1996) occurred after two consecutive, high-rate (4.6 and 4.3 kg ha^{-1}) applications of glyphosate to the gravel platforms of utility substations in Newfoundland, Canada; the sites were on highly permeable subsoil, with no overlying topsoil.

Summary

Residual herbicides are useful for long-term weed control, but problematic when the same characteristic leads to injury to sensitive crops planted in rotation or to natural vegetation in uncropped areas over a long period. Generally no single factor is linked to long herbicide persistence: rather, persistence is due to a combination of herbicide chemistry, soil pH, organic matter content, and texture. Climatic factors also strongly affect degradation and binding of residual herbicides to the soil. In most cases, herbicide persistence increases as pH increases, and soil moisture and temperature decrease.

Careful planning of herbicide applications in relationship to rotational crops is especially needed for the more persistent, biologically-active residual herbicides. Herbicide labels usually have restrictions on replanting or reapplication of the chemical(s); extension publications (e.g., Devlin et al. 1992; Hager and Norby 2004) may provide additional guidance.

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Soil interactions of imidazolinone herbicides used in Canada

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The imidazolinone herbicides were discovered and developed in the 1980s and 1990s. Imazethapyr and imazamox are the mostly widely used imidazolinones in Canada. Although imazamox and imazethapyr are applied early postemergence, they do have residual activity. Imazamox dissipates more rapidly than imazethapyr in the soil. The most important factors affecting the soil activity of the imidazolinones are soil organic matter, pH, moisture and temperature.

Additional Keywords: imidazolinone, imazethapyr, imazamox, soil dissipation, adsorption

Introduction

The imidazolinone herbicides were discovered and developed in the 1980s and 1990s (Shaner and Singh, 1997). Imazethapyr and imazamox are the most widely used imidazolinones in Canada, and are registered to control weeds in soybeans (*Glycine max* (L.) Merr.), field peas (*Pisum sativum* L.), dry beans (*Phaseolus vulgaris* L.), alfalfa (*Medicago sativa* L.), chickling vetch (*Lathyrus sativus* L), and imidazolinone resistant crops. Although imazamox and imazethapyr are applied early postemergence, they do have residual activity. The purpose of this review is to compare the soil activity of imazamox with imazethapyr and to discuss factors that affect their soil residual activity and carryover potential to sensitive follow crops.

Mode of action

Imidazolinones kill plants by inhibiting acetolactate synthase (ALS), the first enzyme in the biosynthesis of the branched chain amino acids (Shaner and Singh, 1997). Imazamox and imazethapyr are equally effective in inhibiting ALS (Little et al. 1994). Since ALS is primarily located in the meristematic tissue of plants, the imidazolinones have to be translocated to the growing points of plants to be effective (Shaner and Singh, 1997).

Root absorption and translocation

Imidazolinones are amphoteric compounds with multiple pK_as, and they can exist in different ionic states depending on pH (Figures 1 and 2). The lipophilicity of these herbicides varies with pH, with both herbicides being more lipophilic in the neutral state versus the cationic or anionic state. Imazamox is a slightly stronger acid compared to imazethapyr. At pH greater than 6 both chemicals exist in the anionic form. However, at pH between 4 and 6, more imazethapyr exists in the neutral form compared to imazamox (Figure 2). This difference is important because it affects the ability of these herbicides to penetrate roots.

The mechanism of root uptake of imidazolinones is via an ion trapping mechanism (Little and Shaner, 1991). The major barrier preventing a herbicide from entering the xylem is the impermeable endodermis. The primary way to cross the endodermis is for a herbicide to be absorbed by the root cells in the outer cortex. A pH gradient exists between the inside and outside of the root cell. Typically the pH outside the cell is between 4.5 and 5 while it is between 7 and 7.5 inside the cell. At the lower pH outside the cell more of the neutral, lipophilic form of the imidazolinone exists and this form can diffuse across the cell membrane. Once the herbicide is in the higher pH environment inside the cell, the anionic form predominates and is trapped within the cell and the herbicide can then diffuse from cell to cell via the plasmodesmata. The absorption of these herbicides by roots is dependent on the pH of the external solution; as pH increases, absorption decreases. However, since more imazethapyr will exist in the neutral form than imazamox at physiological pH, imazethapyr is more readily absorbed and translocated than imazamox (Little et al. 1994). Hence, imazethapyr has greater soil activity than imazamox.

Adsorption to soil

Adsorption of imazethapyr and imazamox to soil affects the activity and persistence of these herbicides. The most important factors that determine how tightly these herbicides bind to soil are organic matter, pH and time (Ahmad et al. 2001). The amphoteric nature of the imidazolinones plays a dominant role in their binding to soil. The anionic form of both herbicides predominates from pH 6 to 9, and this form will be only weakly bound or will be repulsed by the negative charges of the soil colloids, resulting in low adsorption to neutral and high pH soils. As the pH of the soil decreases, the neutral and cationic forms of these herbicides increases and soil adsorption increases.

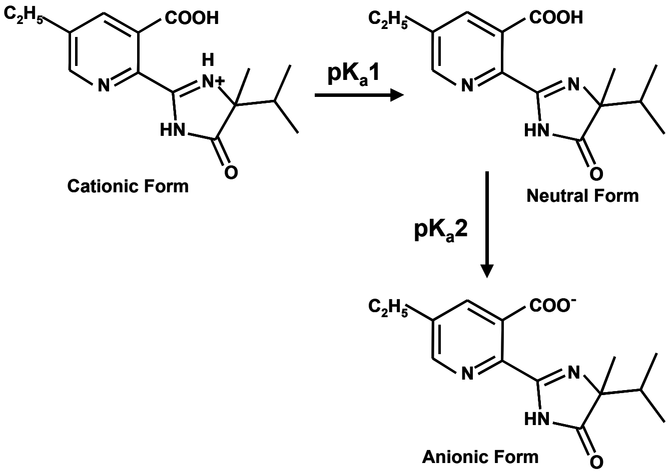

Figure 1: Ionic states of imazethapyr.

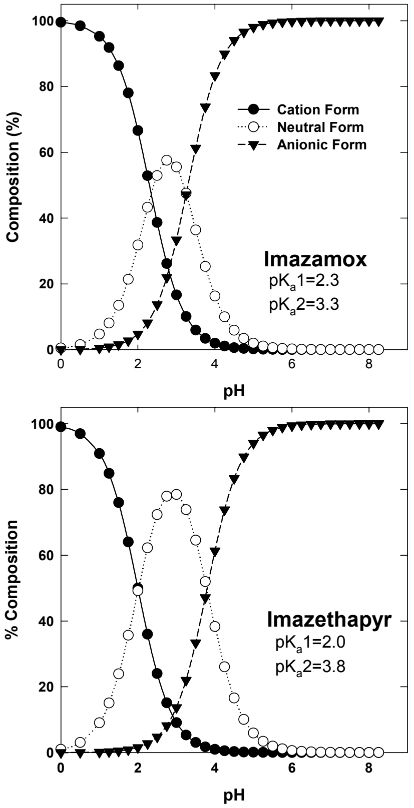

Figure 2: Effect of pH on the distribution of ionic states of imazethapyr and imazamox in solution.

Stougaard et al. (1990) found a complex interaction between soil texture and soil pH and the adsorption of imazethapyr (Table 1). At any given pH, more imazethapyr was bound to the soil as the amount of organic matter and clay increased. Within each soil, more imazethapyr was bound to the soil as pH decreased. Bresnahan et al. (2000, 2002) determined the effect of pH on the binding of imazethapyr and imazamox to a loam soil (Table 2). As pH decreased, adsorption of both herbicides increased. However, more imazethapyr was bound to the soil compared to imazamox.

The adsorption of imazethapyr and imazamox to soil is also dependent on time. The concentration of imazethapyr in the soil solution decreased with time, dropping more than 70% over 30 d in a sandy loam soil, pH 6.8 (Figure 3) (Johnson et al. 2000.) This increased adsorption affected the distribution of imazethapyr in soil columns if the herbicide was allowed to incubate in the top 2 cm of soil before water was applied (Figure 4). Bresnahan et al. (2000, 2002) also found that adsorption of imazethapyr and imazamox to soil increased with time, particularly at low pH.

Desorption of imazethapyr and imazamox from soil shows hysteresis. That is, less herbicide desorbs from the soil than would be predicted from sorption isotherms. It appears that desorption is also affected by soil pH. At pH <6 both imazamox and imazethapyr more readily desorbed than at pH >6 (Bresnahan et al. 2000, 2002). Bresnahan et al. (2000, 2002) speculated that the differences in desorption of these herbicides between low and high pH was due to differences in the binding mechanisms. At low pH, the cationic form of the imidazolinones will increase and this form can bind tightly, but reversibly, to the soil colloids. In high pH soil, less herbicide is initially bound, but once bound it is less able to desorb.

Table 1:Effect of soil texture and soil pH on adsorption of imazethapyr (Data adapted from Stougaard et al. 1990).

Soil Type	pH	Kf
Silty Clay Loam	**5**	**232.2**
(OM=2.5%)	**6**	**41.6**
	7	**12.5**
Silt Loam	**5**	**49.7**
(OM=1.5%)	**6**	**11.5**
	7	**7.3**
Sandy Loam	**5**	**12.5**
(OM=1.0%)	**6**	**2.8**
	7	**0.7**

Table 2: Effect of soil pH on adsorption of imazethapyr and imazamox to Ves loam (Data adapted from Bresnahan et al. 2000 & 2002).

Soil pH	**Kf Imazethapyr**	**Kf Imazamox**
5.4	**3.6**	**1.3**
5.7	**2.8**	**1.2**
6.2	**2.1**	**0.8**
7.7	**0.5**	**0.3**

Dissipation in the soil

The imidazolinones dissipate in soil through microbial degradation (Flint and Witt, 1997). The rate of degradation depends on the herbicide, temperature, moisture, soil texture and pH. Imazamox degrades more rapidly than imazethapyr. The half lives ($T_{1/2}$) of these herbicides under normal conditions ranges from 20-30 d and 45-90 d for imazamox and imazethapyr, respectively (Shaner, 2003).

Any factor that affects microbial activity, also affects the rate of dissipation of these imidazolinones. Flint and Witt (1997) found that $T_{1/2}$ for imazethapyr increased from 24 day to 53 d as the temperature decreased from 30C to 15C. Vischetti et al. (2002) reported that the $T_{1/2}$ for imazamox increased from approximately 20 d to 52 d as the temperature decreased from 25C to 10C. Soil moisture also affects the rate of degradation of these two herbicides. The $T_{1/2}$ for imazethapyr increased more than two fold if it was incubated in soil held at 15% field capacity (FC) versus 75% FC (Flint and Witt, 1997). Under average conditions in Canada imazethapyr and imazamox are applied when the soil temperature is between 15-25C from late May until September and there is an average of 250 mm of precipitation. These conditions are conducive to the microbial degradation of imidazolinones.

The rate of degradation is affected by soil texture. In general, these two herbicides are more persistent in heavy soil compared to light soils. Imazethapyr degraded more slowly in a silty clay loam ($T_{1/2}$=180 d), than a silt loam ($T_{1/2}$=60 d) under laboratory conditions. Cantwell et al. (1989) found that the rate of degradation of imazethapyr depends on the concentration of the herbicide in the soil solution. This would explain the differences in degradation in different soil types.

The effect of soil pH on degradation of imazethapyr and imazamox is not clear. Loux and Reese (1993) found that the persistence of imazethapyr increased as soil pH decreased in a silt loam soil, but in clay soil there was no relationship between pH and dissipation. Bresnahan et al. (2000, 2002) found that the rate of dissipation of both imazethapyr and imazamox was the same in a loam soil across a pH range of 5.4 to 7.7 although imazamox dissipated approximately 5 fold faster than imazethapyr.

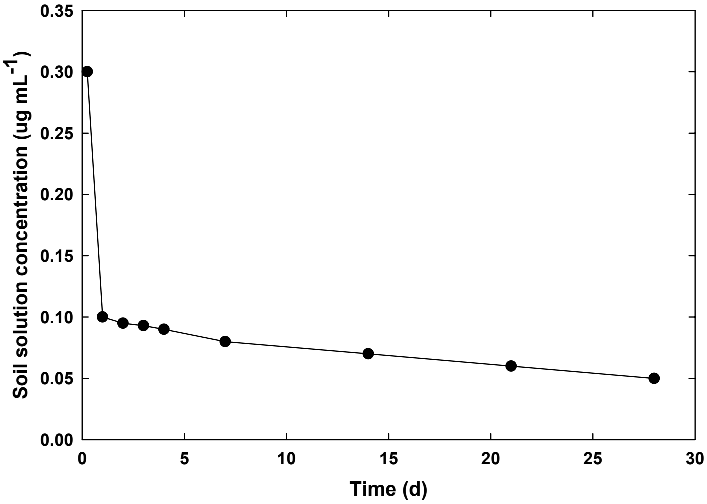

Figure 3: Effect of time on soil solution concentration of imazethapyr in a sandy loam soil, pH 6.8 (adapted from Johnson et al. 2000).

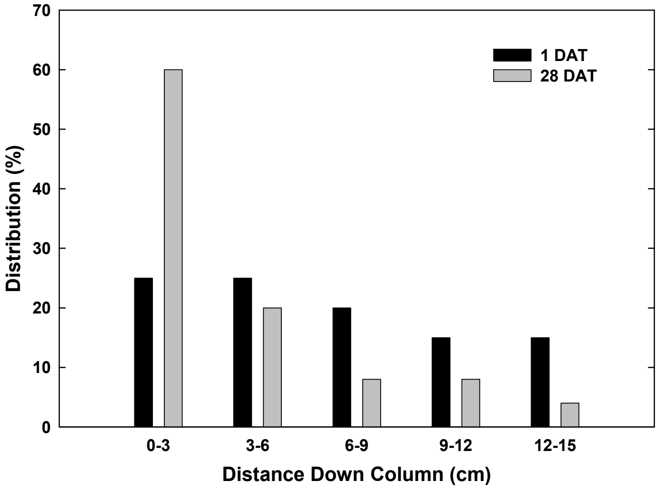

Figure 4: Effect of time on movement and distribution of imazethapyr in soil column. Soil was a sandy loam, pH 6.8. Herbicide was applied to top 2 cm of soil at field capacity and incubated for 1 or 28 d. 40 ml of water was applied over 24h to each column (adapted from Johnson et al. 2000).

Carryover to sensitive follow crops

The carryover of imazamox and imazethapyr to follow crops depends on the environmental conditions between time of application and time of planting of the follow crop, soil pH, and the sensitivity of the follow crop. Under normal conditions, both imazamox and imazethapyr will degrade sufficiently to allow the planting of most crops after a reasonable interval. However, some crops, such as sugar beets (*Beta vulgaris* L.) are extremely sensitive to these herbicides and injury can occur under adverse environmental conditions or low soil pH.

If there is insufficient precipitation between the time of application of the herbicide and time of planting of the follow crop, there may not be adequate degradation of the herbicide in the soil to prevent injury to sensitive follow crops, as described above. If precipitation is insufficient to produce a crop, it will be insufficient to allow microbial degradation of the imidazolinones. Persistence of abnormally low temperatures could also slow down the degradation of these herbicides and increase the opportunity for injury to a sensitive follow crop.

Soil pH can affect the response of crops such as sugar beet and canola (*Brassica napus* L.) to both imazethapyr and imazamox (Corbucci et al. 1998). Bresnahan et al. (2000, 2002) found that the response of sugar beets and canola to the same soil residue levels of imazethapyr and imazamox was greater when the soils had $pH<6$ than at $pH>6$. They suggested that the herbicide becomes more bioavailable as pH decreases. However, others have found that the soil activity of imazethapyr decreases as soil pH decreases due to greater binding. In the case of carryover, there may be an interaction between the response of the crop to soil pH and the stress induced by the herbicide. Sugar beets do not grow well in low pH soils, even in the absence of herbicide. If these stressed plants are then exposed to low rates of herbicide residue, the combination of the two factors could cause greater injury than either one alone.

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The science of DuPont's soil residual herbicides in Canada

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Sulfonylurea herbicides are characterized by their low use rates, and their proper use according to label recommendations results in low risk to the environment. Their ionization to anionic and nonionic forms affects their adsorption to soil and degradation through aqueous hydrolysis. Field studies often show that sulfonylureas do not readily leach under normal agronomic conditions. Many sulfonylureas degrade in soils through multiple mechanisms, which are affected by pH, soil temperature, and soil moisture. Each sulfonylurea herbicide degrades at different rates in soils and this is affected differently in each field situation, thus generalizations cannot be made over the entire class. Certain rotational crops can be injured by low concentrations of sulfonylurea herbicides, but with a good understanding of the dynamics of degradation mechanisms, soil properties, climate and plant response, proper recommendations for replanting can be made.

Additional Keywords: degradation, leaching, recropping, soil behaviour, soil adsorption

Introduction

Sulfonylurea herbicides were discovered by George Leavitt of DuPont in 1975 and the first product, Glean® (chlorsulfuron), was commercialized for cereal crops nearly twenty-five years ago in 1980 (1982 in Canada). DuPont has commercialized worldwide a total of 13 sulfonylurea herbicides which have an unprecedented range of utility in crops including cereals, canola (*Brassica napus* L), sugar beet (*Beta vulgaris* L.), maize (*Zea mays* L.), soybeans (*Glycine max* L. Merrill), and rice (*Oryza sativa* L.). DuPont began an active research program to understand the effects of these sulfonylurea herbicides on different rotational crops in order to provide information to growers making replanting decisions. This research program lead to the development of shorter residual sulfonylurea herbicides, which offer the grower a broad range of residual attributes in crops such as cereals.

Soil residual leads to the maintenance of weed control over an extended period, enabling crops to maximize yield in response to decreased weed competition. However, when a soil-active herbicide persists at phytotoxicologically active concentrations which can affect a sensitive crop beyond the growing season for the target crop, it can result in rotational crop damage. It also can contribute to the selection of resistant weed species, particularly when applied without mixture partners of other modes of action with similar persistence . As with all soil residual herbicides, management of weed resistance and rotational crops are important factors when considering their intended future uses in crops.

The main factors which affect the potential of any herbicide to injure rotational crops are the use rate, sensitivity of the rotational crop to soil residues and the degradation rate in the particular soil to which it has been applied. This paper will briefly review some of the important aspects of the science of DuPont's soil residual herbicides in Canada.

Chemical properties affecting soil residual behaviour

Sulfonylurea herbicides are weak acids which can lose a proton from an amino group located on the sulfonylurea bridge to form the negatively charged (anionic) species. The negatively charged species is more water soluble than the neutral species and is less susceptible to aqueous hydrolysis. The proportion of molecules in either the anionic or neutral form is controlled by the pH of the soil solution and the pK_a of the particular herbicide. Because the pK_a values of sulfonylurea herbicides range between 3 and 5, most remain in the negatively charged form in Canadian soils. This results in generally greater soil sorption of sulfonylurea herbicides at lower soil pH (acidic conditions).

Removal processes affecting soil residual behaviour

Removal processes that can affect the soil residual behaviour of herbicides include volatilization, plant uptake, adsorption and desorption and leaching.

Volatilization

The vapour pressure of sulfonylurea herbicides are typically less than 1×10^{-8} Pa (Figure 1), and can range to below 10^{-12} Pa (Schmuckler et al. 2000). Thus, sulfonylurea herbicides do not volatilize and volatility is a removal process which does not contribute to losses in the field.

Adsorption and desorption

Laboratory studies show that sulfonylureas do not strongly adsorb to soil constituents. Results from batch-equilibrium studies in which a slurry of soil and an aqueous herbicide solution (usually 1:1 solution:soil ratio or higher) are shaken for generally 6-24 h show that the K_{OC} values (soil adsorption coefficient, K_d, normalized for soil organic content) are low, generally < 100 (Figure 2), which is interpreted to indicate that they are very mobile in soils and thus leach readily.

Other herbicides, particularly phenoxy acids like 2,4-D or moderately water soluble compounds like acetanilides, are in the same general range of mobility classification. Sulfonylurea soil mobility depends partly on soil organic matter (OM) content, with higher OM levels resulting in stronger sorption. Sorption by sulfonylureas to soil is stronger at lower soil pH levels due to the stronger sorption by neutral species and the reduction in negatively charged sites on soil constituents.

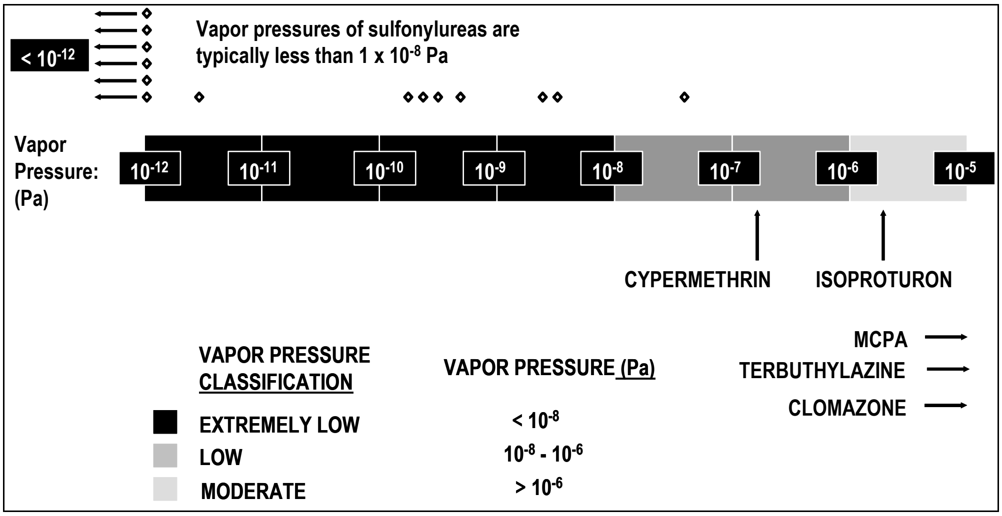

Figure 1. Perspective on the vapour pressure of sulfonylurea herbicides (source of data USDA 2004).

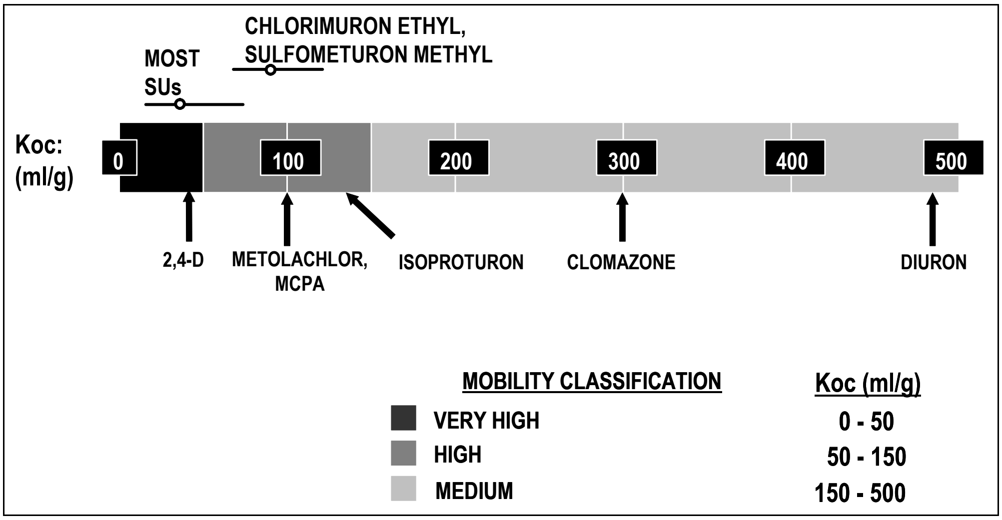

Figure 2. Perspective on the soil mobility classification of sulfonylurea herbicides (source of data USDA 2004).

At DuPont we have developed a different type of test to measure sorption under field-moist conditions using incubation under static conditions and centrifugation to extract soil water. This technique does not destroy secondary soil structure and allows for measurement of adsorption under more realistic soil moisture conditions. The results have shown an increase in adsorption with lower water content as compared with the batch-equilibrium method (Figure 3). The adsorption coefficient (K_d) of chlorsulfuron to a clay loam soil (pH 8.0, 1.2% OC, 36% clay), increased from 0.33 at solution:soil ratio of 1:2 (result identical to that measured using 1:1 batch equilibrium technique) to 0.68 at a 1:4 solution:soil ratio, representing a 2-fold increase in adsorption. The soil moisture content at the 1:4 solution:soil ratio is equivalent to 0.1 bar, or field capacity. Under unsaturated conditions, the soil solution becomes more concentrated resulting in a decrease in the effective pH near soil constituent surfaces (diffuse double-layer). This results in more chlorsulfuron being in the neutral state or in the formation of neutral species formed from positive cations complexing with negatively charged species which can adsorb more strongly to soil constituents. The decrease in effective pH can also result in a decrease in negative charges on soil constituent surfaces, which do not repel negatively charged species as strongly.

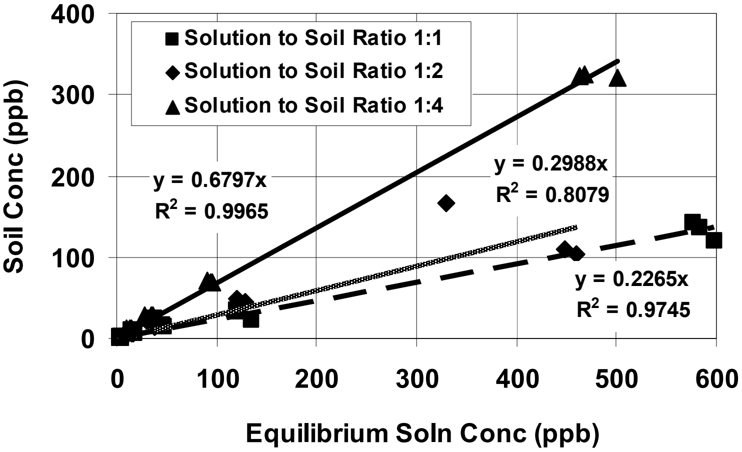

Figure 3. Adsorption of chlorsulfuron to soil at various soil moisture contents (source Strek et al. 2004).

It has been shown that adsorption of sulfonylureas can increase over time. Using the field-moist sorption technique based upon centrifugation, the chlorsulfuron K_d at the 1:2 solution:soil ratio increased from 0.33 to 0.63 over 22 days, while over 7 days the K_d at the 1:4 solution:soil ratio increased from 0.68 to 1.82, representing a 3-fold increase (Figure 4). The increase in adsorption over time is partly the reason that leaching under field conditions consistently shows a different type of behaviour than predicted by laboratory studies. Field studies have generally shown that most of the sulfonylurea herbicide applied to a field soil remains in the upper 15-50 cm over time. For example, in a field study conducted in Idaho on a silt loam soil of pH 6.1-6.7 and an OM content of 1.3-2.2% and with 25-29% clay (Strek 1998), total radioactivity applied as C^{14}-chlorsulfuron, which represents the active ingredient and degradation products, generally remained in the upper 20 cm (Figure 5). When the total radioactivity was characterized, chlorsulfuron was only found in the upper 10 cm.

Leaching under field conditions depends on the inherent adsorption potential of the particular sulfonylurea, its rate of breakdown (faster breakdown results in less compound to move in soil), its pK_a (higher pK_a results in stronger soil sorption at a particular pH), the soil pH (lower pH results in stronger soil sorption), and soil texture (sandier soil results in more leaching). Although in regions which receive precipitation (including supplemental irrigation) predominantly in summer it is logical to assume that leaching will mainly occur when most of the rains occur. However, summer is also the time when the soil is warm and microbes are most active degrading the compound, plants are growing and are taking up the compound into the roots along with the water they transpire, and more water is lost through evaporation. Therefore what affects leaching potential is not only the total precipitation but the water balance, or recharge, which are water inputs minus water lost. Although it has been shown that sulfonylureas can move upward through capillary action, the effective depth from which this occurs is relatively near the soil surface. Another factor to consider is the freezing of soil, which stops all movement of water and thus the movement of any compound.

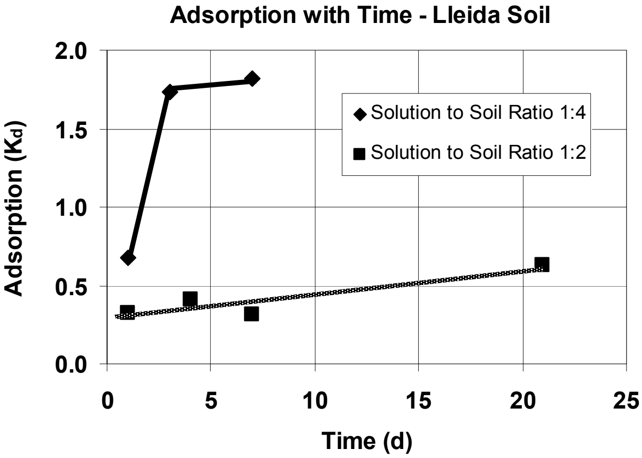

Figure 4. Adsorption of chlorsulfuron to soil over time at different soil moisture contents (source Strek et al. 2004).

Surface water and groundwater monitoring studies have shown very few detections of sulfonylureas. When observed, they have been found at very low concentrations (<1 ppb).

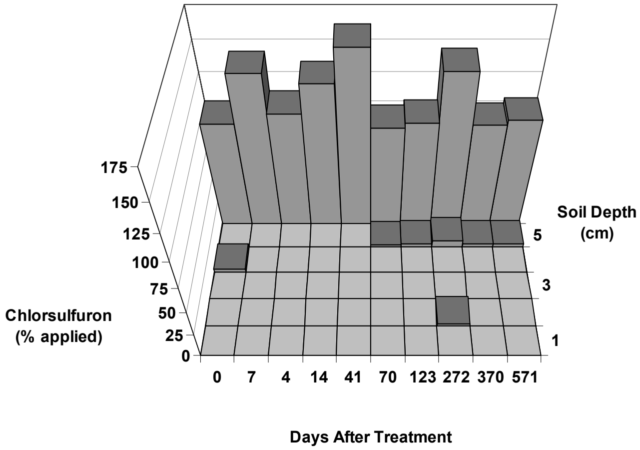

Figure 5. Distribution of total radioactivity (phenyl label) in a field trial conducted in Moscow, Idaho (source Strek 1998).

Degradation processes affecting soil residual behaviour

The major mechanisms of sulfonylurea degradation in soils are aqueous hydrolysis and microbial degradation; indirect photolysis is a minor mechanism. The rate of degradation is dependent upon soil temperature, pH and soil moisture. Because aqueous hydrolysis is a chemical process, the rate increases linearly with temperature and essentially ceases at 0°C. Because microbial degradation is a biological process, the rate generally increases to an optimum level (generally at 30 to 35°C), above which it decreases rapidly because of the negative effects of high temperature on the microbes themselves.

For example, laboratory studies in aqueous buffered solutions with tribenuron methyl show that the DT_{50} (time required for degradation of 50% of the compound) in solutions (at 25° C) of pH 5 is 0.2 days, in solutions of pH 7 is approximately 13 days, and in solutions of pH 9 is much longer (Figure 6). Although many sulfonylureas show the greatest stability in alkaline solutions, others respond differently. For example, metsulfuron methyl shows an increase in DT_{50} (corresponding to a decrease in degradation rate) as the pH increases from acidic to neutrality (pH 7), and then show a decrease in DT_{50} (increase in degradation rate) thereafter as the pH increases from neutrality to alkaline (Figure 6). For flupyrsulfuron the DT_{50} decreases from pH 5 to 9 and it is most stable in acidic solutions. Rimsulfuron DT_{50} values change relatively little in response to pH. Thus the change in chemical hydrolysis rate with a change in pH is different for different sulfonylureas. The range in DT_{50} values also indicates a large degree of variability in the hydrolysis rates between different sulfonylureas. The maximum DT_{50} value for the compounds presented for the pH at which they were most stable ranged from approximately 1500 days (highly extrapolated value) to <10 days. When discussing the rate of sulfonylurea aqueous hydrolysis, it is important to avoid generalizations.

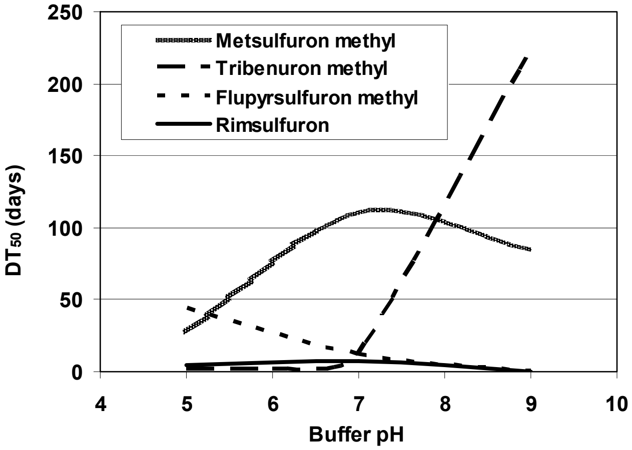

Figure 6. Aqueous hydrolysis DT_{50} values at different solution pH for selected sulfonylureas (source USDA 2004).

Both aqueous hydrolysis and microbial degradation contribute to the degradation of sulfonylureas in laboratory soil degradation studies conducted in the dark. In studies conducted with chlorsulfuron on a variety of soil types, the soil pH exerted a significant effect on the degradation rate (Beyer et al. 1987, Fredrickson and Shea 1986, James et al. 1999, Joshi et al. 1985, Marucchini et al. 1991, Ravelli et al. 1997, Sarmah et al. 1999, Strek 1998, Thirunarayanan et al. 1985, Walker and Brown 1983). Chlorsulfuron showed an overall slower rate (higher DT_{50}) at alkaline soil pH levels (Figure 7). A higher degree of variability in DT_{50} values is generally observed in alkaline soils. Since the rate of aqueous hydrolysis is slower in alkaline solutions, microbial degradation is relatively more important in alkaline soils. Because microbial degradation is a biological process, it is inherently more variable than aqueous hydrolysis, a chemical degradation process. This type of behaviour cannot, however, be applied uniformly to all sulfonylureas. Rimsulfuron, for example, shows relatively little change in degradation rate over a wide range in soil pH (data not shown).

The complex network of factors operative in field studies may result in very different results than those observed in controlled laboratory experiments. The dynamics of soil drying and rewetting, temperature fluctuations and the presence of light are but a few factors present in field soils that are absent in laboratory experiments and which can contribute to the faster degradation generally observed in field soils. Sulfonylureas exhibit a relatively wide range of degradation rates in field studies, with DT_{50} values ranging from days to weeks (Figure 8). The degradation rates of most sulfonylureas (as determined by DT_{50} values) can be considered to be relatively rapid to moderate.

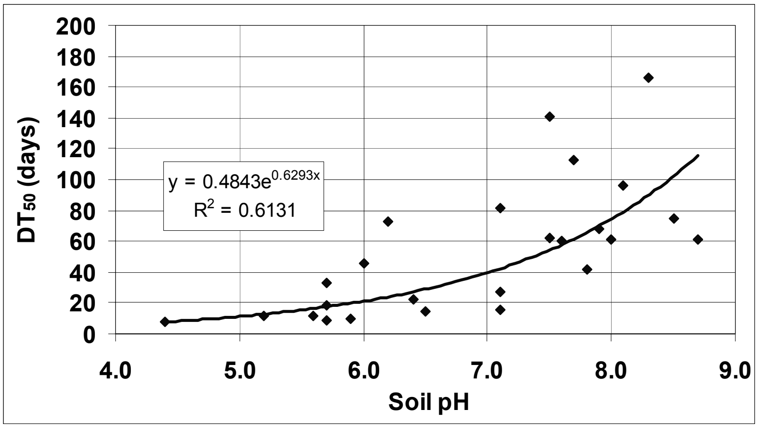

Figure 7. Soil degradation rate for chlorsulfuron in response to soil pH. Values are corrected to 20°C and to PF2 moisture.

Factors which influence microbial degradation of sulfonylureas in field soils include temperature, moisture, depth and microbial viability. Soil temperature varies daily and seasonally and is generally higher near the soil surface during spring, summer and autumn. Soil moisture can inhibit sulfonylurea microbial degradation when the soil is very dry or saturated. The soil depth is important because microbial populations and activity decrease significantly below the plow layer. Thus microbial degradation is generally faster nearer to the soil-air interface, but it is inherently more variable near the soil surface because microbes are susceptible to extremes in soil moisture and temperature. Since the aqueous hydrolysis rate responds to soil pH and temperature, the rate of degradation by this mechanism can also vary with depth as these parameters change.

Indirect photolysis can occur at the soil surface where light energy drives the formation of free radicals or super oxides which can attack a molecule and degrade it. This degradation mechanism can play a minor role in sulfonylurea degradation in field soils. Field studies with chlorsulfuron have shown the presence of a particular degradation product is only found in soil studies in which the soil has been exposed to light. This product attributed to indirect photolysis is not found in very high concentrations, thus it is not believed to be a major degradation pathway. However, over time it could contribute significantly to overall degradation particularly in alkaline soils located in arid climates where microbial degradation may be limited by a lack of soil moisture and aqueous hydrolysis may be limited by the high pH.

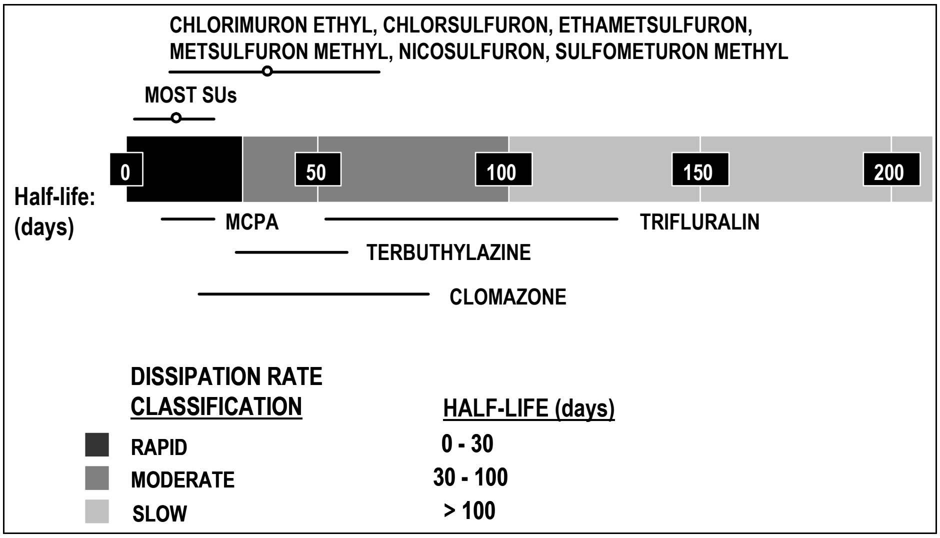

Figure 8. Perspective on the field soil degradation rates of sulfonylurea herbicides (source of data USDA 2004).

The effect of drought on the degradation of sulfonylureas depends on the relative importance of microbial degradation versus aqueous hydrolysis, on soil parameters and on the particular sulfonylurea. Under conditions where soil temperatures and moisture are adequate for normal plant growth, the relative importance of each degradation mechanism may be theoretically allocated as in Figure 9, where microbial degradation is major, hydrolysis is secondary and indirect photolysis is minor. Under drought conditions, degradation attributed to soil microbes becomes much smaller due to negative effects on the microbes. This causes a decrease in the overall rate of degradation for those compounds which degrade only through microbial activity. During drought, the soil temperature generally increases to considerably deeper soil depths than under normal conditions, resulting in faster aqueous hydrolysis. Additionally, as the soil water decreases to levels which negatively affect plant growth, enough moisture remains for aqueous hydrolysis to continue. The loss of moisture results in an increase in the concentrations of the remaining ions and substances in the soil water. Since pH is a measure of the concentration of hydrogen ions, as the soil water decreases and the electrolytes are not physically displaced, the pH near the soil constituent surfaces effectively decreases, sometimes as much as 1 to 2 units below that typically measured in 1:1 soil:water slurries. This can result in an increased rate of hydrolysis which may compensate partially or entirely for the loss in microbial degradation. Additionally, during drought cloud cover tends to be much less than during normal climatic conditions, resulting in more light energy hitting the soil surface. Coupled with an increase in soil temperature, this can lead to an increase in degradation through indirect photolysis. The overall effect may be no significant decrease, or only a slight decrease (or even an increase), in sulfonylurea degradation rate under drought conditions when compared to normal conditions. However, plants under drought stress may exhibit more severe phytotoxicity symptoms from the same level of herbicide soil residues due to the addition of multiple stress factors than they would under normal conditions.

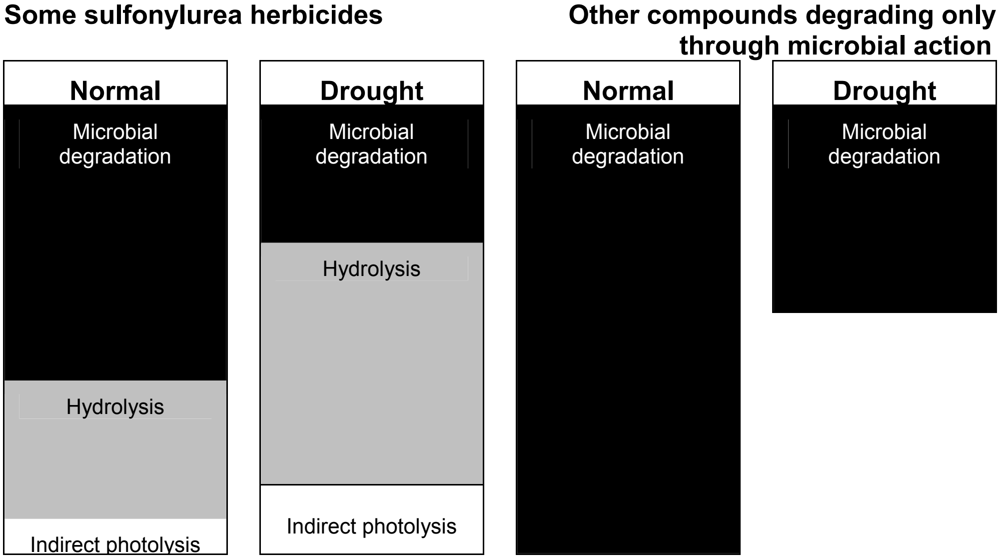

Figure 9. Theoretical relative allocation of degradation mechanisms for certain sulfonylureas under drought and normal conditions.

Susceptible plant response to soil residues

Sulfonylureas belong to the class of herbicides which inhibit the enzyme acetolactate synthase, responsible for the production of key amino acids valine, leucine and isoleucine. Susceptible plants generally respond to phytotoxic levels of soil residues by ceasing growth, and at high soil concentrations, by dying. When describing phytotoxic symptoms of sulfonylureas it is common to include reddening or yellowing and perhaps malformations of leaves, particularly actively growing ones. Many other factors can cause the expression of such symptoms. However, root pruning damage from sulfonylureas, particularly lateral roots, is often overlooked because plants must be dug out of the soil and the roots must be washed soil-free. Injury to recropped species in the field does not often show a uniform distribution and generally occurs in patches. Because soil properties which affect degradation and bioavailability vary in three dimensions across a field, this results in different soil concentrations with depth across a field (spatial variability). Areas which appear relatively unaffected can be found beside areas which show severe injury even though the field was applied uniformly with a herbicide.

Plant response to sulfonylurea soil residues is often described mathematically using a logistic curve (Figure 10), in which an initially slow increase in injury level with herbicide rate is followed by a relatively steep response that is followed by a relatively slow increase in injury level at high relative levels of injury. The GR_{50} (rate resulting in 50% growth reduction) is the preferred parameter to use to classify the sensitivity of crops because the prediction interval is at its narrowest in the midpoint of a line. The GR_{25} and GR_{10} are generally acknowledged to be the rates at which a herbicide causes no significant long-term injury and without significant visible injury, respectively.

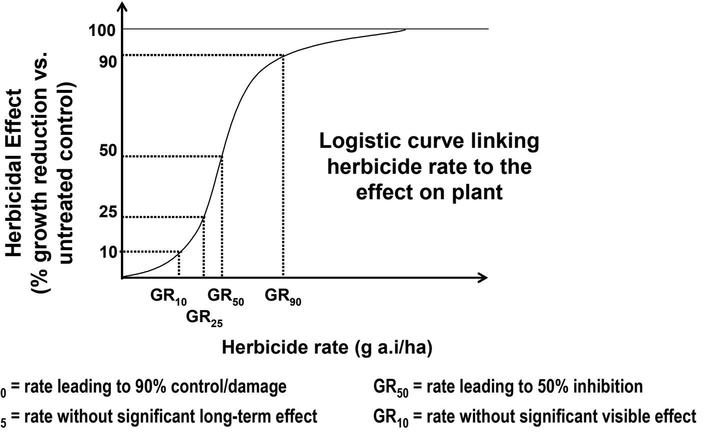

Figure 10. Generalized plant response of sulfonylurea herbicides as described by a logistic curve (source P. Favier 2004).

Figure 11 shows a degradation curve for a sulfonylurea which is biphasic under certain conditions and which depends on the particular sulfonylurea, soil and climate. Degradation can initially be rapid and then can become slower, with the last few percent (seen in the insert) requiring longer to degrade. One of the major reasons for this type of behaviour is that over the course of a year (in areas with temperate climates) winter will cause a slowdown in degradation due to a decrease in soil temperature. Another reason is that sulfonylurea adsorption and diffusion into micropores increases over time resulting in increased adsorption, and consequently, decreased bioavailability to microbes that can degrade the compound. This type of degradation behaviour is not unique to sulfonylureas; it is observed for many other compounds if we look at low enough concentrations in the soil. What makes sulfonylureas and other ALS-inhibiting herbicides unique is that relatively few herbicides have plant injury thresholds at such relatively low percentages of their initial soil concentration (following application). This is one of the properties that make sulfonylurea herbicides such effective and valuable herbicides. Using a hypothetical example we can see that a sulfonylurea which can cause injury in a particular soil at concentrations as low as 0.1 ppb to a highly sensitive crop (see Obrigawitch et al., 1998), when applied at 15 g ai ha^{-1} to a soil of bulk density of 1.5 g cm^{-3} and evenly distributed to a depth of 5 cm, it results in a concentration of 20 ppb. Thus, to allow the highly sensitive crop to grow safely in this soil, 99.5% of the sulfonylurea must be degraded. A convenient parameter with which to classify the tolerance level of rotational crops is to use the number of half-lives required for safe replanting, in which the original concentration is halved until it is at or below the injury threshold level (Figure 12). Using the example above, application at 15 g ai/ha would require 8 half-lives (99.6% degradation) to allow safe replanting at or below 0.1 ppb. Crops requiring 7-9 half-lives of degradation are typically considered to be highly sensitive in rotations. An important point to note is that sulfonylureas degradation products are generally non-herbicidal and thus once degraded a sulfonylurea will not cause injury to plants.

Recropping work in Canada

It is important to have analytical methods with detection limits that are below the threshold of biological activity. Partly because sulfonylureas can be phytotoxic to certain sensitive plants in soils at such relatively low concentrations, DuPont has been in the forefront of developing more sensitive but very specific analytical methods. Studies have shown that some sulfonylureas can affect crop yield and quality down to 1.0 to 0.1 ppb soil concentration. Each sulfonylurea is unique and the biological threshold concentration depends upon the particular sulfonylurea, soil properties, crop species and climate. The use of liquid chromatography coupled with tandem mass spectrometry with quantification limits in soils down to 0.05 ppb have been developed, providing another tool for developing and making rotational crop recommendations.

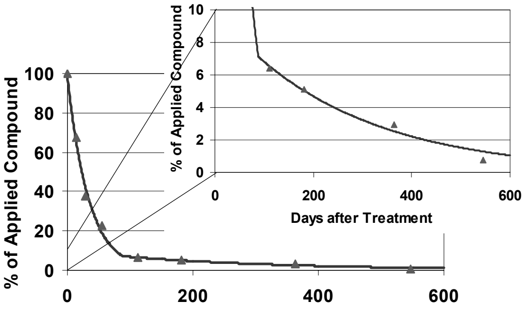

Figure 11. Biphasic degradation curve of a sulfonylurea herbicide in soil.

Setting proper rotational intervals for crops requires rigorous and well-designed field testing. Crop rotation intervals are based on a minimum of a 2-fold safety factor, and since spray overlaps are not that uncommon in field practice, this is a sound basis for the establishment of recommendations. DuPont has conducted nearly 500 field tests in Canada from 1980 to 2003, with over 40 conducted yearly from the period of 1985 to 1989 (Huston, 2003). Safe recropping intervals have thus been established for chlorsulfuron, metsulfuron methyl, ethametsulfuron methyl, chlorimuron, nicosulfuron, and products containing thifensulfuron methyl and tribenuron methyl, the short-residual sulfonylurea herbicides.

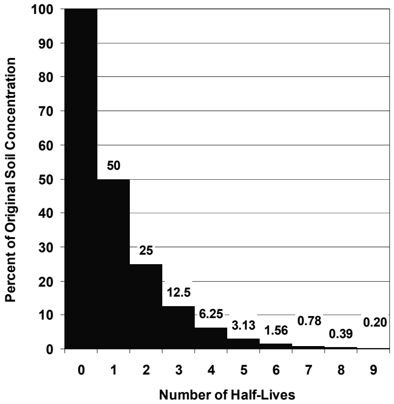

Figure 12. Relationship of the number of half-lives to soil concentration.

Summary

Sulfonylurea herbicides are characterized by their low use rates, and their proper use according to label recommendations results in low risk to the environment. Their ionization to anionic and nonionic forms, which is controlled by pH, affects their adsorption to soil and degradation through aqueous hydrolysis. Sulfonylurea herbicides do not readily volatilize, thus this mechanism is not responsible for losses in field soils. Many sulfonylureas degrade through multiple mechanisms. Sulfonylurea herbicides degrade in soils mainly through aqueous hydrolysis and microbial degradation. Indirect photolysis is believed to be a minor degradation mechanism for some sulfonylureas. Degradation in soils is dependent upon pH, soil temperature, and soil moisture. A wide range in DT_{50} values, from days to weeks, has been observed for sulfonylureas, thus the generalization that all sulfonylurea herbicides are soil persistent is not accurate. Each sulfonylurea herbicide has unique properties which determine the degradation rate in each field situation. Drought conditions do not necessarily result in higher soil residues given a decrease of microbial degradation because aqueous hydrolysis (and to a limited extent indirect photolysis) can increase under the same conditions. Thus, soil residues combined with plant response to multiple stresses during drought may result in more severe, similar or less severe symptoms than observed under more normal climatic conditions. Certain rotational crops can be injured by low concentrations of sulfonylurea herbicides, but with a good understanding of the dynamics of degradation mechanisms, soil properties, climate and plant response, proper recommendations for replanting can be made.

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The effect of landscape position on residual herbicide activity in Prairie soils

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The topographic position in the field (depression, knoll) can significantly influence the residual behavior of herbicides. Of particular interest are those compounds in the Group 2 category, for which rotational cropping choices may be restricted due to persistence of the compound beyond the year of application. Higher organic matter and clay contents typical of lower slope positions and depressions favour herbicide sorption and reduced phytotoxicity while high pH, low organic matter and drier soil conditions common on eroded knolls contribute to increased phytotoxicity and persistence of herbicides such as imazethapyr and flucarbazone. The landscape effects should be taken into consideration when making recropping decisions, especially when choices can be made about crops to seed in different landscape positions. Soil sampling for bioassay purposes may be best accomplished by sampling the different landscape positions separately, so as to allow for assessment of injury potential according to landscape position.

Additional Keywords: landscape effects, topography, herbicide phytotoxicity, herbicide persistence, soil residual activity, recropping injury

Introduction

Herbicides that persist in the soil months or years following application are of potential environmental and agronomic concern. Cropping options may be restricted in the years following application due to injury risk from carryover of the compound in soil. The potential for carryover injury is determined by a herbicide's persistence in the soil, the bioavailability of the herbicide, and susceptibility of the rotational crop to damage (Hartzler et al. 1989). Alternatively, depending on the rotational crop grown, some residual effect in the year following application may be desirable in providing a degree of weed control in the second year. Herbicides that have residual properties and that may be of concern in Western Canada include compounds from a number of different Groups (Guide to Crop Protection, 2005, Saskatchewan). Because of the high plant toxicity of Group 2 herbicides (acetolactate synthase inhibiting herbicides) at low concentrations in the soil, the residual activity of Group 2 herbicides is of special interest.

Knowledge of how soil properties affect the phytotoxicity and persistence of herbicides in the soil environment is important in making sound recropping decisions within farm field landscapes as well as in entire farm fields. In the undulating topography common throughout the Canadian prairies, depressions that remain wet until later in the spring are often seeded later, and sometimes to a different crop than the rest of the field. Managing different landscape positions in the field effectively requires an understanding of how residual soil herbicides behave in the different slope positions. To a large extent, the observed differences in herbicide activity in different landscape positions are explained by variations in soil properties. Greater organic matter and clay content and higher soil moisture are factors contributing to the reduced phytotoxicity of many herbicides in lower slope positions of prairie landscapes. In particular, the impact of soil organic matter on reducing herbicide bioavailability through sorption processes has been identified as important. The objective of this paper is to review the effect of soil properties and environmental conditions on soil residual herbicide activity, with emphasis on observed impacts of landscape position on the phytotoxicity and persistence of Group 2 herbicides.

The nature of soils in Prairie landscapes

Agricultural landscapes on the Canadian Prairies are a product of glacial activity that ended about twelve thousand years ago. The melting ice deposited parent materials that created unique landscape patterns, depending on the nature of the glacial retreat. These landscape patterns include regions of undulating topography in which the calcareous parent material is comprised of unsorted sand, silt and clay sized particles (glacial till), as well as other more level regions derived from lacustrine materials of typically high clay content formed from the settling of ancient glacial lakes. Areas of rapid outwash by glacial melt water produced sandy parent materials derived from fast moving water.

Much of the Canadian prairie landscape is dominated by undulating topography containing lime-rich glacial till parent material upon which the soils we see today were formed. The soils in these landscapes are largely the product of varying moisture content across the landscape (Pennock et al. 1987). Soil properties like moisture content, organic matter, texture and pH tend to vary with landscape position in a relatively predictable manner (Malo et al. 1974). Upslope, convex regions of the prairie landscape (knolls) are usually characterized by low soil moisture content, lower organic matter, sandier texture and higher pH due to water runoff and erosion. Lower slope, concave regions of the landscape (depressions) are where runoff water accumulates, and are more moist, have higher organic matter and clay contents, greater topsoil depth and lower pH due to greater weathering. Since cultivation, accelerated water, wind and tillage erosion have further contributed to variability in key soil properties across prairie landscapes (Moulin et al. 1994).

Soil properties and herbicide phytotoxicity and persistence

Soil properties have a major influence on the activity of herbicides in the soil, because they affect sorption to soil constituents and the rate of herbicide degradation (Pool and Villiers 1993). Important soil properties in this regard include pH, texture, organic matter and microbial activity as influenced by environmental factors such as temperature and moisture.

Soil pH

The stability of some herbicides is pH dependent and acidic soils may enhance the degradation of the phytotoxic portion of some herbicide molecules (Joshi et al. 1985). For example, sulfonylurea herbicides are reported to be increasingly persistent with increasing soil pH (Beckie and McKercher 1989). The phytotoxicity of imidazolinones was noted to increase as soil pH increases (Jourdan et al. 1998). However, relationships between soil pH and herbicide phytotoxicity and persistence can be complex. Herbicides that exist in soil solution in an anionic form will tend to be more strongly adsorbed at lower pH with potentially less availability to plants. However, lower pH can also increase the number of uncharged herbicide molecules which may increase plant availability due to increased lipophilicity and root affinity for the compound (Stougaard et al. 1990).

Texture

The clay - sized fraction of the soil exhibits colloidal properties and a reactive surface due to high surface area and a net negative charge. Herbicides tend to adsorb to clay surfaces, particularly those compounds with a high density of charged functional groups This sorption can reduce phytotoxicity (Eliason et al. 2004) but also increase persistence as the sorption reduces accessibility of the herbicide to microbial degradation (Walker 1991). The texture of the soil through its impact on soil moisture storage and drainage can also affect persistence, as sandier textured soils have lower water holding capacities and tend to be droughtier and have lower microbial activity than soils with high clay content.

Organic matter

Organic matter has been identified as a key property controlling herbicide phytotoxicity and persistence in soil (El Azzouzi et al. 1998; Eliason et al. 2004). Like clay, soil organic matter in the form of humus is colloidal in nature with a highly reactive surface containing many functional groups capable of binding with herbicide molecules. Sulfonylureas and imidazolinones have shown increased sorption in soils with high organic matter (Szmigielska et al. 1998; Morrica et al. 2000). Increased herbicide sorption with increasing soil organic matter content has been used to explain reduced phytotoxicity of flucarbazone in prairie soils of high organic matter content. Organic matter is also positively correlated with microbial activity and therefore greater microbial degradation. However, increased sorption of the herbicide to organic matter can also reduce herbicide availability to microbial processes, increasing the persistence of the compound (Walker 1991). For some herbicides, such as trifluralin, organic matter was found to have little effect on persistence (Gerwing and McKercher 1992).

Environmental conditions: Temperature and moisture

Microbial decomposition is an important mode of degradation for many herbicides. It is not therefore, surprising that temperature and moisture exert a significant influence on the persistence of many herbicides in soil via their effect on microbial activity. Degradation of sulfonylurea herbicides was reported to show a linear response to increasing temperature, with higher temperature resulting in increased dissipation rates (Beckie and McKercher 1989), and low temperatures have been linked to slower degradation rates for many herbicides (Gaynor 1985). Decreased soil moisture was shown to increase persistence of flucarbazone as a result of reduced microbial activity (Eliason 2003). As moisture content decreased from 85% of field capacity to 50% of field capacity in a Dark Brown Chernozem (Asquith association) soil, the half-life of flucarbazone was found to be 50% longer. It was reported that the bioavailability of imazethapyr is higher under low moisture conditions compared to moderately high soil moisture conditions, but as soil moisture approaches field capacity, bioavailability may increase again under low soil pH conditions (Jourdan et al. 1998).

Examples of landscape controls on herbicide activity

The higher soil organic matter, clay and moisture contents that are generally found in lower slope positions of prairie landscapes have been used to explain reduced phytotoxicity and lower crop injury from residual herbicides in these landscape positions as compared to upslope regions. The damage potential from herbicide residues is recognized as being particularly high on eroded knolls due to low soil moisture content, low organic matter, sandy texture and high pH. A laboratory study with metsulfuron applied to soils collected from three different slope positions (upper, mid and lower) from a landscape in southern Saskatchewan showed that a higher proportion of herbicide was removed as exchangeable ions from the upper slope soil compared to the mid and lower slope soils (Szmigielska et al. 1998). In this study, anion exchange membranes were used as a rudimentary plant root surface simulator to adsorb the exchangeable fraction. Inhibition of lentil root growth followed a similar trend with greatest inhibition in the upslope soil and least in the lower slope soil (Figure 1).

Reduced phytotoxicity of metsulfuron in the lower slope positions was explained by three fold higher soil organic carbon concentrations and a slightly lower soil pH compared to the upslope soil.

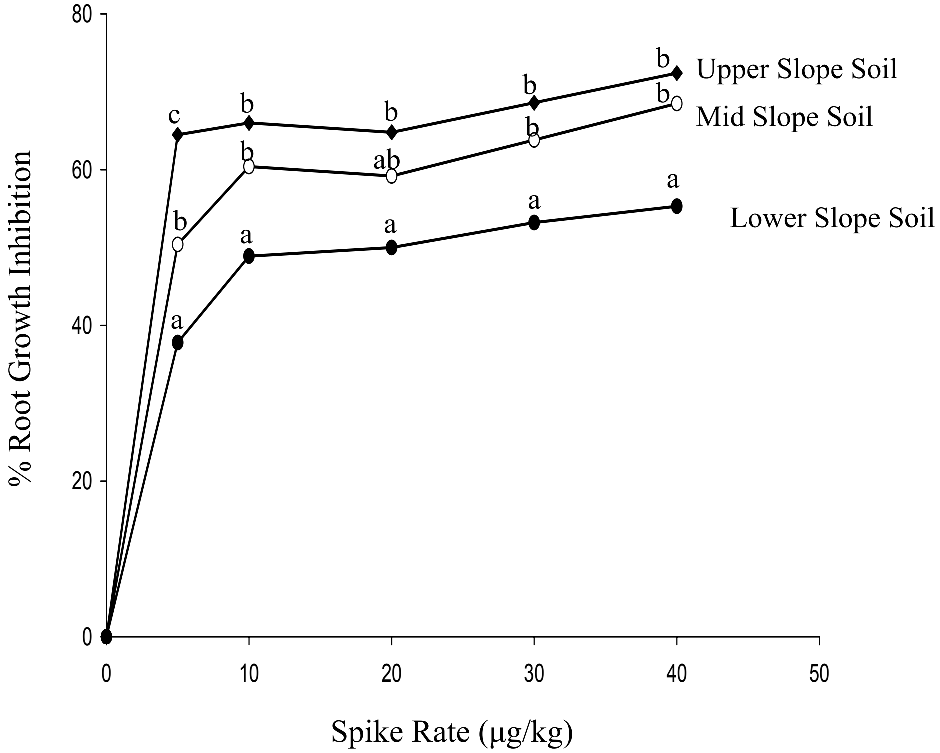

Figure 1. Lentil root response to varying metsulfuron concentration, in soils from three landscape positions in southern Saskatchewan (Szmigielska et al. 1998).

Imazethapyr was reported to follow a similar trend to metsulfuron with respect to the effect of landscape position on phytotoxicity (Szmigielska and Schoenau 1999). Recovery of imazethapyr from spiked soils using ion exchange membrane extraction ranged from 25% on an upslope soil to 0 % on the low slope soil along the same landscape sequence. In line with this, the root growth inhibition in a five day canola root bioassay on the spiked soils showed the expected relationship of highest root growth inhibition on the upper slope soil (pH 8.0, organic carbon 1.4%) and lowest root growth inhibition on the lower slope soil (pH 6.6, organic carbon 2.11%).

In the study by Szmigielska and Schoenau (1999), as a follow-up to spiking of soil with imazethapyr in the laboratory, a field trial was conducted in which imazethapyr was applied to the field landscape using a field sprayer. Soils were sampled from control and treated portions of the landscape over a one year period following imazethapyr application. As expected, the canola root bioassay applied to the collected soils revealed significantly greater root growth inhibition and therefore persistence in the upper and mid-slope soils as compared to lower slope soils. In the following year, canola was planted across the landscape as a field bioassay and, consistent with extractions and lab bioassays, the greatest yield reductions and apparent injury from herbicide residue was found on the upper and mid-slope positions. However, another landscape sequence from another region in southern Saskatchewan did not show differences in root length inhibition among landscape positions, reflecting a lesser impact of landscape position on soil properties in this instance. Therefore the landscape dependency may not always be consistently observed, as the relationship between landscape position and soil properties is complex and can be variable.

The activity of Flucarbazone is also closely related to landscape position. Using a mustard root length bioassay, flucarbazone phytotoxicity was compared according to landscape position using the same landscape sequence sampled for the imazethapyr study described above (Eliason 2003). Root growth inhibition was greatest in the upper slope soil (Figure 2) where soil organic matter content was much lower. Eliason et al. (2004) observed that soil organic carbon content was the dominant factor controlling flucarbazone phytotoxicity in a range of Saskatchewan soils.

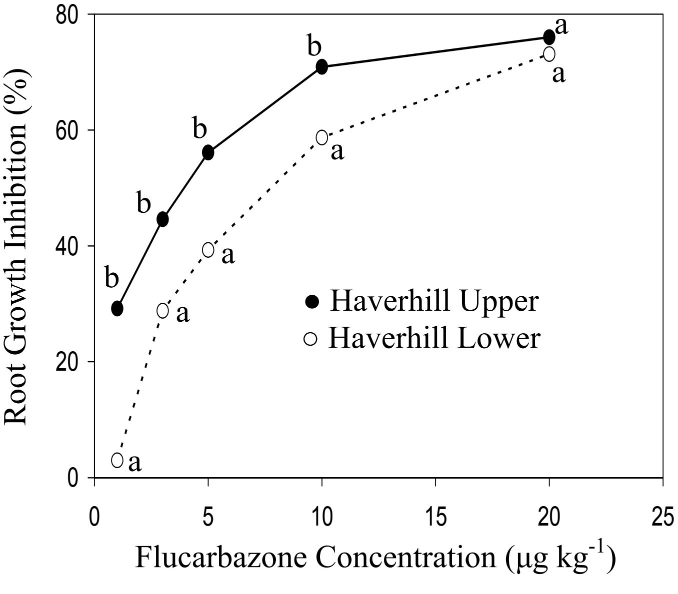

Figure 2. Oriental mustard root length inhibition response to landscape position in a landscape sequence of upper (pH 7.9, organic carbon 0.7%) and lower (pH 6.9, organic carbon 2.2%) slope position soils from southern Saskatchewan (Eliason 2003).

Conclusion

Landscape position has significant effects on soil residual activity of herbicides in prairie farm fields through relationships among landscape position, soil properties and environmental conditions. Higher organic matter and clay contents found in lower slope positions favour herbicide sorption and reduced phytotoxicity, although sorption may increase persistence of herbicides by protecting herbicide molecules from degradation. High pH conditions typically found on eroded knolls, along with dry soil conditions may increase phytotoxicity and persistence of some herbicides on upper slope positions. Landscape effects on the residual nature of herbicides in the soil should be taken into consideration when making re cropping decisions, especially when choices can be made about crops to seed in different landscape positions. In addition, it may be wise when collecting soil samples for bioassay purposes to sample and assess the different landscape positions separately. Similarly, the most valid field bioassay would encompass all the different landscape positions within the field, with yield assessments made at different slope positions.

Relationships between landscape position, soil properties and subsequent herbicide activity can vary and do not always follow the expected pattern. For example, in some landscapes the discharge of carbonate- laden groundwater at foot slope positions can result in higher soil pH values moving down slope. Repeated application of animal manures to eroded knolls can produce higher soil organic matter contents in upslope regions than in low slopes, altering the typical pattern of organic matter distribution. Flooding of depressions will produce anaerobic conditions and lower redox potentials that may cause deviations from the expected dissipation rate of some herbicides. While small plot experiments on uniform topography at several locations serve a useful purpose in revealing the factors controlling herbicide residue in the soil, landscape scale experiments are also needed to better elucidate the complex factors and interactions controlling the phytotoxicity and persistence of a wide range of herbicide compounds in soil.

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Do repeated applications of residual herbicides result in herbicide stacking?

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The introduction of a number of soil residual acetolactate synthase (ALS) inhibitors to the Canadian Prairies over the past two decades has raised concerns about repeated application and the potential for “stacking” of herbicide residues. Stacking is defined as the repeated application of different residual herbicides which results in additive or synergistic phytotoxicity to rotational crops. Provincial surveys

indicate that about 15 to 20% of prairie producers use a soil residual ALS inhibitor and 25 to 37% of those producers apply them in successive years. The effect of repeated applications of residual herbicides on rotational crops is reviewed in this paper. Research on the impact of repeated applications has concentrated on the accumulation of residues and the potential for environmental contamination. Very little research has been conducted on the crop response from the interaction of different soil residual herbicides with the same mode of action. Theoretically, herbicide residues should not accumulate over time unless they are extremely stable compounds; however, short-term accumulation may occur in some soil types, particularly under drought conditions. Unpublished results from ongoing field trials are presented and provide an indication that stacking may occur in some soils and environments. The high frequency with which soil residual ALS inhibitors are applied in successive years indicates that there is a need to provide information to producers on the potential risks associated with this practice.

Additional Keywords: herbicide persistence, herbicide carryover, acetolactate synthase inhibitors, soil residual herbicides, recropping phytotoxicity

Introduction

Herbicides that provide extended weed control are beneficial for growers; however carryover and injury to sensitive rotational crops can occur. There is particular concern during extended droughts like those experienced on the Canadian Prairies from 2000-2003. Industry agronomists feel that there is a lack of information on the consequences of repeated applications of the same herbicide or different herbicides with the same mode of action.

The first research on the Canadian Prairies investigating the effect of herbicide persistence on soil and crop productivity occurred in the 1930's (Bowser and Newton 1933). Smith (1982) stated that research demonstrating no deleterious effects from 35 years of continuous 2,4-D application did not reduce public concern with soil persistence from repeated annual herbicide application. There has been little attention paid to repeated residual herbicide applications in annual grain crop production since the 1980's. In the past ten to fifteen years, soil residual herbicides whose mode of action is the inhibition of the acetolactate synthase enzyme (ALS) have been commercialized in Western Canada. These include imazamethabenz, imazethapyr, imazamox, sulfosulfuron, flucarbazone and florasulam. Since these herbicides are registered on a number of different cereal, oilseed, and pulse crops, there is potential for repeated application even by producers who follow a diverse crop rotation.

The impact of repeated application of phenoxyalkanoic acids is largely understood (Smith 1989). Plots that received annual applications of 2,4-D and MCPA at Indian Head, Saskatchewan did not result in cumulative residues after 35 and 33 years, respectively, as levels were below the detectable level of 0.05 $\mu g\ g^{-1}$ (Smith et al. 1991). In addition, there were no significant long-term effects on spring wheat (*Triticum aestivum* L.) production, soil biochemical processes, nutrient cycling, and microbial population or biomass (McCurdy and Molberg 1974; Smith et al. 1991). However, this level of understanding of repeated applications is not the case with herbicide chemistries such as the imidazolinones and sulfonylureas.

In 2001, concerns with repeated application of soil residual ALS inhibitors were raised by the Weed Subcouncil of the Saskatchewan Advisory Council on Soils and Agronomy (Brenzil, personal communication). Field agronomists reported an alleged higher incidence of injury to field pea (*Pisum sativum* L.) when flucarbazone was applied the previous year and imazamox:imazethapyr (1:1) was applied postemergence to the crop. It was hypothesized that the combined activity of the two compounds was causing either an additive or synergistic phytotoxic effect. These field observations also raised the question of whether repeated residual ALS inhibitor herbicide application could result in herbicide residue "stacking", a term coined by industry agronomists. Stacking is not defined in the literature; therefore "the repeated application of different residual herbicides which results in additive or synergistic phytotoxicity to rotational crops" will be used to define this term.

Long-term accumulation of herbicide residues

Past research has shown that problems with long-term accumulation of herbicide residues rarely occur (Walker 1987). Hill et al. (1955) derived the following equation [1] to predict the accumulation of residues for herbicides which degrade at a rate that is proportional to their concentration (first-order kinetics):

$$R = \frac{AP\,(1 - P^n)}{1\text{-}P} \qquad [1]$$

where R = residue at the end of the *n*th year, P = proportion of the applied dose which remains after one year, and A = rate applied each year. Therefore, if a herbicide is applied at a rate of 30 g ai ha^{-1} and the annual rate of degradation is 70%, then theoretically 9 g ha^{-1} remains after one year and stabilizes at 12.5 g ha^{-1} after three years. In order for residues to accumulate over time, the rate of degradation must be less than 25% annually (Smith 1982; Walker 1987). Pesticides that possess that degree of stability include the banned or restricted insecticides dieldrin and DDT.

Validation of the equation by Hill et al. (1955) is illustrated with data from Johnstone et al. (1998) where trifluralin was repeatedly applied to three soil types (Figure 1). After 6 years, the percentage of the initial trifluralin concentration remaining was quite stable; however, the amount present on an annual basis was highly dependent on soil texture (Figure 1). The percentage of trifluralin remaining in the sandy loam soil was more influenced by environmental conditions than the fine textured soils. Severe carryover occurred on the sandy loam soil following a drought year in 1984.

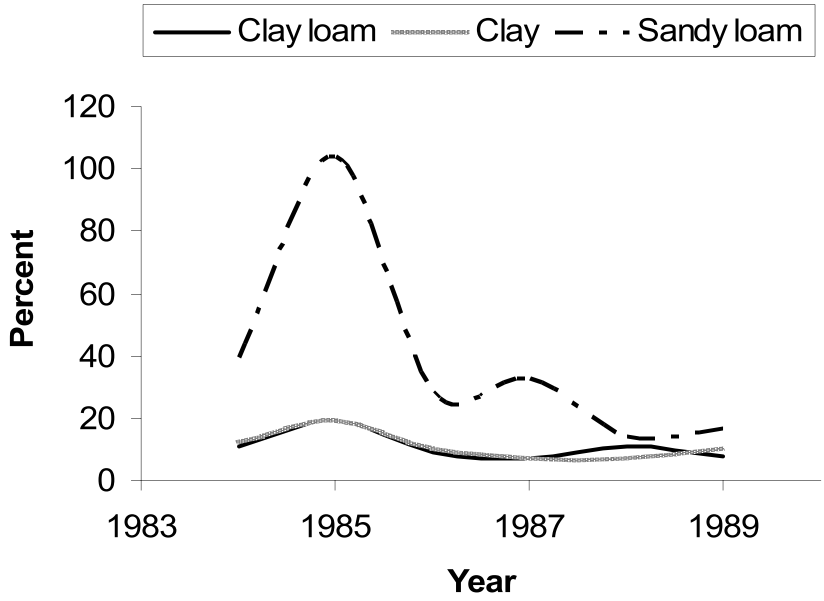

Figure 1. Effect of repeated trifluralin application on the percentage of initial measured trifluralin concentration remaining in soils of varying texture. Adapted from Johnstone et al. 1998**.**

Most of the research on repeated application has concentrated on perennial fruit crops where repeat application of the same herbicide is required (Rouchard et al. 2000). Tworkoski et al. (2000) reported that the herbicides diuron, simazine, terbacil and their metabolites did not accumulate after 14 years of repeated application in fruit orchards. Eighteen years of continuous isoxaben application in a pear tree orchard did not result in residue accumulation (Rouchard et al. 1997). Most studies on repeat herbicide applications investigate the potential for groundwater contamination from residue accumulation rather than the potential for rotational crop phytotoxicity. On the Prairies, the potential for pesticide leaching into groundwater is generally low due to the relatively dry climate and the occurrence of deep bedrock aquifers (Reynolds et al. 1995). Even though herbicide residues do not appear to accumulate, Walker (1987) reported that some soils can attain an "equilibrium" residue level that will be sufficiently high to injure sensitive crops. Colquhoun (2004) concurs with this assessment in that repeated diuron applications did not result in residue accumulation greater than the concentration of the initial application; however, it reduced perennial ryegrass (*Lolium perenne* L.) groundcover and seed yields. The potential for phytotoxic carryover in the arid prairie region is high since degradation of most herbicides is highly dependent on soil moisture (Eliason et al. 2004).

Enhanced degradation

Repeat herbicide applications may also lead to enhanced or accelerated herbicide degradation. Enhanced degradation is an increase in the decomposition rate of a herbicide when applied to a field that received a prior herbicide treatment (Roeth 1986). The terms "history soil" and "non-history" soil are used to designate soils with repeat applications and an untreated check soil, respectively. There is usually a lag phase where there is little decomposition of herbicide following an initial application to a non-history soil (Kaufman and Edwards 1983). This lag phase is not present when enhanced degradation occurs. Pendimethalin was found to have a much higher rate of degradation when applied to a history soil that received more than five consecutive applications compared to a non-history soil (Kulshrethra et al. 2000). When applied to the history soil, 54% of pendimethalin was degraded five days after treatment compared to 10% for the non-history soil. It is believed that enhanced degradation occurs from increased activity of microbial degraders or by microbial adaptation (Cullimore 1981; Kaufman and Edwards 1983; Roeth 1986). Enhanced degradation has been reported for 2,4-D and MCPA (Smith et al. 1991); diuron, chlorotuluron, propyzamide and to a lesser degree, simazine (Rouchard et al. 2000); isoxaben (Rouchard et al. 1997); EPTC and butylate (Harvey 1991; Harvey 1987); and chlorsulfuron (Ravelli et al. 1997). Roeth (1986) provides a review of herbicides which exhibit enhanced degradation from studies conducted prior to 1986.

Not all herbicides have shown enhanced degradation from repeat applications. Alachlor, atrazine, cyanazine, or metolachlor did not exhibit enhanced degradation after five years of continuous application (Harvey 1987). Diflufenican residues were not affected by repeat applications; however, it was only applied in three consecutive years so it is not known whether the lack of enhanced degradation is due to the relatively short time frame of the study or due to the herbicide's resistance to soil degradation (Rouchard et al. 2000). Repeated applications of imazethapyr, imazaquin, and chlorimuron did not result in enhanced rates of soil degradation (Young and Barrett 1999).

Enhanced degradation can be a positive phenomenon because the residues dissipate much quicker; however, there have been situations where enhanced degradation resulted in reduced weed control. Harvey et al. (1986) reported a reduction in wild proso millet (*Panicum miliaceum* L.) control from enhanced degradation of EPTC.

Soil residual herbicide interactions

There is very little information in the literature on the combined effect of different herbicide residues on crop phytotoxicity (Moyer and Hamman 2001). Johnstone et al. (1998) stated that it is possible that combined herbicides could "accelerate or slow degradation by their impact on soil microbial populations or adsorption". In one of eighteen site-years, trifluralin residues were 2.1 times higher in the presence of bromoxynil-MCPA than when absent (Johnstone et al. 1998). Smith (1982) reported that MCPA or 2,4-D residues were not affected by the presence of a number of herbicides and that triallate or trifluralin residues did not interfere with the degradation of the other herbicide. The lone experiment examining the combined effects of residues on crop phytotoxicity was conducted in a greenhouse by Moyer and Hamman (2001) who reported that residues of sulfosulfuron combined with either imazethapyr, metsulfuron, or triasulfuron resulted in additive injury to sugar beet (*Beta vulgaris* L.).

There are no reports in the literature of a soil residual herbicide predisposing the following crop to injury from a postemergence herbicide application such as the flucarbazone – imazamox:imazethapyr (1:1) sequence in field pea discussed earlier. It is possible that interactions like this could occur. Simpson and Stoller (1996) reported that imazethapyr combined with thifensulfuron resulted in synergistic phytotoxicity to sulfonylurea-tolerant soybean [*Glycine max* (L.) Merr.]. The synergism between the two ALS inhibitors was not due to increased absorption, translocation, or metabolism of either herbicide; therefore, another mechanism must be responsible for the synergism. It has been well established that the application of certain soil-applied insecticides combined with a postemergence herbicide can result in injury to corn (*Zea mays* L.) that is greater than the injury from the pesticides applied individually (Kapusta and Krausz 1992). Nicosulfuron injury in corn was magnified by terbufos application as the insecticide caused slightly higher absorption of the herbicide and interfered with the cytochrome P450 monoxygenases involved in nicosulfuron metabolism (Diehl et al. 1995). Field research is required to investigate interactions of residual herbicides and whether there is potential for stacking to occur.

Soil residual ALS inhibitor use on the Prairies

To assess the use patterns of residual ALS inhibitor herbicides, questionnaire data from the 2001-2003 Alberta, Saskatchewan, and Manitoba weed surveys were analyzed (Leeson et al. 2001, 2002, 2003). The analysis involved the use patterns of the following herbicides: imazamethabenz (half life: 25-36 days); imazethapyr (half-life: 60-90 days); imazamox (half-life: 20-30 days); flucarbazone (half life: 17 days); sulfosulfuron (half-life: 14-75 days) and florasulam (half life: 2-18 days). The half-lives of the compounds are from Vencill (2002), although

Eliason et al. (2004) reported the half-life of flucarbazone in Saskatchewan soils ranged from 6 to 110 days depending on soil organic matter content.

The number of survey respondents is reported in Table 1. The percentage of respondents who used residual ALS inhibitors was relatively uniform across provinces, with a trend of increased use in recent years. The percentage use in the final year of the surveys was about 15 to 20% (Table 1), which is consistent with market data (BASF, unpublished data).

Table 1: Number of respondents and the percentage that applied a soil residual ALS inhibitor herbicide[a], Weed Survey Questionnaire[b], Prairie Provinces, 2001-2003.

	Alberta		Saskatchewan		Manitoba	
Year	No. of respondents	% using residual ALS	No. of respondents	% using residual ALS	No. of respondents	% using residual ALS
2003			1018	15		
2002			915	13	362	23
2001	758	19	922	12	346	19
2000	697	15	816	13	329	20
1999	669	16	794	7	321	11
1998	624	13	607	12	300	9
1997	577	13			260	11
1996	464	12				

[a] imazamethabenz, imazethapyr, imazamox:imazethapyr (1:1), flucarbazone, sulfosulfuron, and florasulam

[b] Leeson et al., unpublished data.

The percentage of respondents who used the residual ALS inhibitors and applied them in successive years ranged from 25 to 37% in the final survey year for each province (Table 2). There is a definite trend for a higher percentage of back-to-back applications in recent years.

The use patterns of the individual herbicides varied somewhat by province. Imazamethabenz was more commonly used by respondents in Manitoba and Alberta compared to Saskatchewan (Table 3). Imazamox:imazethapyr (1:1) and imazethapyr were used more frequently in Saskatchewan than in Manitoba and Alberta. Flucarbazone was used by a relatively high percentage of growers in Manitoba in 2001 and 2002. The higher use of imazamethabenz and flucarbazone in Manitoba is likely due to an increased incidence of Group 1-resistant wild oats (*Avena fatua* L.) in that province (Beckie et al. 1999, 2004).

Table 2: Percentage of respondents applying soil residual ALS inhibitor herbicides[a] in successive years, Weed Survey Questionnaire[b], Prairie Provinces, 2001-2003.

Year	Alberta	Saskatchewan	Manitoba
		(%)	
2003		25	
2002		15	37
2001	27	20	26
2000	17	4	11
1999	17	9	3
1998	19		8
1997	15		

[a] imazamethabenz, imazethapyr, imazamox:imazethapyr (1:1), flucarbazone-sodium, sulfosulfuron, and florasulam

[b] Leeson et al., unpublished data.

To assess the most common successive applications of residual ALS inhibitors, the herbicides were grouped into the imidazolinones and others (sulfonylurea, sulfonylamino carbonyltriazolinone and triazolopyrimidine sulfonanlide) (Table 4). The most common back-to-back usage involved an imidazolinone herbicide applied after another imidazolinone herbicide (Table 4). Imazamethabenz applied two years in a row was the most frequent application and accounted for 30% of the back-to-back imidazolinone applications (data not shown). The second most common sequence was the other class following an imidazolinone application (Table 4). Florasulam following imazethapyr or imazamox:imazethapyr (1:1) was the most frequent application, accounting for about 40% of the other-imidazolinone sequence (data not shown).

Current research

In response to allegations from field agronomists, laboratory and field studies investigating the potential phytotoxic interactions from repeated application of residual ALS inhibitor herbicides were initiated in 2002. The field studies consist of multi-year crop/herbicide sequences at eight locations in Saskatchewan and Alberta. The objectives of the field studies are:

1. To determine if crop phytotoxicity from a postemergence ALS inhibitor herbicide is increased if a soil residual ALS inhibitor was applied the previous year.

2. To determine if the repeated application (two successive years) of different residual ALS inhibitors results in increased phytotoxicity to susceptible rotational crops grown in years three or four. In other words, does stacking of herbicide residues occur?

Table 3: Residual ALS inhibitor herbicide[a] use by province and year, Weed Survey Questionnaire[b], Prairie Provinces, 2001-2003.

Year	Imaza-methabenz	Imazamox: imazethapyr	Imazethapyr	Sulfosulfuron	Florasulam	Flucarbazone
			% of respondents			
			Alberta			
2001	39	20	7	15	13	6
2000	47	31	12	9	0	2
1999	51	31	9	7	0	1
1998	45	35	17	4	0	0
1997	63	15	22	0	0	0
1996	75	11	15	0	0	0
			Saskatchewan			
2003	9	29	23	5	35	0
2002	8	43	22	7	18	1
2001	14	32	38	9	6	1
2000	10	52	25	9	2	3
1999	20	48	25	7	0	0
1998	17	44	37	3	0	0
			Manitoba			
2002	19	24	3	10	16	29
2001	25	35	9	6	13	12
2000	45	27	8	9	2	9
1998	65	15	3	18	0	0
1997	42	46	12	0	0	0
1996	61	7	32	0	0	0

[a] imazamethabenz, imazethapyr, imazamox:imazethapyr (1:1), flucarbazone-sodium, sulfosulfuron, and florasulam

[b] Leeson et al., unpublished data.

Table 4: Chemical family sequences of soil residual ALS inhibitor herbicides applied in successive years, percentage of respondents, Weed Survey Questionnaire[b], Prairie Provinces 2001-2003.

Sequence (2nd application on 1st application)	Percent
Other [a] on Other	6
Imidazolinone on Other	9
Other on Imidazolinone	26
Imidazolinone on Imidazolinone	59

[a] Other group includes sulfosulfuron (sulfonylurea), flucarbazone- sodium (sulfonylamino carbonyltriazolinone) and florasulam (triazolopyrimidine sulfonanlide)

[b] Leeson et al., unpublished data

Field studies

Two field experiments are being conducted at 8 sites in Saskatchewan and Alberta. These sites represent a range of soil types that differ in organic matter content, pH, and texture (Table 5). The two field experiments were initiated in 2002 and involve different crop and herbicide sequences. Preliminary results from one of the experiments are presented. The experiment involves a field pea – wheat – canola (*Brassica napus* L.) sequence. The field pea phase of the sequence received either a postemergence treatment of bentazon (check treatment) or imazamox:imazethapyr (1:1) at rates of 840 and 30 g ai ha^{-1}, respectively. The wheat phase received one of the following postemergence herbicide applications: imazamethabenz (500 g ai ha^{-1}); flucarbazone (30 g ai ha^{-1}); sulfosulfuron (20 g ai ha^{-1}); and florasulam-MCPA (5 and 500 g ai ha^{-1}, respectively). A check treatment of clodinafop-propargyl (56 g ai ha^{-1}) and bromoxynil-MCPA (280 and 280 g ai ha^{-1}, respectively) was also included; In year three, glyphosate-tolerant canola was seeded over the entire study and treated with glyphosate at 450 g ai ha^{-1}. The wheat phase of the sequence addresses the first objective of the study, while the canola phase addresses the second objective.

Only results from Scott, SK are presented since it was one of the more responsive sites. In the spring wheat phase of the cropping sequence, high levels of visual injury were observed 7 DAT, particularly with the imazamox:imazethapyr (1:1) / sulfosulfuron sequence when compared to the check year 1 / check year 2 (CHY1 / CHY2) sequence, the imazamox:imazethapyr (1:1) / CHY2 sequence or the CHY1 / sulfosulfuron sequence. (Table 6). The wheat plants recovered over time with only slight injury reported 28 DAT (Table 6). Single degree of freedom contrasts indicated that imazamox:imazethapyr (1:1) followed by flucarbazone or florasulam resulted in lower yields than the CHY1 / CHY2 sequence, while the sequences of imazamox:imazethapyr (1:1) / CHY2, CHY1 / flucarbazone or CHY1 / florasulam were not lower yielding than the CHY1 / CHY2 sequence (Table 6). The sequence of imazamox:imazethapyr followed by sulfosulfuron resulted in a similar trend (*p*=0.12); however, yield differences were not significant. To assess the nature of the herbicide interactions, expected values of yield reduction were calculated according to Colby (1967):

$$E = X + [Y(100 - X)]100 \qquad [2]$$

where X is the inhibition of growth from herbicide A (ALS inhibitor applied in year 2) at p g ai/ha, Y is the inhibition of growth from herbicide B [imazamox:imazethapyr (1:1) applied in Year 1]. E is the expected growth inhibition of herbicides A and B applied at respective p and q concentrations to previous crops. If observed yield reductions are equal to expected yield reductions, then the interaction of the two herbicide treatments are considered additive. If observed is greater than expected, then the response from the two herbicide applications are considered synergistic.

Table 5: Soil characterization of sites for repeated ALS inhibitor herbicide application studies.

Site	Soil Zone	%O.M.[a]	pH	Texture
Scott, SK[b]	Dk. Brown	3.0	5.9	Loam
Lethbridge, AB[c]	Dk. Brown	3.6	7.8	Clay loam
Saskatoon, SK	Dk. Brown	3.8	7.4	Clay
Vanscoy, SK	Dk. Brown	5.3	7.1	Loam
Fairview 1, AB	Gray	6.0	6.3	Sandy loam
Fairview 2, AB	Gray	7.1	6.1	Sandy clay loam
Vegreville, AB	Black	7.2	6.3	Clay loam
Melfort, SK	Thin Black	11.3	6.6	Clay
Ellerslie, AB	Black	12.2	6.2	Silty clay loam

[a] % Soil organic matter
[b] Saskatchewan, Canada
[c] Alberta, Canada

Table 6: Effect of repeat application of residual ALS inhibitors on visual injury and yield of spring wheat in a field pea-spring wheat-canola sequence. (unpublished data, Scott, SK. 2002-03).

	Visual Injury (0-100 %)[a]			
Herbicide Sequence[b]	7 DAT[c]	14 DAT	28 DAT	Yield (kg ha^{-1})
CHY1[d] / CHY2[e]	0	0	0	2380
CHY1 / imazamethabenz	5	3	1	2140
CHY1 / flucarbazone	10	4	5	2160
CHY1 / sulfosulfuron	11	5	0	2330
CHY1 / florasulam	1	0	0	2410
I:I[f] / CHY2	3	0	1	2330
I:I / imazamethabenz	9	4	1	2220
I:I / flucarbazone	14	8	6	1870
I:I / sulfosulfuron	20	15	1	2100
I:I / florasulam	4	3	1	1960
LSD$_{0.05}$	4	4	2	380
Contrasts	*p value*			
CHY1 /imazamethabenz vs CHY1 / CHY2	0.001	0.07	0.56	0.19
CHY1 / flucarbazone vs CHY1 / CHY2	<0.0001	0.05	<0.0001	0.24
CHY1 / sulfosulfuron vs CHY1 / CHY2	<0.0001	0.01	1.00	0.76
CHY1 / florasulam vs CHY1 / CHY2	0.49	1.00	1.00	0.90
I:I / CHY2 vs CHY1 / CHY2	0.17	1.00	0.39	0.76
I:I / imazamethabenz vs CHY1 / CHY2	<0.0001	0.04	0.29	0.38
I:I / flucarbazone vs CHY1 / CHY2	<0.0001	<0.0001	<0.0001	0.01
I:I / sulfosulfuron vs CHY1 / CHY2	<0.0001	<0.0001	0.39	0.12
I:I / florasulam vs CHY1 / CHY2	0.04	0.07	0.39	0.03

[a] 0 = no injury symptoms; 100 = complete kill

[b] Application made in Year 1 / Year 2

[c] DAT = days after treatment

[d] CY1 = check applied in year 1 (bentazon)

[e] CY2 = check applied in year 2 (clodinafop-propargyl and bromoxynil-MCPA)

[f] I:I = imazamox: imazethapyr (1:1)

The yield reduction from imazamox:imazethapyr (1:1) followed by flucarbazone or florasulam was synergistic at Scott in 2003 since the observed yield reduction was much higher than the expected yield reduction (Table 7). This was the only site out of eight sites where the application of two sequential ALS inhibitor herbicide applications resulted in a synergistic yield reduction. The soil pH at Scott is low (Table 5), thus there is a greater likelihood of crop injury from imidazolinone carryover (Bresnahan et al. 2000, 2002; Chamberlain et at. 1995). In addition, the Scott soil is low in organic matter and growing season precipitation was below normal in both 2002 and 2003. Ball et al. (2003) reported that imidazolinone carryover injury to sensitive crops was highest in drier locations.

Table 7: Predicted vs. observed yield reductions in spring wheat from repeat application of residual ALS inhibitors in a field pea-spring wheat-canola sequence. (unpublished data, Scott, SK. 2002-03).

Herbicide Sequence[a]	Expected Yield Reduction (% ± S.E[b])	Observed Yield Reduction (% ± S.E.)
I:I[b] / imazamethabenz	12 ± 4	7 ± 10
I:I / flucarbazone	11 ± 2	22 ± 8
I:I / sulfosulfuron	5 ± 4	12 ± 8
I:I / florasulam	1 ± 4	18 ± 10

[a] Application made in Year 1 / Year 2
[b] Standard error
[c] I:I = imazamox: imazethapyr (1:1)

In the canola phase of the cropping sequence, the sequential application of imazamox:imazethapyr (1:1) followed by imazamethabenz resulted in the highest visual injury 7 days after crop emergence (Table 8). As time progressed, injury from the imazamox:imazethapyr (1:1) / sulfosulfuron sequence was evident (Table 8). The visual injury observed was consistent with canola yield reductions (Table 8). The sequences of imazamox:imazethapyr (1:1) followed by imazamethabenz or sulfosulfuron were the only treatments that were lower yielding than the CHY1 / CHY2 sequence (Table 8). The sequences where the three herbicides were applied in isolation (imazamox:imazethapyr (1:1) / CHY2; CHY1 / imazamethabenz; CHY1 / sulfosulfuron) were not lower yielding than the CHY1 / CHY2 sequence. Applying Colby's formula suggests that the sequences of imazamox:imazethapyr (1:1) followed by imazamethabenz or sulfosulfuron resulted in a synergistic yield reduction in canola (Table 9). In greenhouse studies, Moyer and Hammon (2001) reported that sulfosulfuron residues were additive with imazethapyr; therefore, it appears that environment has an important influence on the nature of the crop response from different repeated residual herbicide applications. The crop response at Scott was consistent with the Vanscoy site (data not shown). Additive or synergistic yields reductions were not as evident at other locations.

Table 8: Effect of repeat application of residual ALS inhibitors on visual injury and yield of canola in a field pea-spring wheat-canola sequence. (unpublished data, Scott, SK. 2002-04).

	Visual Injury (0-100%)[a]			
Herbicide Sequence[b]	7 DAE[c]	14 DAE	28 DAE	Yield (kg ha^{-1})
CHY1[d] / CHY2[e]	0	0	0	940
CHY1 / imazamethabenz	8	16	10	660
CHY1 / flucarbazone	0	2	0	800
CHY1 / sulfosulfuron	0	1	3	940
CHY1 / florasulam	0	2	0	800
I:I[f] / CHY2	0	4	1	860
I:I / imazamethabenz	20	53	45	440
I:I / flucarbazone	3	9	4	790
I:I / sulfosulfuron	3	25	18	550
I:I / florasulam	3	3	3	760
LSD$_{0.05}$	8	13	13	376
Contrasts		*--- p-value ---*		
CHY1 /imazamethabenz vs CHY1 / CHY2	0.07	0.02	0.17	0.15
CHY1 / flucarbazone vs CHY1 / CHY2	1.00	0.81	0.88	0.44
CHY1 / sulfosulfuron vs CHY1 / CHY2	1.00	0.88	0.82	0.98
CHY1 / florasulam vs CHY1 / CHY2	1.00	0.76	0.88	0.45
I:I / CHY2 vs CHY1 / CHY2	1.00	0.57	1.00	0.67
I:I / imazamethabenz vs CHY1 / CHY2	<0.0001	<0.0001	<0.0001	0.01
I:I / flucarbazone vs CHY1 / CHY2	0.54	0.18	0.68	0.41
I:I / sulfosulfuron vs CHY1 / CHY2	0.54	0.01	0.03	0.04
I:I / florasulam vs CHY1 / CHY2	0.54	0.69	0.70	0.32

[a] 0 = no injury symptoms; 100 = complete kill

[b] Application made in Year 1/ Year 2

[c] DAE = days after crop emergence

[d] CY1 = check applied in year 1 (bentazon)

[e] CY2 = check applied in year 2 (clodinafop-propargyl and bromoxynil-MCPA)

[f] I:I = imazamox: imazethapyr (1:1)

Table 9: Predicted vs. observed yield reductions in canola from repeat application of residual ALS inhibitors in a field pea-spring wheat-canola sequence. (unpublished data, Scott, SK. 2002-04).

Herbicide Sequence[a]	Expected Yield Reduction (% ± S.E.[b])	Observed Yield Reduction (% ± S.E.)
I:I[c] / imazamethabenz	36 ± 12	53 ± 17
I:I / flucarbazone	21 ± 11	16 ± 14
I:I / sulfosulfuron	8 ± 11	41 ± 14
I:I / florasulam	22 ± 8	19 ± 15

[a] Application made in Year 1 / Year 2

[b] Standard error

[c] I:I = imazamox:imazethapyr (1:1)

Conclusions

Long-term repeat applications of residual herbicides do not generally result in accumulation of residues. However, droughts may lead to short-term accumulation in certain soils. Preliminary field tests suggest that the application of a residual ALS inhibitor can predispose the following crop to higher levels of phytotoxicity from postemergence ALS inhibitor herbicide application. In addition, short-term stacking of different herbicide residues can result from repeated applications; however, it also appears to be limited to low organic matter soils that have received less than average precipitation. Research is ongoing to provide a better understanding of the frequency of stacking and the environmental and soil conditions that lead to its occurrence. Survey data indicates that producers are frequently applying ALS inhibitors in successive years; therefore, there is a need to provide information to growers on the risks associated with this practice.

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Soil residual herbicide bioassays: Science and practice

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Soil residual herbicide activity has been investigated since the early 1960s and one objective of this research has been to provide growers with specific recrop recommendations. Numerous whole-plant and root growth bioassays have been developed to meet this need. The Alberta Research Council (ARC) has been providing a bioassay service to detect symptoms consistent with herbicide carryover since 1986. The objective of this paper is to describe our bioassay methodology and to provide basic information arising from our experience. Soil samples suspected of containing active residues are submitted to the ARC. Once the soil sample is received, the target crop and a sensitive species are planted in both the submitted soil and a check soil, known to be herbicide-free. Samples are evaluated for initial severity of symptoms and recovery over time and this information is reported. Symptoms consistent with herbicide carryover were found in 77% of all samples submitted since 1999. The most common crop-herbicide type combination requested is canola-imidazolinone. The primary limitation of bioassays is that damage in the bioassay may not reflect yield loss in a producer's field. However, bioassays are the only risk-management tool available to growers and can detect the presence of residues below chemical detection thresholds.

Additional Keywords: sulfonylurea, imidazolinone, herbicide carryover, peas, wheat, oats

Introduction

The effects of residual herbicides on subsequent crops have been investigated since the early 1960's (Chubb 1963). Early research used field experiments (Wicks et al. 1969) to detect residual herbicide effects. However, this type of research offered general recommendations, recognizing that herbicide residual activity was affected by factors such as crop sensitivity, soil texture, organic matter and precipitation (Wicks et al. 1969). Growers' need for specific recrop recommendations for specific fields was recognized (Anonymous 1977; 1980) and bioassays were developed to mitigate this problem (Anonymous 2004).

Bioassays to detect herbicide residual activity have examined root growth reduction in soil media (Eliason et al. 2002; Holloway et al. 1999) and petri dishes (Jourdan et al. 1998), and whole-plant bioassays in soil media (Loux et al. 1989) and hydroponics (Sandín-España et al. 2003) for a number of herbicide-crop combinations. A common research goal in these studies has been to compare the bioassay with other methodologies to detect herbicide residues, thereby preventing yield loss. In general, this research has found that bioassays are suitable screening tests for herbicides employed at low rates and can be useful in the detection of low levels of phytotoxic soil residues (Anonymous 2000).

The Alberta Research Council (ARC) has been providing a bioassay service to detect symptoms consistent with herbicide residue since 1986 and has considerable expertise in this area. This service has been provided to growers, extension agronomists, chemical companies, and the research community. It has been used as a risk management tool to aid recrop decisions by agronomists and growers, and, to detect symptoms consistent with residue after injury is observed on crops. The objective of this paper is to describe the bioassay methodology and to provide basic information arising from our experience.

Materials and methods

Sampling fields

Soil analysis can provide detailed information on nutrients or herbicide residues. Information, obtainable from a soil analysis, useful in assisting interpretation of bioassay results include pH, organic matter, soil texture, and soil moisture (or alternatively, precipitation records) (Bresnahan et al. 2002; Eliason et al. 2002; Loux et al. 1989; Moyer 1995; Rubem et al. 1999). However, a small soil sample may not be representative of the whole field unless the sample is carefully selected (Rubem et al. 1999). It is important to have a full record of the field sample including information on location and topography (Rubem et al. 1999), crop history and agronomic practices (Jensen et al. 1995) and herbicide use history.

Two soil sampling strategies are commonly used, and either may be appropriate for a bioassay. Topographic soil sampling entails obtaining samples from eroded knolls, mid-slopes and low-lying areas and each soil sampling site can be subjected to a bioassay. This sampling system is useful for fields having rolling landscapes and can detect “hot spots” of carryover in the field as well as areas less likely to be affected. Our experience indicates this sampling methodology is most useful after injury has been observed. By contrast, random soil sampling avoids potential problem areas such as saline areas, poorly drained areas, and eroded knolls that should not be sampled unless they represent a significant portion of the field.

Sampling accuracy is improved by dividing fields into smaller units (e.g. 80-acre segments). Each soil sampling site can be subjected to a bioassay. Agrologists and growers may find that one or both methods may be used on the same field.

Our sample requirements for a single bioassay are a minimum of 2 kg of soil per sample area to provide sufficient soil to conduct a bioassay with three plant species. Sampling depth is suggested to be 0-7.5 cm for direct-seeded fields and 0-15 cm for tilled fields based on expected differences in distribution due to tillage effects (Berger et al. 1999). Check soil samples may also be submitted if a herbicide free area can be found, but all bioassays are conducted using a known herbicide-free soil from ARC as a check. Ideally, soil samples should be collected and submitted prior to fall freeze to facilitate timely transmittal of results.

Bioassay method

Once the soil sample for the bioassay is received, the target crop, a check crop, and a sensitive species are planted in both the submitted soil and a check soil, known to be herbicide-free. Using glyphosate-tolerant canola (*Brassica napus* L.), testing for imidazolinone residues as an example (Figure 1), we would seed in the submitted and check soils: 1) glyphosate-tolerant canola (target crop), 2) imidazolinone-tolerant canola, and, 3) sugar beet (*Beta vulgaris* L.) as a sensitive species. Since imidazolinone-tolerant canola is not sensitive to imidazolinone, this approach ensures we detect bioavailable herbicide and do not confuse other symptoms, such as sulphur deficiency, pH response, or salinity, with herbicide activity. For other crop-herbicide combinations, different check and sensitive species are used. Samples are visually evaluated for initial severity of symptoms and recovery over time. This information is reported to the agronomist or producer. Mild injury may not include chlorosis or substantial growth reduction. Symptoms may be limited to short-term purpling and cupping of leaves in the target species with more severe symptoms present in the sensitive species. Severe injury (Figure 1) can include substantial chlorosis, purpling and cupping of leaves and disruption of meristems. This can result in significant growth reduction and excessive lateral branch production in the target species, sensitive species, or both.

Interpreting bioassay results

Since the ARC does not chemically evaluate the presence or concentration of specified herbicides, we do not state that these herbicides are present. Instead, we evaluate for "symptoms consistent with herbicide damage". Consequently, the ARC does not provide advice or recommendations to agronomists or growers. Agronomists and growers receiving reports jointly make decisions based on the information provided and experience as to the course of action. However, bioassays are most difficult to interpret and make reliable recommendations from when they are not either completely "dirty" or completely "clean".

Feedback from agronomists indicates that when we report severe symptoms on the target species (e.g. canola), the decision is undertaken not to plant that crop.

In the Peace River area of Alberta, where the soil is relatively acidic, damage to sugar beet (sensitive species) indicates a canola recrop may not be suitable. The ARC is currently involved with Agriculture and Agri-Food Canada (AAFC) and Alberta Agriculture, Food and Rural Development (AAFRD) in a validation study to determine how to optimize the bioassay recommendations.

Figure 1. Bioassay showing severe damage to the target species (canola) on the left and the sensitive species (sugar beet) on the right.

Results and discussion

The ARC, formerly the Alberta Environmental Center (AEC), has provided a residual bioassay service since 1986. Under the AEC, this diagnostic service was free and many hundreds, possibly thousands, of samples were received. Early sample submissions consisted largely of samples containing picloram (Tordon) and later chlorsulfuron (Glean). After the AEC was taken over by the ARC, a fee was charged for the bioassay and the number of samples declined sharply. Since record-keeping commenced in 1999, approximately 900 samples have been received (Table 1). These samples have come primarily from agronomists, but since the drought of 2002, there has been a substantial increase in the number of samples coming from industry and research (Table 1).

Most samples are submitted to aid recrop decisions, and interest has focused predominantly on high-acreage, high-value crops. Approximately 63% of all samples received request canola as a target crop (Table 2). The next most frequently requested crop is peas (*Pisum sativum* L.), however, it is the requested target crop less than 10% of the time. Major crops, wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), lentil (*Lens culinaris* Medik.), and tame oats (*Avena sativa* L.) are also represented. In addition to these crops, bioassays have been requested for: 1) forage crops such as brome (*Bromus* spp.), fescue (*Festuca* spp), fescue/alfalfa (*Medicago sativa* L.) mixes, and timothy (*Phleum pratense* L.), 2) various bean crops (*Phaseolus* spp.) such as faba, navy, pink, and soy (*Glycine max* L. Merr.), 3) oilseeds such as sunflower (*Helianthus annuus* L.) and flax (*Linum usitatissimum* L.), and, 4) specialty crops such as canaryseed (*Phalaris canariensis* L.), coriander (*Coriandrum sativum* L.), corn (*Zea mays* L.), mustard (*Sinapis alba* L. and *Brassica juncea* L.), potatoes (*Solanum tuberosum* L.) and sugar beets. This represents a wide range of experience in inspecting and interpreting symptoms.

Table 1. Sample sources and number of samples received for residual bioassay from various sources since 1999.

Year	Agronomist	Industry	Research	Producer	Government	Other	Total
1999	24	-	6	-	-	-	30
2000	36	-	4	5	3	-	48
2001	51	-	-	13	3	-	67
2002	98	61	-	6	3	-	168
2003	229	15	-	31	2	1	278
2004	118	59	76	22	-	2	277
Total	556	135	86	77	11	3	868

Table 2. Target species for residual bioassay since 1999.

Year	Canola	Peas	Wheat	Barley	Lentil	Tame Oats	Other	Total
1999	19	-	-	5	6	-	6	36
2000	18	2	1	5	4	1	16	47
2001	45	23	5	1	8	7	10	99
2002	77	9	12	13	-	6	14	131
2003	240	21	19	13	1	1	30	325
2004	76	9	16	9	-	1	7	118
Total[1]	475	64	53	46	19	16	83	756

[1] Excludes missing data and some samples submitted by industry.

Sample submissions have been received from a wide geographic range in western Canada (Table 3). Most samples come from Alberta, excluding the South region, and Saskatchewan (Table 3). A considerable increase in samples from all areas was observed after the drought of 2002 (Tables 1-3). Fewer samples from southern Alberta may be attributable to label restrictions and heightened awareness of the potential for herbicide soil residual activity due to: 1) drier conditions than are found in the central and northern parts of Alberta, and 2) research initiated in that part of the province (Moyer 1995). By contrast, Manitoba tends to receive more rainfall and herbicide soil residual activity should be generally less problematic, possibly resulting in less awareness of potential problems.

Table 3. Location of sample submissions for residual bioassay since 1999.

Year	BC	AB				SK	MB	Total
		South	Central	East Central	Peace			
1999	2		13	5	8	2	-	30
2000	2	3	8	11	20	-	-	44
2001	3	8	7	22	14	5	8	67
2002	-	11	27	9	17	34	9	107
2003	-	38	55	58	53	45	26	275
2004	1	6	14	19	22	29	16	107
Total[1]	8	66	124	124	134	115	59	630

[1] Excludes missing data and some samples submitted by industry.

Sample submissions have requested tests for herbicide activity from herbicide Groups 2, 3, 4, 5 and 6, but have been dominated by Group 2 herbicides (Table 4). More than 85% of samples received have requested testing for Group 2 herbicides and greater than 68% of these have requested imidazolinone activity (Table 4), generally using canola as the target species (data not shown). These results may arise from 2 factors. Firstly, imidazolinone herbicides were introduced in Alberta relatively recently. Imazethapyr (Pursuit) was introduced to Alberta in 1995, followed by imazamox + imazethapyr (1:1) (Odyssey) in 1998. Secondly, imidazolinone and sulfonylurea herbicides may have extended residual activity under some conditions (Moyer 1995, Moyer and Esau 1996). Unknown herbicides (Table 4) frequently represent situations where a producer is renting, or planning to rent, land and has no cropping history to make recrop decisions. In these cases multiple target species and herbicides may be evaluated.

Symptoms consistent with herbicide soil residual activity have been found in approximately 77% of submitted samples (Table 5). In 52% of samples submitted, the target species showed some herbicide damage. In addition, 25% of samples showed damage to the sensitive species, but not the target species. The remainder of samples showed no symptoms to either the target or sensitive species. These results suggest that growers expecting soil residual activity are likely to find it.

Table 4. Herbicides tested for with residual bioassay since 1999.

Year	Herbicide Group										Total
	2				3	4	5	6	Picloram	Unknown	
	IMI	SU	IMI & SU	2,4							
1999	17	2	-	-	-	-	-	-	7	5	31
2000	23	4	5	-	-	4	-	-	-	12	48
2001	26	25	2	-	-	14	-	-	-	7	74
2002	69	26	9	3	3	3	1	-	1	1	116
2003	179	92	18	6	1	13	1	3	1	2	316
2004	69	29	-	4	1	10	1	-	-	1	115
Total[1]	383	178	34	13	5	44	3	3	9	28	700

[1] Excludes missing data and some samples submitted by industry.

Table 5. Presence or absence of symptoms consistent with herbicide residue for the residual bioassay since 1999. Symptoms in the target species were always associated with symptoms in the sensitive species.

Year	Symptoms Present		Symptoms Absent	Total
	Target species	Sensitive species only		
1999	16	5	4	25
2000	16	3	14	33
2001	20	20	18	58
2002	60	23	18	101
2003	130	70	54	254
2004	38	13	12	63
Total[1]	280	134	120	534

[1] Excludes missing data and some samples submitted by industry.

In conclusion, soil residual herbicide bioassays have both limitations and benefits. Limitations include that sampling may not adequately reflect whole-field variability. For example, agronomists and growers may sample in strips where overspray has occurred and a 2x concentration is present. Growing the sample out in a small pot or cup is not reflective of a field situation where roots have the opportunity to grow out of the herbicide layer. Additionally, samples can fall in a grey area where there is damage to the sensitive species, but not the target species. In this case reliable recommendations to growers may be difficult. Finally, when minor damage to the crop occurs, little is known about recovery and yield loss under different climatic and edaphic conditions.

Benefits of the bioassay are that whole-plant bioassays show biological effects of herbicides present, often at levels below chemical detection thresholds. They can be more useful than chemical detection methods due to interactions with soil organic matter, pH, soil moisture and soil texture. Finally, it is the only risk management tool available to growers at this time. Results from the bioassay should not be interpreted alone. Interpretation needs to include other tools and information such as label recommendations, rainfall restrictions, pH, organic matter, soil texture, and perhaps most importantly, grower and agronomist experience.

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Development of a grower-friendly bioassay to determine the potential effect of imazethapyr residues in soil on vegetable crops

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A plant bioassay is a simple, inexpensive, accurate and direct method to determine if it is safe to grow crops in soil treated with known herbicides or in soils with an unknown history of herbicide use. A greenhouse, grower-friendly, bioassay, to detect imazethapyr residues in the rotation was developed. Imazethapyr was applied to soybean in 2001, 2002, 2003 at 0X, 1X and 2X rates of application. Cole crops were planted in the spring and fall of 2002, 2003 and 2004. At planting, soil samples were collected and used to conduct a greenhouse bioassay to detect imazethapyr levels in this soil, using sugar beet. Imazethapyr residue in the field caused injury and reduced yields in all plantings. The severity of injury and yield reductions declined over time. In the greenhouse, sugar beets showed injury and plant growth reduction at all sampling dates. Greenhouse results were compared to growth of sensitive crops (e.g. cauliflower) in the field. Plant growth reductions in the greenhouse were related to yield reductions in the field. The greenhouse bioassay was capable of detecting imazethapyr residues in the field that could cause injury and yield reduction to cole crops more than two years after imazethapyr application to soybean. The extent of sugar beet growth reduction in the greenhouse can be used to predict yield potential in the field. The greenhouse bioassay helps to predict potential herbicide residue problems so a grower can make better decisions about crop rotation, herbicide selection, planting date and other cultural practices. If the bioassay results are correlated with field results and field variability is accounted for in sampling, bioassays can be effectively used to predict follow crop injury.

Additional Keywords: bioassay, imazethapyr, sugar beet, herbicide residue, rotation

Introduction

Herbicide persistence is an important consideration in crop production since residue levels of some herbicides can persist to the next growing season and may injure sensitive crops in the rotation (Jensen et al. 1995; Leuschen and Getting 1996; Moyer and Esau 1996). Residues of some herbicides persist in the soil for long periods. Extremely small amounts of residues can be devastating to some crops that are planted in the following year. Herbicides vary in their potential to persist in the soil. Persistence is dependent on herbicide characteristics (method of degradation, water solubility and rate of application) and site characteristics (soil type, rainfall and temperature). Drought conditions in the year prior to planting rotational crops result in higher levels of herbicide carryover and consequently more injury to the crops grown in the rotation (Mangels 1991).

Recent herbicide introductions for field crops, especially soybeans (*Glycine max* L Merr.), have found significant use in weed control programs (Krausz et al. 1992). These herbicides are particularly attractive because of the high activity that allows them to be used at very low rates of application (g ha^{-1} rather than kg ha^{-1}). In addition, the mode of action of these herbicides is to inhibit an enzyme [acetolactate synthase (ALS)] found in plants. They, therefore, have very low mammalian toxicity. The herbicides are also tightly bound to the soil making it virtually impossible for the herbicide to leach into groundwater thus reducing any potential environmental hazards, an increasingly important goal in the development of all new herbicides. The favourable toxicological profile, low mammalian toxicity and environmentally friendly nature of these herbicides make them extremely valuable tools in agriculture (Hart et al. 1991). While these herbicides provide substantial benefit to growers and also to the environment, it is also important to recognize the potential for wide-scale carryover problems with these herbicides (Cantwell et al. 1989; Goetz et al. 1990; Leuschen and Getting 1996).

The importance of managing herbicide applications to prevent problems with herbicide residues in the rotation cannot be overemphasized. Damage to high value susceptible crops can result in a considerable economic loss to growers. Herbicide carryover from persistent herbicides has been a particular problem to growers of fruit and vegetable crops (O'Sullivan et al. 1998). There has been concern about imidazolinones persistence since they have long residual activity in the soil. Imazethapyr, an imidazolinone, has persisted to injure corn in the year following application (Curran et al. 1991). A number of fruit and vegetable crops are affected by imazethapyr residues in the rotation also. Results from trials conducted to determine the effect of imazethapyr residues on some vegetable crops showed that these crops could not follow soybeans in the rotation where imazethapyr has been applied at the label rate (O'Sullivan et al. 1998). This effect may carryover into the second year. Imazethapyr currently has strict rotational cropping restrictions. Winter wheat (*Triticum aestivum* L.) can be planted in the season of application after 120 days. Only soybeans, corn (*Zea mays* L.), spring barley (*Hordeum vulgare* L.) and spring wheat can be planted in the following year. All other crops cannot be planted for two years.

One method used to determine if injurious herbicide residues might exist in the soil is to conduct a bioassay (Hager and Sprague 2002). A bioassay is the measurement of a biological response by a living organism to determine the presence and/or concentration of a chemical in a substrate (Santelmann 1997). A bioassay uses susceptible plants to identify if the herbicide is present in concentrations high enough to inhibit germination or growth. This technique can be used to determine if herbicide residues are present in soil at high enough concentrations to adversely affect crop growth, yield and quality. A bioassay is unique in that it measures plant susceptibility, unlike a chemical assay (Santelmann 1997). Chemical detection identifies a substance not biological activity. Herbicide concentrations alone may not allow predictions of herbicide phytotoxicity in the soil (Hance 1987). Bioassays are conducted by growing species of plants known to be sensitive to specific herbicide or class of herbicides in the sample soil. This is a simple and direct method to determine if it is safe to seed or plant into areas treated with herbicides (Stek et al. 1989). Crop response to herbicide residue depends on various factors including species and variety, soil type and environmental conditions after planting.

Predicting crop injury is often difficult. This is due to soil spatial variability which results in an non-uniform distribution of herbicide residues across the field and in depth (Hance 1987). However, a bioassay can help in deciding whether a potential problem exists and in choosing the appropriate crop or variety. There is a great need to develop simple bioassay methods that facilitate the early field detection of herbicide residues (Hall et al. 2000). The objective of this research project was to develop rapid, easy, economical and reliable bioassay for the detection of imazethapyr residues in soil.

Materials and methods

Field experiments

Imazethapyr was applied preemergence, to soybeans after planting, in the spring of 2001 at 1X (100 g a.i. ha^{-1}) and 2X rates (200 g a.i ha^{-1}). This crop was grown to maturity and harvested in the fall of 2001. In the spring of 2002 a sensitive rotation crop, (cauliflower, *Brassica oleracea* L.) was planted into this site. Plots were replicated four times in each of the three treatments, 0X, 1X, and 2X application rates of imazethapyr. At the same time, soil samples were collected for the bioassay study. The effect of imazethapyr residues on the cauliflower was monitored by way of injury ratings and final yield. A late planting of cauliflower was made approximately August 1, 2002. Further collection of soil samples was taken at that time for the bioassay. The extent of imazethapyr residues on this crop was also monitored by way of injury rating and yield. In the spring of 2003 cauliflower was again planted into this site and soil samples were again collected for the bioassay study. A late planting of cauliflower was made approximately August 1, 2003. Further collection of soil samples was taken at that time for the bioassay. The extent of imazethapyr residues on these crops was also monitored by way of injury rating and yield. This sequence was repeated in 2002, 2003 and 2004.

Greenhouse bioassay

Labelled, double, styrofoam cups (237 ml) were filled with 205 g of treated soil, collected from the field at the time of planting of cauliflower. Each 237 ml cup received 180 g of soil, 15 seeds of sugar beet (*Beta vulgaris* L.) (a highly sensitive crop to imazethapyr residues) and another 25 gm of soil to cover the seeds, as described by Hall et al. (2000). A known volume of water was added to each cup until the soil was saturated with moisture. Soil samples from each treatment (0X, 1X and 2X of imazethapyr) were replicated six times. The cups were placed in flat plastic trays to which a known amount of water was added to bring the soil to field capacity. Depending on the temperature in the greenhouse, water was added as required to keep the soil at 80% field capacity.

Immediately after planting, the cups were covered with plastic and placed in the dark. Once germination began, the plastic was removed, supplemental lighting was turned on. Light intensity was at 500 umol/m^2/s. Temperature was kept at approximately 24°C by day, 16°C by night. The photoperiod was 16 hours light and eight hours dark. Each cup was thinned to five sugar beet plants, about 10 to 12 days after planting. Emergence was recorded and the cups were fertilized weekly. Harvesting took place 26 days after planting. A visual rating system of the shoots was made to determine injury as compared to the controls. The plants from each cup were removed from the soil and washed to remove soil from the roots. The shoots and roots from each cup were removed, separated from each other and placed in separate envelopes. The envelopes were placed in a drying chamber set at 55-65C° for 48 hours and then dry weights were measured and recorded. Data was analyzed by appropriate ANOVA and means separated by a protected LSD test. The injury noted with the sugar beet plants in the greenhouse bioassay was compared to the injury in the field on the cauliflower crop. Regression analysis was performed to determine best fit for the relationship between sugar beet injury in the bioassay and cauliflower yield reduction in the field. These experiments were repeated over two years so that different soil types with different characteristics from different locations were included in the bioassay.

Results and discussion

Imazethapyr at 1x and 2x application rates resulted in severe crop injury and reduced yields one year and two years after application to soybean (Table 1). The greenhouse bioassay also showed significant injury to sugar beet as well as reduced plant dry weight. To use bioassays to predict the risk of injury to follow crops, bioassay results from soil samples were correlated with field grown injury to cauliflower (Figure 1). At lower levels of injury, the sugar beet bioassay in the greenhouse was more sensitive than cauliflower in the field. At high levels of injury this relationship did not hold. Sugar beet injury less than 20% had no effect on cauliflower yield. Injury at 60% resulted in a 40% cauliflower yield reduction.

At greater than 25% sugar beet injury, cauliflower yield reduction can be expected. There is likely considerable species variation. If injury occurs to bioassay test-plants, then the potential exists for significant field crop injury, if the crop grown is sensitive to that particular herbicide. Imidazolinone herbicides affect root and shoot growth and development (Hart et al. 1991). Symptoms of plant injury includes inhibited root development, stunted plants and interveinal chlorosis or leaf striping. Bioassay plants should be grown for 21 to 25 days. Depending on the type and concentration of residues, injury symptoms usually appear within 10 to 12 days after plant emergence. The approximate concentration of herbicide residues in the soil is estimated by comparing the test plants with standard dose response curves. By setting the risk threshold for unacceptable crop injury at a relatively low level (<25%) an underestimation of field crop injury risk by a bioassay species can be prevented. For other crop species this bioassay may over estimate the risk of injury in the field. This illustrates the conservative nature of the predictions made with the bioassay, a desired characteristic when those data are used to predict the risk of follow crop injury.

Table 1. The effect of residual imazethapyr on field-grown cauliflower and greenhouse-grown sugar beet.

	Field (Cauliflower)		Greenhouse (Sugar beet)	
Imazethapyr rate	Injury (%)	Yield (t/ha)	Injury (%)	Dry Weight (mg/plant)
		Year One - 2002[a]		
0 X	0	16.4	0	335
1 X	44	6.7	92	27
2 X	84	0.9	97	11
LSD(0.05)	45.7	12.2	9.3	5.1
		Year Two - 2003[b]		
0 X	0	18	0	146
1 X	39	12.6	33	98
2 X	50	12.8	62	55
LSD(0.05)	46.3	10.2	0.6	42.7
		Year One - 2004[a]		
0 X	0	36.1	0	107
1 X	38	16.3	90	14
2 X	83	1.3	98	6
LSD(0.05)	7.6	11.6	0.6	6.9

[a] One year after imazethapyr application to soybeans.
[b] Two years after imazethapyr application to soybeans.

Some herbicides are biological active below the level of detection. The bioassay measures the biological activity of the herbicide especially the phytotoxic portion of the herbicide. By conducting a bioassay, growers can save time and money. The bioassay can help predict potential crop injury. The test is inexpensive and can be done with a few simple supplies. A bioassay does not measure the amount of herbicide residue presents in the soil. A bioassay is not 100% accurate in predicting herbicide residue problems but it can indicate whether or not enough residue is present to injure a sensitive crop. Soil sampling has a major influence. Predictions of crop injury are only as good as the sampling techniques. Adequate samples are required, taking into account the soil characteristics. High-risk areas should be sampled separately. Otherwise the risk of injury may be underestimated.

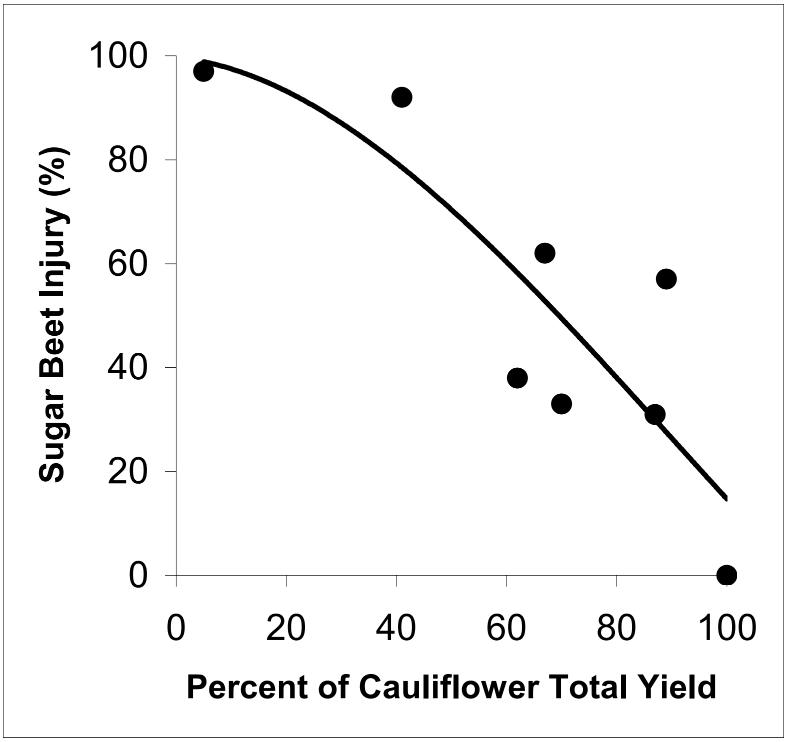

Figure 1. Relationship between sugar beet injury (in bioassay) and field grown cauliflower yield reduction

The potential for imazethapyr to injure sensitive crops in the rotation depends, not only on the imazethapyr application rate but also on soil pH, soil organic matter, rainfall in the year of application and soil texture. All of these factors affect the rate of imazethapyr breakdown in the year of application. An effective bioassay will eliminate these variables and identify the potential for injury in the rotation crops. This grower-friendly bioassay will help determine which vegetable crops, commonly grown in rotation with corn or soybeans, can be grown without injury and yield effects following imazethapyr application in prior years. Identifying the magnitude of imazethapyr residues in the soil prior to planting sensitive vegetable crops in the rotation will help to minimize economic losses due to imazethapyr residue damage. It will allow crops to be planted in the rotation that are not affected by the magnitude of the residues present at planting and clearly identify those crops that are and thus allow growers to take appropriate strategies to avoid any residue problems with these crops. This information can be used to change the cropping restrictions that are currently on the label for this herbicide, based on the sensitivity/tolerance of the crops grown. The goal is to be able to determine the extent of imazethapyr residues in any soil prior to planting sensitive crops in the rotation.

Bioassays can also be used to estimate herbicide concentration in soil and to identify unknown herbicide residues from the injury symptoms. Bioassays should be conducted when seeding or planting into an area previously treated with herbicides known to be residual, such as imazethapyr, and when using land with an unknown history of herbicide use. A bioassay is especially valuable when investigating field complaints where sampling often follows the appearance of injury. When a newly seeded or established plant shows unexplained symptoms of injury, stress, or decline, a bioassay is also warranted. If the suspected herbicide contaminant is unknown, a broad range of crop species is grown to help identify the culprit.

Summary

A bioassay is a simple, economical and accurate way to determine if herbicide residues are present at high enough concentrations to affect seedling growth, emergence or development. The greenhouse bioassay helps to predict potential herbicide residue problems so the grower can make better decisions about crop rotation, herbicide selection, planting date and other cultural practices. Sugar beets were a sensitive indicator of injury risk to field -grown cauliflower with a comfortable safety margin. If the bioassay results are correlated with field results and soil spatial variability is accounted for in sampling (Hance 1987), bioassays can be effectively used to predict follow crop injury. This project demonstrated that a bioassay is an economical and accurate way to determine if herbicide residues are present at high enough concentrations to affect seedling growth, emergence or development. In this way, imazethapyr-type herbicides can be used in agriculture by learning to manage the residue problems that they present.

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Residual herbicides: An integral component of weed management systems in Eastern Canada

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Soil applied residual herbicides have been an integral part of weed management systems in Eastern Canada for decades. They provide effective control of a wide range of annual grass and broadleaf weed species plus control of selected winter annual, biennial and perennial weed species. Weed control with soil applied residual herbicides is affected by weed species composition, environmental conditions, soil type, soil pH, and application timing. Crop tolerance with soil applied residual herbicides is affected by environmental conditions, soil type, soil pH, application timing, and hybrid/variety selection. One concern with the use of soil applied residual herbicides is injury to subsequent crops in rotation. Weed management practitioners must be aware of the injury potential to subsequent crops and adjust their herbicide selection accordingly. One of the primary benefits of soil applied residual herbicides is weed control early in crop development when yield losses due to weed interference is the greatest.

Additional Keywords: residual herbicides, weed control, crop injury, preplant incorporated herbicides, preemergence herbicides, postemergence herbicides

Introduction

Residual herbicides provide control of weeds present at the time of application and weeds germinating and emerging after application. They have been an integral component of weed management systems in field and horticultural crops in Eastern Canada for decades. One of the primary benefits of soil applied residual herbicides is that they provide weed control during the early part of the growing season when crop yield losses due to weed competition are the greatest. In addition, soil applied residual herbicides provide control of some weed species for which there are no effective postemergence applied herbicide alternatives. This is especially true in some horticultural crops where there are a limited number of registered herbicides.

Soil applied residual herbicides can be classified into those which primarily provide control of annual grasses or annual broadleaves and those which have activity on both annual grass and broadleaves. Examples of soil applied residual herbicides that provide primarily annual grass control include dimethenamid, EPTC, flufenacet, pendimethalin, S-metolachlor, and trifluralin. Those with primarily annual broadleaf weed activity include atrazine, cloransulam-methyl, dicamba, flumetsulam, linuron, mesotrione, and metribuzin. Imazethapyr and isoxaflutole have activity on both annual grass and broadleaf weeds. Generally, soil applied residual herbicides do not provide control of perennial grass and broadleaf weeds, however there are exceptions such as yellow nutsedge (*Cyperus esculentus*) which is effectively controlled with soil applied applications of dimethenamid and S-metolachlor. There are three accepted application timings for soil applied residual herbicides: preplant, preplant incorporated, and preemergence. Preplant applications are made prior to planting and left on the soil surface. This application timing is used primarily in reduced and no-till crop production systems but is also frequently used in stale seedbed weed management crop production systems in horticultural crops. Preplant incorporated herbicides are applied prior to planting and incorporated into the soil with a secondary tillage implement. A double disc or cultivator with rolling basket harrows are the most common implements used for incorporation. Preemergence herbicides are applied after planting the crop but before the emergence of the crop and weeds. The application timing of soil applied residual herbicides affects both the level of weed control and the degree of crop injury.

Weed control

Each soil applied residual herbicide has a defined spectrum of weeds that it controls. For optimal control with soil applied residual herbicides it is imperative that weed control practitioners scout and keep accurate records of the weed species composition in each field from previous years. The weed species composition must be known because the herbicides are applied before weed seedling emergence. The activity of the selected herbicide must match the weed spectrum in each field. In addition, crop advisors must have a thorough knowledge of weed biology for successful weed control with soil applied residual herbicides. Herbicides with long residual activity must be used for control of weeds that germinate for an extended period such as fall panicum (*Panicum dichotomiflorum*) and proso millet (*Panicum miliaceum*). Pendimethalin provides better full-season control of the above weeds than EPTC because it has longer residual activity in the soil. Similarly, dicamba does not provide full-season residual control of velvetleaf (*Abutilon theophrasti*) due to its relatively short residual activity in the soil, while mesotrione provides season long control of velvetleaf. Conversely, some weed species are not effectively controlled with the currently registered soil applied residual herbicides in some crops. The annual grasses, fall panicum, proso millet, and sandbur (*Cenchrus spp*.) are more effectively controlled in corn (*Zea mays* L.) with postemergence herbicides than the currently registered soil applied herbicides. Also, the perennial grasses, quackgrass (*Elytrigia repens*) and wirestem muhly (*Muhlenbergia frondosa*), and almost all perennial broadleaves are controlled more effectively with postemergence herbicides. The herbicide rate should be adjusted depending on the weed species composition. For example, the low rate of imazethapyr provides excellent control of species such as redroot pigweed (*Amaranthus retroflexus*), Eastern black nightshade (*Solanum ptycanthum*) and wild mustard (*Sinapis arvensis*). In contrast, the high label rate is recommended for weed species such as common ragweed (*Ambrosia artemisiifolia*) and common lamb's-quarters (*Chenopodium album*). The rate of soil applied residual herbicides should be adjusted dependent on weed density. The S-metolachlor label recommends that the highest rate be applied in fields with high weed densities. Liphadzi and Dille (2001) reported 88, 24, and 20% giant foxtail (*Setaria faberii*) mortality with isoxaflutole at 20, 50, and 100 seeds m^{-2}, respectively.

Weed control with soil applied residual herbicides is affected by environmental conditions. Most soil applied residual herbicides provide better weed control if there is adequate soil moisture. The herbicide must be dissolved in soil water solution so that the developing weed seedling can absorb the herbicide while it is taking up water to support plant growth and development. During periods of low soil moisture, weed control with most soil applied residual herbicides is reduced. If extremely dry conditions persist, weed control can be improved through a light cultivation or rotary hoeing to uproot small emerged weed seedlings and to activate the herbicide. Rainfall shortly after application moves the herbicide into the soil thereby reducing losses due to photodegradation and volatilization. Improved weed control with herbicides such as dimethenamid, pendimethalin and S-metolachlor is obtained if rainfall moves the herbicide into the soil to reduce losses by photodegradation. In contrast, too much rain after the application of a highly water soluble soil applied herbicide can leach the herbicide below the weed seed germination zone resulting in reduced levels of control. Reduced levels of control of velvetleaf with dicamba and common ragweed with linuron has been observed in seasons with excessive rainfall.

The level of weed control with soil applied residual herbicides is affected by soil type, organic matter content, cation exchange capacity, and soil pH. Soils with high clay content, high organic matter content and high cation exchange capacity bind herbicides making them biologically unavailable for uptake by developing weed seedlings. The rate of soil applied residual herbicides must be adjusted depending on soil type, organic matter content, and cation exchange capacity. For example the recommended rate of trifluralin is 600 g ai ha^{-1} on sandy textured soils and 1155 g ai ha^{-1} on clay textured soils. On extremely high organic matter content soils most applied residual herbicides are not recommended since the herbicide is bound so extensively that it results in reduced levels of weed control. Soil pH affects the metabolites formed in the soil. At low soil pH the triazine herbicides form a cation in the soil which is more readily bound by the negatively charged clay and organic matter fraction in the soil. This results in reduced levels of weed control. Conversely, at high pH the triazines form a negatively charged ion in the soil which is repelled by the soil colloids making the herbicides more biologically available for uptake by developing weed seedlings resulting in improved weed control. Similarly, flumetsulam forms a more active metabolite in high pH soils resulting in improved weed control. In a study conducted by Kegode (2001), flumetsulam provided 45, 85, and 100% control of biennial wormwood (*Artemisia absinthium*) on soils with pH's of 5,4, 6.5, and 7.8, respectively.

Time of application with soil-applied residual herbicides can affect weed control levels. For example, the control of yellow nutsedge with dimethenamid and S-metolachlor is improved when it is applied preplant incorporated compared to preemergence. In contrast, Eastern black nightshade control with the same herbicides is improved when it is applied preemergence compared to preplant incorporated. With imazethapyr, lamb's-quarters control is improved with soil applied applications while common ragweed control is better with postemergence applications. For some weed species, such as spreading atriplex (*Atriplex semibaccata*) and prickly lettuce (*Lactuca serriola*) in conventional soybeans (*Glycine max* L. Merrill) it is imperative that they be controlled with a tankmix of glyphosate plus a soil-applied residual herbicide since there are no effective postemergence herbicide options for the control of these weed species after the crop has emerged.

Care must be exercised with preplant herbicides that have relatively short residual activity to not apply them too far in advance of planting the crop. When dicamba, which has relatively short residual activity, is applied three weeks prior to planting corn, it effectively reduces the residual weed control in the crop by about the same length of time. This may result in the requirement of an additional in-crop postemergence herbicide to control late-emerging weeds. Conversely, with some preemergence herbicides, it is important that they be applied before the weeds emerge because weed control decreases rapidly after weed emergence. Control of small-seeded annual broadleaf weeds such as lamb's-quarters, redroot pigweed, and common ragweed with dimethenamid, pendimethalin, and S-metolachlor decreases rapidly after these weed species have emerged.

Herbicides that are susceptible to photodegradation and volatilization, such as the dinitroanilines and thiocarbamates, should be uniformly incorporated immediately after application. A delay in incorporation will result in reduced efficacy.

One of the advantages of the use of soil applied residual herbicides is the control of weeds early in crop development when yield losses due to weed interference can be dramatic. In sixteen studies conducted by Hamill and Sikkema from 2000 to 2002 (unpublished) yield losses of 50.2 kg ha^{-1} day^{-1} occurred in soybeans if herbicide application was delayed until after the second trifoliate stage. In twenty studies conducted by Hamill and Sikkema from 2000 to 2003 (unpublished) yield losses of 29.2 kg ha^{-1} day^{-1} occurred in corn if herbicide application was delayed until after the first leaf stage. In four studies conducted by Sikkema (unpublished data) in corn and soybeans the use of preemergence herbicides programs resulted in yields comparable to postemergence herbicide programs. Effective weed control with soil applied residual herbicides protects the yield potential of the crop from yield losses due to early weed competition.

Crop injury

Environmental conditions affect the tolerance of crops to soil applied herbicides. Heavy rainfall after the preemergence application of dicamba, isoxaflutole or pendimethalin in corn may move the herbicide into the seed zone of the crop resulting in greater herbicide uptake and a corresponding increase in crop injury. Rainfall when dry beans (*Phaseolus vulgaris* L.) are cracking through the soil surface results in greater uptake of dimethenamid and S-metolachlor and greater crop injury. With a preemergence application of linuron in soybeans, heavy rainfall after soybean emergence may result in splash injury and severe necrosis of the lower leaves. Furthermore, a heavy rain after planting may result in soil crusting thereby delaying crop emergence and increased potential for injury from soil applied residual herbicides. Extremely dry conditions at the time of EPTC application in dry beans results in greater binding of the herbicide to the soil colloids which may be released later in the season resulting in increased injury. Growers are advised to delay dry bean planting by ten days under extremely dry conditions if EPTC was applied preplant incorporated. Cold, wet conditions after seeding increases the time for germination and crop emergence and increases the potential for injury from soil applied residual herbicides. The crop does not begin active plant growth as quickly and it cannot metabolize the herbicide resulting in greater crop injury. Under cold and wet conditions increased injury had been observed from dimethenamid, flufenacet, isoxaflutole, and S-metolachlor in corn, from dimethenamid, flufenacet, metribuzin, and S-metolachlor in soybeans, and from imazethapyr and S-metolachlor in lima bean (*Phaseolus lunatus* L) (McNaughton et al. 2004).

Selection and rate of soil applied residual herbicides must be adjusted according to soil type, organic matter content, cation exchange capacity and pH due to the possibility of crop injury. Soils with low clay content, low organic matter content and low cation exchange capacity do not strongly bind herbicides and this results in increased herbicidal activity and the potential for greater levels of crop injury. For example, the use of isoxaflutole for weed control in corn is not recommended on light textured sandy and loamy sand soils due to the increased potential for crop injury and yield loss. Dicamba is only recommended for weed control in corn on medium to fine textured soils with greater than 2.5 % organic matter because injury may occur on coarse textured, low organic matter content soils. The rate of metribuzin for weed control in soybeans must be adjusted from 560 to 1120 g ai ha^{-1} depending on the soil texture and pH. Complete crop loss has occurred on light textured, high pH soils with the high rate of metribuzin. Soil pH affects the metabolites formed in the soil. At low soil pH the triazine herbicides form a cation in the soil which is more readily bound by the negatively charged clay and organic matter fraction in the soil. This can result in greater crop safety. Conversely, at high pH the triazines form a negatively charged ion in the soil which is repelled by the soil colloids making it available for absorption by the developing crop seedlings. This can result in greater crop injury. It is for this reason that metribuzin and flumetsulam are not recommended for weed control in soybeans on soils with pH greater than 7.5 and 7.8, respectively.

Crop safety with soil applied residual herbicides is affected by application timing. The tolerance of processing peas (*Pisum sativum* L.) with S-metolachlor is greater when it is applied preemergence versus preplant incorporated. In a study conducted by Sikkema and Lambregts (1995), there was 8 and 1 % visual crop injury in processing peas when S-metolachlor was applied preplant incorporated and preemergence, respectively. There was a corresponding decrease in yield of 0.5 t ha^{-1} with the preplant incorporated application. In contrast the tolerance of dry beans to dimethenamid, imazethapyr, and S-metolachlor is greater when these herbicides are applied preplant incorporated versus preemergence. Similarly, there is a greater margin of crop safety in white beans to flumioxazin when it is applied preplant incorporated versus preemergence. The preplant incorporated and preemergence application of flumioxazin resulted in 2 and 17% visual crop injury, respectively, in white beans seven days after white bean emergence. There was no yield loss in white beans when flumioxazin was applied preplant incorporated, but there was a yield loss of 0.3 t ha^{-1} with the preemergence application (Soltani et al. 2005).

The rate of some soil applied herbicides must be adjusted depending on the crop or market class grown. The maximum registered rate for imazethapyr in soybeans is 100 g ai ha^{-1} while in dry beans it is 75 g ai ha^{-1}. It has been documented in numerous studies that the margin of crop safety with imazethapyr in soybeans is greater than in dry beans and therefore the higher recommended label rate in one crop might not be acceptable in other crops. The rate of soil applied residual herbicides may even need to be adjusted depending on the market class, hybrid or variety within a crop species. The maximum rate of flumioxazin where there was no yield loss was 70 g ai ha^{-1} in white and black beans while it was safe to apply up 140 g ha^{-1} in cranberry and kidney beans (Soltani et al. 2005).

A knowledge of hybrid/variety sensitivity to soil applied residual herbicides is necessary to minimize crop injury and maximize crop profitability. Severe crop injury has been observed in some hybrids/varieties with some registered soil applied herbicides. Many seed corn companies have identified hybrids that are sensitive to soil applied Group 4, 15 and 27 herbicides. Similarly, many soybean seed companies have identified varieties that are sensitive to soil applied Group 5 herbicides. The tolerance of dry beans to soil applied herbicides such as flumioxazin, imazethapyr and linuron is market class specific. In studies conducted in Ontario cranberry and kidney beans have a greater margin of crop safety to flumioxazin, imazethapyr and linuron than do black and white beans (Soltani et al. 2004, 2005).

Seeding/transplanting techniques affect crop injury with soil applied herbicides. The crop must be seeded to a minimum depth to reduce the potential for the herbicide to move into the seed zone of the crop. There are minimum seeding depth recommendations on the labels of a number of herbicides. For example, in corn the minimum seeding depth when isoxaflutole and dicamba are being used is 4 cm. Similarly in soybeans the minimum seeding depth when linuron is being used is 4 cm. The tolerance of transplanted tomatoes (*Lycopersicon esculentum* L.) to preplant incorporated herbicides is improved if the transplants are set at least 10 cm deep. In contrast, seeding too deep increases the time for the crop to emerge and begin active plant growth. This may result in greater injury from soil applied residual herbicides especially if it is compounded by cool, wet conditions after seeding. Proper seed furrow closure after seeding ensures that the herbicide does not come in direct contact with the seed after preemergence applications. Isoxaflutole injury in corn is increased if there is poor seed furrow closure.

Crop rotation

One of the concerns with the use of residual herbicides is the potential for carryover injury to subsequent crops in rotation. The length of time a residual herbicide is present in the soil at concentrations that will cause injury to rotational crops (the recropping interval) is affected by degradation and transfer processes (Weber et al. 1973), which, in turn, are dependent upon climatic factors, soil factors, and the physicochemical properties of the herbicide. Degradation of residual herbicides occurs primarily by: 1) chemical decomposition, which includes oxidation, reduction and acid hydrolysis, and is primarily affected by rainfall, temperature and soil pH (Cheng and Lehman 1985); 2) biological decomposition, which includes microbial degradation (Cheng and Lehman 1985) and breakdown by higher plants; and 3) photodecomposition of residues left on the soil surface (Monaco et al. 2002). The primary transfer processes likely to influence injury from herbicides applied in a previous year are: 1) adsorption to soil colloids, which is affected by the base ion exchange capacity of the soil (soils in North America typically have a net negative charge, and therefore will bind cations), organic matter and clay content [organic matter and clay increase herbicide adsorption levels (Weber 1987), which reduces herbicide carryover], 2) leaching, or the downward movement of herbicide molecules that are not adsorbed onto soil particles. Herbicide leaching is primarily a function of soil texture, the solubility of the herbicide in water, and the amount of water moving through the soil at a given time (Weber 1972), 3) volatilization, which occurs when the herbicide vaporizes and is lost to the atmosphere or moves through pore spaces in the soil, and 4) surface runoff, which may occur during heavy rainfalls that carry the herbicide laterally over the soil surface away from the treated area also influence herbicide persistence (Baker et al. 1995; Weber 1972). There have been detailed reviews of herbicide degradation (Kearney and Kaufman 1988) and transfer processes (Hunnicut and Schabacker 1994). Here, we present a few examples commonly observed today to demonstrate how these factors influence the potential for herbicide residues to cause injury to subsequent crops in rotation.

Climatic factors, especially cool temperatures and low precipitation have a significant impact on the microbial degradation of a range of herbicides of varying chemistries, such as the imidazolinones, triazolopyrimidines, dinitroanalines, triazines, carboxylic acids, diphenylethers, callistemones, and isoxazoles (Vencill 2002). Cool weather conditions (i.e. below 15°C) reduce metabolism of soil microorganisms enough to significantly reduce their ability to break down organic substrates, including organic herbicides, while temperatures between 20 and 30°C are considered optimal for microbial metabolism (Monaco et al. 2002). For example, under controlled conditions, an increase in soil temperature from 15 to 30°C increased dissipation of imazathepyr two-fold in non-sterilized soil (Flint and Witt 1997). Similar changes in rate of degradation in response to temperature have been shown for pendimethalin, (Zimdahl et al. 1984), isoxaflutole (Beltran et al. 2003), and several other residual herbicides (Walker 1987). Dry soil conditions will reduce the ability of soil microbes to degrade herbicide residues by reducing microbial activity and survival, and reducing the amount of herbicide present in the soil solution (Anderson 1981). Microbial degradation of isoxaflutole (Taylor-Lovell et al. 2002) and imazethapyr (Flint and Witt 1997) was faster in soil maintained at less negative levels of water potential, such that as soil moisture levels approached 75% field capacity, the half-lives of these herbicides were two- or three- times shorter than when soil was maintained at permanent wilting point. Degradation of triallate (Anderson 1981), pendimethalin (Zimdahl et al. 1984) and DCPA (Choi et al. 1988) also increased as moisture levels increased. For example, high value crops, such as sugar beet (*Beta vulgaris* L.) are sensitive to residues of field crop herbicides such as imazethapyr (O'Sullivan et al. 1998). One consideration that growers and agronomists must consider when using residual herbicides, is how weather conditions will affect herbicide degradation. The potential for carryover injury is greater following a cool, dry year, and should be considered when selecting rotational crops.

Soil factors, such as pH and organic matter, also have an impact on herbicide degradation and/or movement in the soil. Soil pH affects carryover of the sulfonylurea, imidazolinone, triazolopyrimidine, and triazine herbicides differently.

Sulfonylurea herbicides such as chlorimuron, are more persistent in high pH soils, because their breakdown is primarily by non-microbial acid hydrolysis, which decreases when pH is greater than 7.0 (Kearney and Kaufman 1988). Chemical hydrolysis and microbial degradation are both important in the dissipation of atrazine, however atrazine is more persistent at pH 7.5-8.0. At high pH, atrazine molecules are less likely to become cations, so they not strongly adsorb to soil particles (Best et al. 1975), and cannot undergo degradation by either mechanism. As a result, the herbicide is more available for uptake by crops grown later in the rotation. Soil pH and organic matter can interact to influence herbicide carryover, as in the case of the imidazolinone (e.g. imazethapyr) and triazolopyrimidine (e.g. flumetsulam) herbicides (Lehmann et al. 1992). Imazethapyr and flumetsulam adsorption decreases as pH increases, and increases as organic matter increases, which reduces their availability to soil microbes, and therefore makes each herbicide more persistent in acidic soils (especially below pH 5.8) that are high in organic matter (Stougaard et al. 1990; Shaw and Murphy 1997). Accordingly, injury caused by herbicide residues may be accentuated in those fields with extreme pH levels and high organic matter (Greenland 2003), and should also be taken into consideration when planning crop and herbicide rotations.

Summary

Soil applied residual herbicides are an integral component of current weed management programs in Eastern Canada. They provide control of annual grass and broadleaf weeds in field and horticultural crops. The early weed control provided by soil applied residual herbicides reduces weed interference and minimizes crop losses due to weed competition. Weed management practitioners should combine the use of soil applied residual herbicides and non-residual postemergence herbicides to provide effective long-term weed management strategies and ensure the long-term effectiveness of all these essential weed management tools.

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Managing soil residual herbicide use in Western Canada

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Introduction

Residual herbicides have been used in western Canada since the early 1960's, with the release of soil- applied herbicides such as triallate Avadex™, EPTC ™ and trifluralin Treflan™. In the 1980's and 1990's, sulfonylureas (SU's) such as chlorsulfuron Glean™, metsulfuron methyl Ally™, triasulfuron Amber™, were introduced as a key management tool for difficult to control broadleaf species. The first introduction of a Group 2 grass herbicide was imazamethabenz Assert™, an imidazolinone (Imi) herbicide registered in 1988 for control of wild oats in cereal crops. Group 4 herbicides with residual properties were also registered for use in canola and cereal crops: clopyralid Lontrel™ and quinclorac Accord™. Both herbicides provide control of a unique spectrum of weed species; clopyralid for Canada thistle (*Cirsium arvense* (L.) Scop) control in canola and quinclorac for cleavers (*Galium aparine* L.) and green foxtail (*Setaria viridis* (L.) Beauv.) control in cereals. Two other imidazolinones, imazethapyr Pursuit™ and imazethapyr/imazamox Odyssey™ were introduced for control of grass and broadleaf weeds in field peas, revolutionizing weed control in this non-competitive crop. The release of the Smart Canola™system, an imidazolinone tolerant canola now known as the Clearfield™ system, extended the use of residual herbicides into widely grown broadleaf cropping systems. Additional residual herbicides were released over this time-frame: sulfosulfuron Sundance™ and flucarbazone sodium Everest™. By 2000, there were numerous residual herbicides options used in all the major crops in western Canada. The challenge for growers and agronomists then became how to integrate these valuable weed control products into their complex and diverse cropping systems.

Benefits of residual herbicides

Residual herbicides can be used effectively to provide season-long weed control. Weeds that emerge throughout the season, such as chickweed (*Stellaria media* L.), green foxtail (*Setaria viridis* (L.) Beauv.) and cleavers (*Galium aparine*

L.) have been serious weed issues for crop production in western Canada. The introduction of herbicides with soil residual properties ensured the suppression of weed emergence throughout the growing season, in addition to providing a high level of weed control. These products effectively eliminated the need for a follow-up application in-crop. Residual herbicides also provided the additional benefit of offering continued weed suppression in non-competitive crops or crops that are slow to close the canopy. Furthermore, the introduction of these residual products provided alternative herbicide Groups in crops where very few choices previously existed, an example being the introductions of Odyssey/Pursuit in field peas. In perennial crop stands and in chemical fallow systems as well, this extended weed control is a considerable benefit (ACE™ Specialist Agricore United – personal communication).

In the late 1990's, many agronomists were challenged by inquiries from growers who used herbicides with residual characteristics several years in a row in the same field. It was apparent that the growers using these products did not have a good understanding of the recropping restrictions associated with them. In the early 2000's, drought challenged our understanding of the dynamics of herbicide carryover. The label guidelines that were used in the past were effective but were brought into question under these extremely dry conditions. Further complicating the issue was the diverse crop rotations that included many species highly sensitive to many of the residual products available in the market place.

When applied at recommended rates, most herbicides break down within a few days or weeks after application and impose no restrictions on cropping options the next year. Some residual herbicides, however, do not degrade as quickly and can persist in the soil for weeks, months or years following application (Curran 1998). These residues can limit the choice of crops that can be grown in rotation. Growers initially did not anticipate any concerns that might result from the extensive and frequent use of these residual herbicides on their farm. It became apparent that growers and agronomist needed to better understand the factors that influence carryover and breakdown so they could assess risk and determine the appropriate follow crop. More importantly, they needed to understand how these factors could be used to predict the risks for herbicide carryover. If the possibility of herbicide carryover was suspected, knowing the appropriate sampling procedures and testing required would assist in determining and minimizing herbicide carryover for future crop planning.

Factors affecting herbicide carryover

Herbicide factors

The herbicide used, the time of application and in some cases the soil factors can influence the extent of the residual carryover. It is well understood that herbicides differ in their physical and chemical properties such as water solubility, volatility and susceptibility to breakdown by sunlight and microbes. Herbicides are classified into Herbicide Groups based on their mode of action. Commonly used persistent herbicides used in western Canada are in Groups 2, 3 and 4. Persistence within these herbicides Groups can vary from a few days to several months. Their method of breakdown also ranges from simple chemical reactions to more complex microbial degradation (Table 1).

Table 1. Soil characteristics that influence the persistence of the most commonly used residual herbicides in Western Canada. Source: Vencill 2002 - Herbicide Handbook 8th edition Weed Science Society of America 2002.

Herbicide Family	Group	Trade Name	Breakdown	Soil Factors increasing persistence
Sulfonylureas	2	Ally	hydrolysis	>pH 7.5
	2	Muster	hydrolysis	>pH 7.5
	2	Sundance	hydrolysis, microbial	< 4% OM >pH 7.5
Imidazolinones	2	Pursuit, Odyssey, Absolute, Adrenalin, Assert	microbial	<pH 7.0
Sulfonylamino	2	Everest, K2	microbial	< 4% OM >pH 7.5
Dinitroaniline	3	Edge, Advance, Treflan, Fortress, Heritage, Rival	microbial, photodegradation	OM
Phenoxy	4	2,4 D	microbial	n/a
Benzoic acid	4	Banvel, Dyvel	microbial	n/a
Carboxylic acid	4	Absolute, Curtail M, Eclipse, Lontrel, Prestige, Prevail, Spectrum	microbial	n/a
Quinaline carboxylic acid	4	Accord	microbial	n/a

Although the principles of herbicide degradation were well understood, basic knowledge of the implications of herbicide carryover by the user was not.

The patterns of use of these residual products further reinforced the need for awareness of the factors influencing carryover and recropping restrictions. Knowledge of these factors could then be used to develop a crop rotation that utilized the benefits of residual herbicides while effectively managing the recrop restrictions.

Microbial decomposition

Soil bacteria, algae and/or fungi metabolize some herbicides. This action is enhanced by conditions that favour the growth and multiplication of microorganisms. Warm, moist, fertile soil favours the growth of the soil microorganisms and as a result stimulates breakdown of certain herbicides (Figure 1). Most of the residual herbicides used in western Canada are degraded by microbes in the soil environment (Moyer and Coen, 1999).

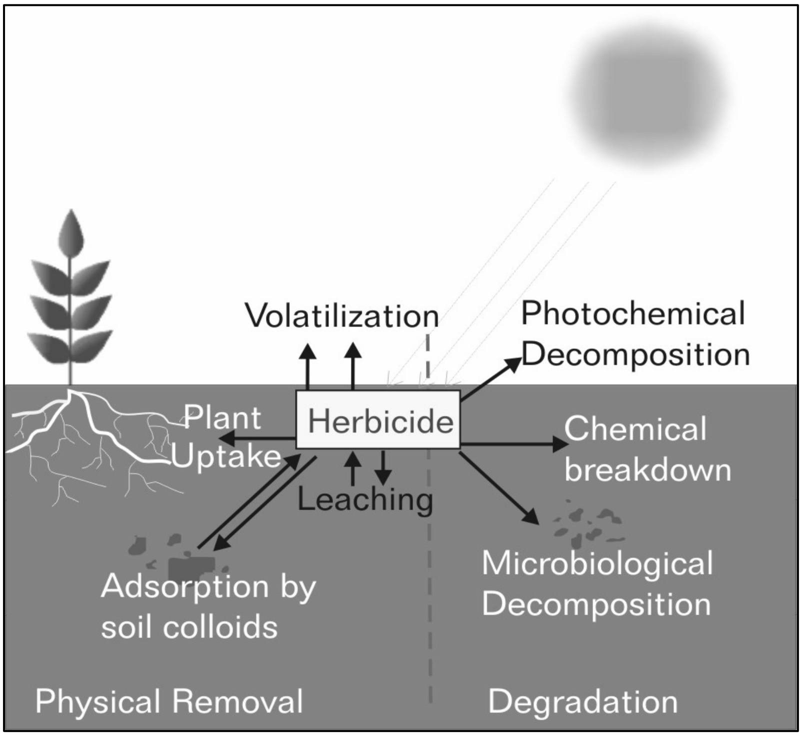


Figure 1. Summary of the factors contributing to the herbicide dissipation.

Chemical degradation and photodecomposition

Some herbicides may react with water or other chemicals in the soil, affecting their herbicidal activity. For example, the sulfonylureas (SU) chemically react with water in a process called hydrolysis. Once the SU is in contact with water, the chemical breakdown is initiated until eventually the herbicide is no longer biologically active (Moyer 1995).

Some herbicides will degrade when exposed to sunlight or ultra-violet light on the soil or leaf surface. These include trifluralin, ethalfluralin and the cyclohexanediones (Poast, Achieve, Select). Specific management strategies such as soil incorporation and the use of effective surfactants minimize the impact of photodegradation.

Plant uptake

Plants play a role in the physical removal of herbicides. They will intercept some foliar herbicide application before it reaches the soil, and depending on species, the plant may metabolize and inactivate the herbicide. Species, size and density are important factors here. A herbicide that remains active in or on the plant, such as picloram (Tordon), may be removed from that field when the crop is harvested.

Soil moisture is the critical factor influencing all forms of degradation. As agronomists working in the field we needed predictors that would assist in recommending recropping options in the context of the growing season conditions. Although label guidelines assisted in this consultation process it was evident that they were inadequate under the more extreme climatic conditions experienced in 2002, and 2003. Record drought was experienced in most locations in western Canada, and the implications and subsequent effect on recropping were not well understood (Moyer and Essau 1996). It was in this context that a strategy to forecast herbicide risk due to moisture conditions was developed (personal communication Clark Brenzil, Weed Specialist, Saskatchewan Agriculture, Food and Rural Revitalization).

Climatic factors

Moisture

All herbicides bind to soil particles and organic matter (OM) to some degree. The strength and extent of the binding will affect the persistence and carryover of the herbicide in the soil. Soil factors such as moisture, pH and OM significantly affect the adsorption of herbicides in the soil (Devlin et al. 1992). Binding of the herbicide to soil particles increases as moisture content decreases and is particularly important for herbicides that are usually weakly adsorbed. Under dry soil conditions the herbicide is bound to the soil and unavailable for breakdown. When soil moisture increases, some of the herbicide will dissolve into solution and become available for breakdown.

The more water-soluble the herbicide is, the more readily it can break down or leach in the soil. While high solubility in water can reduce the potential for herbicide carryover, other factors such as biological activity and persistence influence the recrop restrictions (Hill et al. 1998).

So how can we use this scientific knowledge to build a forecast of herbicide carryover risk? Some pesticide manufacturers attempted to describe risk of carryover to a specific location by utilizing the percent of normal precipitation figures. Although this was a good attempt at risk assessment, the choice of years considered normal for precipitation would affect the forecast. For example should the last 5, 10, 20, or 30 years be taken into consideration?

Field investigations of herbicide carryover illustrated a stronger correlation between total accumulated rainfall and the incidence of injury to sensitive crops (Brian Wintonyk, Dow AgroScience pers. comm.). The total accumulated precipitation assessed covered the period from early to mid-June, to the end of August. These timeframes were considered representative since herbicide applications usually occur in June, and most microbial degradation would occur during that time as soils were warmest. A risk map was developed to determine the areas that would be affected. The original maps were developed for Saskatchewan by Clark Brenzil, Weed Specialist with Saskatchewan Agriculture, Food and Rural Revitalization, and were then extrapolated for western Canada. The ranges were established as Extreme (<75 mm rainfall), Very High (<100 mm rainfall), High (<125 mm rainfall) , Moderate (<150 mm rainfall), and Normal (>150 mm rainfall). Based on these guidelines, 2003 precipitation data would indicate significant risk for 2004, while moisture conditions in 2004 would indicate a low risk for carryover into 2005 (Figure 2). However, moisture is only one factor to consider in identifying a risk of carryover, as other climatic factors such as temperature, and soil factors such as soil pH and organic matter (OM) need to be considered.

Soil temperature

In addition to soil moisture, soil temperature influences herbicide breakdown. Herbicide residue will disappear more rapidly when the soil is warm (>15 C). Early freeze up in the fall and late spring thaw reduce the time available for herbicide breakdown and can result in increased herbicide carryover.

Soil temperatures in 2004 were very cool and may be a factor contributing to herbicide carryover into 2005, especially in Manitoba where temperatures were well below normal throughout the growing season. Field experience with this particular climatic factor is not well documented.

Soil factors

Several soil factors are important in determining the persistence of a herbicide. The great variability in such factors as pH, OM and even texture within a field or field-to-field, challenge the decision-making process regarding recrop selection.

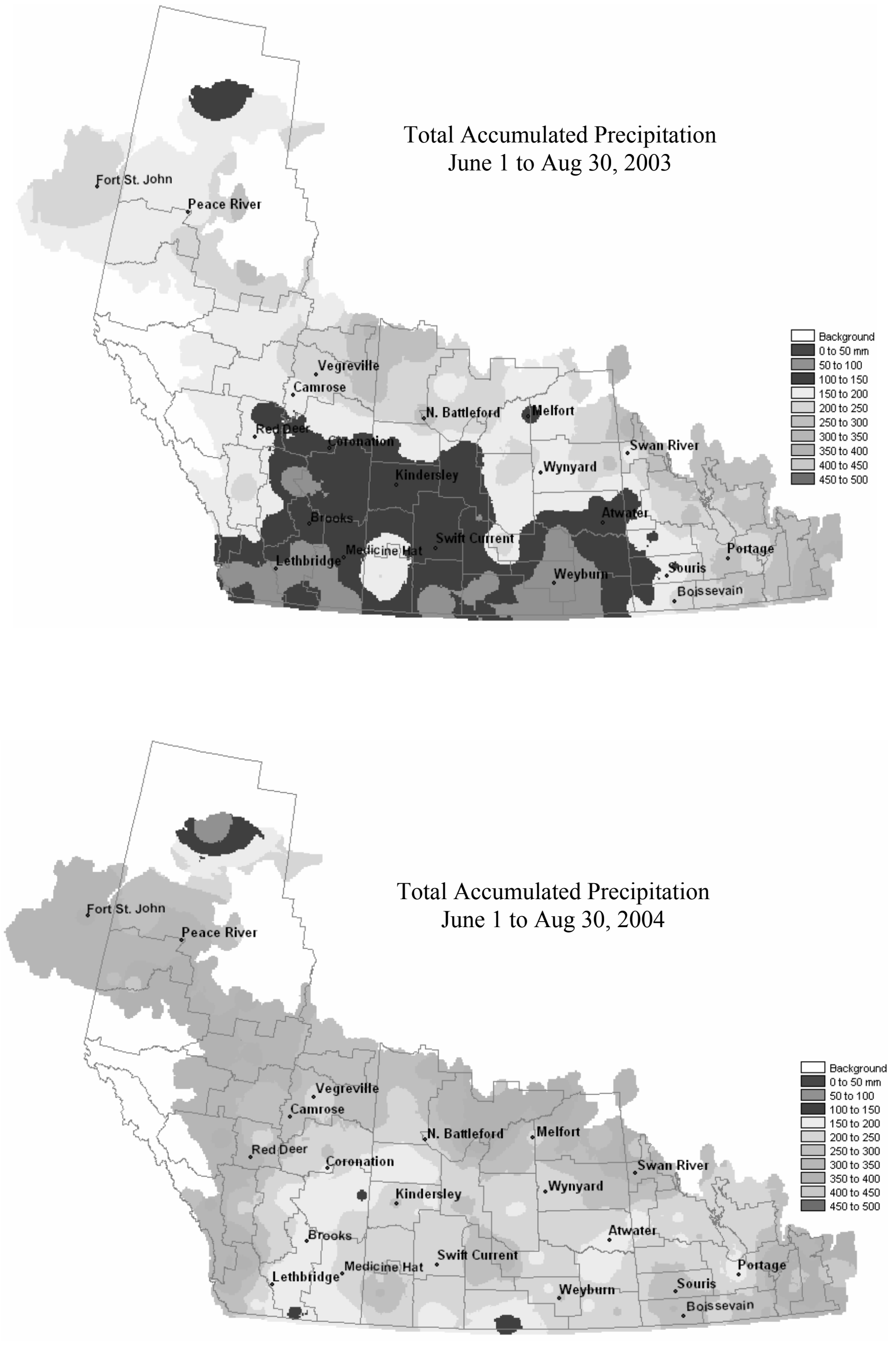


Figure 2. Total accumulated precipitation June 1 to Aug. 30, 2003 and 2004. Source: Canadian Wheat Board, Winnipeg, MB.

Soil pH

The pH of the soil solution is a critical factor in the breakdown of certain herbicides. Soil pH may cause herbicide degradation directly by affecting the stability of the herbicide, or indirectly by its effect on the soil microbes. Many Group 2 herbicides are affected by soil pH in this respect. The sulfonylurea (SU) herbicides (Refine Extra™, Ally™, Express™, Muster™) break down more quickly in acid soils, hence persisting longer in high pH soils (> pH 7.0). The imidazolinones break down more readily in alkaline soils and therefore persistence is increased in low pH (< pH 7.0) soils (Loux and Reese 1993). Two newer herbicides, Sundance™ and Everest™ react similarly to the SU herbicides where higher pH leads to longer persistence

Soil test results should theoretically be an excellent tool to assist in managing herbicide residues in relation to soil factors. This is only somewhat the case, because growers do not routinely request soil pH as part of a standard soil sampling procedure, and the majority of growers in western Canada do not soil sample their fields. Although soil pH maps give a general overview of pH values for a given area, these figures are not sufficient for an individual grower to know and understand pH values on a field by field basis. Furthermore, the standard depth of sampling for a soil test of 0-6 inches or 0-12 inches does not reflect the potential for carryover in the top 3 inches of the soil, where most residual herbicides are located. A study was initiated by Westco at three locations in Alberta to examine pH and OM factors, how they differed by depth in the soil profile, and how they influenced the persistence of commonly used residual herbicides (Table 2). In 2003, the first year of the study, Pursuit and Odyssey were applied. At the locations tested, it was observed that the pH values varied by depth, and lower pH values were observed at the 0-3 inch depth. These 0-3 inch values would more accurately reflect the soil pH that would influence herbicide carryover. Although the numeric value differences in pH recorded in this study may seem low to a grower, they can be significant since pH is measured on a logarithmic scale.

Organic matter

Organic matter (OM) can absorb large amounts of herbicide, so the lower the OM, the more biologically active the herbicide residue will be. Organic matter binds herbicide and slowly releases it. In addition, soil rich in OM supports microorganisms that play a critical role in the degradation of most herbicides. Unfortunately only 50% of all soil tests submitted by growers include a request for OM assessment. This figure is very low, if we also note that less than 15% of agricultural land in western Canada is soil sampled annually (personal communication, Brandon Green, EnviroTest Labs, Calgary). Results from the Westco study indicated that OM values changed dramatically with soil depth. The top 3 inches of the soil tended to have a higher OM level than the 3-6 inch depth (Table 2). Thus, sampling depth can significantly influence the soil test results for both pH and OM. When conducting crop diagnostics for herbicide carryover it is advisable to separate the soil samples according to depth, and this would provide a more accurate assessment of pH and OM values where the herbicide residues are found.

Table 2. Soil pH and organic matter at various depths through the soil profile at three locations in Alberta. Data from unpublished study conducted by R. Karamanos, D. Poisson, D. Maurice, Westco 2003.

Location Alberta	Depth (inches)	Organic Matter (%)	pH	Texture
Olds	0-3 3-6	9.8 7.4	7.1 7.4	Loam Loam
Torrington	0-3 3-6	8.3 4.3	5.1 5.7	Loam Clay/Loam
Trochu	0-3 3-6	5.7 4.8	7.0 7.3	Clay Clay

Soil texture

The relative percentage of sand, silt and clay in a soil determines its texture. Clay particles provide extensive amounts of surface area that can adsorb significant amounts of herbicide. Thus in clay soils, some herbicide residues tend to be less severe. Since water tends not to move as fast or as deep in clay soils, the potential for herbicide leaching is also diminished. In sandy soils, herbicide leaching is more significant since less herbicide can be bound in the soil. It is unclear how soil texture influences the persistence of soil residual herbicides in western Canada.

Integrating climatic and soil factors to predict carryover

According to the risk factors outlined in the previous section, it was predicted that the imidazolinone herbicides used on the sites in the unpublished Wetsco study had the potential to carryover into next season's crop. In 2004 at one of the study sites (Torrington), a significant reduction in wheat yields was documented in treatments where Imidazolinone herbicides had been applied (Table 3). This would suggest that an understanding of the moisture conditions, herbicide and soil factors can enhance the ability to forecast herbicide carryover risk.

Table 3. Integrating soil factors with rainfall June to September 2003 to predict the risk of herbicide carryover at three locations in Alberta. Data from an unpublished study conducted by R. Karamanos, D. Poisson, and D. Maurice, Westco. 2003.

Location in Alberta	Depth (inches)	Organic Matter (%)	pH	Texture	Rainfall 2003 (mm) Herbicide Carryover Risk
Olds	0-3 3-6	9.8 7.4	7.1 7.4	Loam Loam	101.6 High – Very High
Torrington	**0-3** **3-6**	**8.3** **4.3**	**5.1** **5.7**	**Loam** **Clay/Loam**	**97** **Very High** **Wheat yield loss recorded**
Trochu	0-3 3-6	5.7 4.8	7.0 7.3	Clay Clay	147.3 Moderate

Confirming the predicted carryover

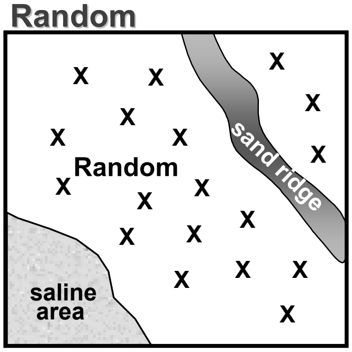
Plant bioassay

Agronomists have found that the use of plant bioassays can assist in advising the grower about recropping into suspected herbicide residues in soil, especially when other factors indicate that the grower may be at risk of injury to a given crop from herbicide carryover. A plant bioassay involves collecting soil samples from soil treated with residual herbicides in the fall or spring. The soil is sent to a commercial laboratory where a simple method is used to indicate whether it is safe to plant into areas previously treated with herbicides or into soil with an unknown history of herbicide use (Jourdan. et al. 1998). A bioassay helps in determining if herbicide residues are present in soil at concentrations high enough to adversely affect plant growth (Van Wyk and Reinhardt, 2001). It should be conducted before seeding into areas previously treated with residual herbicides, or when herbicide stacking is suspected, or when environmental conditions such as extremely dry conditions may cause herbicide residues to persist longer than normal. The plant bioassay should never be used to circumvent label recommendations.

Soil sampling for herbicide residue testing

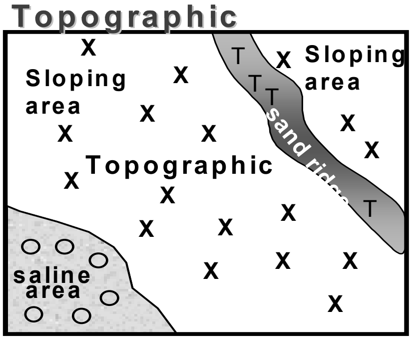
The goal in sampling for herbicide residues is to give an assessment of risk for the whole field or for “problem” areas. Herbicide carryover, as indicated earlier, is influenced by soil moisture, soil temperature, pH, organic matter and the herbicide use history. When sampling soil for herbicide residues, it is crucial that a sample be obtained that is representative of the area (field) (Hager and Nordby 2004). Organic matter, moisture and pH are quite variable within a field, often varying due to topographical features of the landscape. The soil sampling techniques listed below are appropriate for herbicide residue detection:

Random Soil Sampling: This is the most common sampling method. A minimum of 15 to 20 cores need to be collected from the entire area to obtain reliable estimates and it proves relatively accurate on fields of up to 80 acres that have been uniformly managed. Problem areas (saline spots, poorly drained areas, eroded knolls) should not be sampled unless they represent a significant portion of the field.



X= single probe site

Topographic Soil Sampling: This method involves dividing fields into several areas split by landscape position based on topography. When a field has 2 or more topographic areas, each area should be sampled with 15 –20 cores. Separate samples should be taken from: eroded knolls, field mid-slopes, and low areas with better moisture conditions. This may be a better sampling system for fields where the majority of the field is rolling. This is also a useful technique in detecting “hot spots” of carryover in the field.



X=probe sites from sloping areas
O=probe sites from saline area
T=probe sites from sand ridge

One or both of these sampling methods may be used on the same field, for example, submitting a random sample and topographic sample from the same field.

Planning and prevention

Growers should consider the herbicide rotation options when they plan a crop rotation. It is important in limiting the need to apply herbicides that may carryover in the soil in successive years. For example, it is not advisable to apply Sundance ™ or Everest ™ to soil treated with Odyssey the previous year. A crop rotation plan should take into account the best fit for residual herbicides. The grower needs to assess where residual weed control is needed the most, and explore other herbicide options in crops that do not require the residual activity. Choosing a herbicide with little or no carryover, given local soil and weather conditions, will minimize future crop injury problems. If herbicide residue is suspected, growers should grow a tolerant crop. For example, when Odyssey carryover is suspected beyond labelled levels, tolerant crops such as Clearfield canola should be grown. Growers should read the label for each herbicide used, to determine which crops can be safely seeded in rotation, and to determine the length of time before sensitive crops can be grown. They must also keep in mind that there can be differences in tolerance levels between varieties within a crop.

Summary

Soil residual herbicides are an important part of an overall weed management strategy. How these herbicides fit into a grower's crop rotation is a critical part of his or her planning process. Understanding the factors that influence persistence will assist in applying the appropriate management within the crop rotation. Understanding the soil factors that influence the persistence of the various active components will assist in minimizing the impact herbicide residues have on crop yield. There remains a need to further the awareness and communication on herbicide residue management by developing common terminology /usage and consistent use of precipitation data in determining risk. Clear, consistent labelling needs to be established so the growers can quickly and easily assess the fit of these residual herbicide products in their crop rotations.

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Deconstructing herbicide residue problems

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Introduction

A proper diagnosis of crop injury due to herbicide residues in the soil can be challenging. A diagnosis should be based on the facts collected during a thorough analysis of the field information and observations documented during a detailed field investigation. The diagnostic process requires that all potential causes of crop non-performance be considered and then eliminated one-by-one until the correct diagnosis is made. Crop damage caused by soil residual herbicides can often be confused with several other potential causes. Other potential causes of crop non-performance could include: nutrient deficiency, insect damage, herbicide drift, crop injury due to sprayer tank contamination, and adverse climatic or soil moisture conditions (either too wet or too dry). This paper will outline the diagnostic process in cases where crop injury is a result of herbicide persistence. Although the author's experience in performing field inquiries related to herbicide persistence is mostly limited to residual Group 2 herbicides and their effect on canola, many of the diagnostic concepts outlined below can be used for other crops and/or herbicide Groups.

Diagnosing herbicide residue problems

During the early stages of the diagnostic process the management practices used in previous seasons should be examined. The obvious questions to ask include, what crop is impacted and, of course, what crop protection products were applied this year and in previous years? If any of the previously applied products have residual properties it must be determined if they have activity on the current crop. It is also important to determine if the current crop has been grown within the labeled recrop guidelines for all products applied to the field. If recropping guidelines have been followed and crop injury due to herbicide persistence is suspected, a company representative should be contacted. Herbicide application history must go as far back as the recropping guidelines of the various products applied demand. Herbicide application histories may have to go back further in situations where the rate of herbicide degradation may have been impaired due to drought or soil properties (i.e. pH, soil texture and organic matter content)

When arriving at the field there is a tendency to go directly to the most affected part of the field and start making observations. Creating a simple map of the field, demonstrating where good and poor growth areas are located is beneficial. Before proceeding to the most severely injured areas, some field-scale observations need to be made. Do the injured areas appear in discernable patterns across the field? Do these patterns match the dimensions of the equipment used in the field? The soil persistent herbicide may have been applied one or more years previously so patterns would have to be matched to the equipment used in those years. In these cases, crop injury is most obvious in areas that have received more than a single dose of herbicide. These 'overlap' areas typically appear at the corners of the field where one end of the spray boom can remain stationary while negotiating the corners of the field. The 'headland' areas of the field may also have overlapped areas resulting in a staggered pattern of injured crop. Areas of crop injury can also be compared to areas that did not receive any herbicide application in previous years. These areas of missed application can be found around field obstacles such as utility poles, sloughs or in any area of the field that may have been missed due to operator error.

In some cases the injured areas of the field appear randomly with no apparent patterns associated with equipment. If there is no apparent pattern, determine if the injured areas seem related to topography or soil variability. In these situations it is important to have a working knowledge of soil characteristics that impact herbicide degradation as well as the pertinent soil properties of the field in question. For example, imidazolinone herbicides are often more persistence in soils with low pH. As a result, areas of lower soil pH may show increased levels of crop injury compared to areas of the field that have higher pH. Alternatively, sulfonylurea herbicides may persist longer in soils with high pH.

Observations regarding plant coloration and abnormal growth need to be identified in the affected areas of the field after field-scale observations have been made. Symptoms such as chlorosis, necrosis, reddening, purpling, damaged growing points, cupping of leaves, epinasty or swollen roots need to be matched to corresponding herbicide families in order to verify if the crop damage is actually caused by a soil persistent herbicide. Epinasty is often associated with phenoxy-type herbicides. This type of injury may be the result of a drift occurrence rather than herbicide residues. Information regarding neighboring crops and herbicides applied needs to be acquired to rule out herbicide drift. Swollen roots of cereal crops may be associated with the presence of dinitroanaline residues in the soil. Chlorosis may be due to sulphur or nitrogen deficiencies depending on whether or not it appears on older or newer leaves. Frost, insect or photosynthetic inhibitor herbicide damage (from either drift or soil residue) can cause both chlorosis and necrosis on crop plants. Nearby weather stations can provide information regarding temperatures and aid in determining if frost is a variable that could be considered in the diagnosis.

Sulphur and phosphorus deficiencies, frost, poor growing conditions, root disease and Group 2 chemistries (acetolactate synthase inhibiting herbicides) may all cause purpling or reddening of plants. Information regarding the amounts and types of fertilizers applied to the crop coupled with comparative soil samples from poor and good growth areas of the field need to be analyzed in order to determine if a nutrient deficiency is the cause of crop non-performance. Plant tissue analysis also provides supplemental information regarding crop nutrition. If poor climatic conditions are causing reddening or purpling of the crop, additional observations in neighboring fields with completely different herbicide application histories may confirm this diagnosis. Purpling of leaf tissue along with injured or reduced growth at the growing point (broadleaf crops) can be associated with Group 2 herbicide injury via persistence in the soil, herbicide drift or sprayer tank contamination. Application records from previous fields, in conjunction with patterns of crop injury in the field can help determine if crop injury is due to improper tank cleaning. Purpling of plants and injured growing points in broadleaf crops can also be caused by sub-lethal doses of glyphosate (Group 9) via physical drift. Documentation of nearby crops and herbicide applications on neighboring crops would be required to rule out drift as a cause for crop injury. Herbicide drift is usually observed as a wave-like pattern along one side of the field. Gusts of wind carry air-borne droplets further into the affected field resulting in these wave-like patterns.

Crop injury from herbicide drift (for either Group 2 or Group 9 herbicides) and sprayer tank contamination (usually for Group 2 herbicides) is often confused with injury caused by soil residuals of Group 2 herbicides. Plants growing in soils that contain residual herbicide are typically smaller at all stages of crop growth. Plants injured in a drift or tank contamination scenario may have normal (large) leaves up to the time of injury and subsequently exhibit symptoms on the newest growth. Injury patterns in the field could also resemble herbicide persistence damage, especially along the ‘headland’ of the field. As herbicide is being applied, herbicide residue remaining in the sprayer booms or nozzle filters can be released every time the sprayer begins applying herbicide.

Identifying the presence of susceptible weed species is also necessary when conducting a thorough crop injury diagnosis. Injury to susceptible weeds must be matched with the susceptibility they might have to certain residual herbicides. Comparing weed growth in injured and non-injured areas can provide valuable information for the diagnosis.

In order to determine if herbicide persistence is the primary cause of crop injury soil bioassays can be employed as a diagnostic tool. These were initially developed as a risk management tool, but have been successfully used to aid in diagnosis. Soil samples taken from both poor and typical growth areas, can be taken and sent to the Alberta Research Council in Vegreville, Alberta. Under controlled conditions, the crop in question and other sensitive species (determined by herbicide application history) can be grown in the submitted soil samples and any injury is then observed and documented. Bioassay results, along with soil pH and organic matter values, are valuable diagnostic tools for determining if there is a herbicide residue in the soil and whether soil characteristics have contributed to the reduced degradation of the previously applied herbicide.

Summary

The process of diagnosing crop injury problems due to herbicide persistence in soil can be complex. Trying to assess every conceivable management, soil and climatic factor affecting crop growth may seem like an onerous task, but by using information gathered during the diagnostic process and asking the right questions to eliminate various factors as information is gathered the process can be simplified and a correct diagnosis can be made.