

**RUNOFF, PERSISTENCE, AND RUNOFF MODELLING**  
**OF**  
**BROMOXYNIL OCTANOATE, DICLOFOP-METHYL AND ATRAZINE**  
**FROM**  
**THREE MANITOBA SOILS**

**BY**  
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A Thesis  
Submitted to the Faculty of Graduate Studies  
In Partial Fulfillment of the Requirements  
for the Degree of

**MASTER OF SCIENCE**

Department of Soil Science  
University of Manitoba  
Winnipeg, Manitoba

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ISBN 0-315-77965-9

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## Abstract

A study was conducted to determine the losses of residues of the herbicides bromoxynil octanoate, diclofop-methyl and atrazine from treated fields through surface runoff. Field sites used had a runoff collection system in place. The plots had a 9% slope, were 22.1 m long and 4.6 m wide. Three sites were chosen for the experiment, near Miami, Roseisle and Whitewater Manitoba on Gretna clay, Leary sandy loam and Ryerson sandy clay loam, respectively. The active ingredients bromoxynil octanoate and diclofop-methyl were applied as Hoegrass II to the wheat plots and Aatrex, with the active ingredient atrazine, was applied to the corn plots. In addition to runoff samples, soil samples were taken following runoff events to determine the amount of each chemical remaining in the soil. Runoff samples from the plots were extracted with dichloromethane, derivatized by methylating, cleaned up on a Florisil column and analyzed by gas chromatography using either an electron capture detector or a nitrogen phosphorus detector. Total losses of these herbicides in the runoff water over a field season ranged from 0.05% to 0.83%. Highest losses of bromoxynil octanoate and atrazine in runoff were found from the Leary sandy loam. The highest losses of diclofop-methyl were from the Ryerson sandy clay loam.

Soil persistence of bromoxynil octanoate, bromoxynil, diclofop-methyl, diclofop acid and atrazine were determined at each of the three sites. Soil samples were extracted with acetonitrile and analyzed using gas chromatography. The loss of the readily hydrolyzed bromoxynil octanoate and diclofop-methyl was detected shortly after application to the phenol and acid form respectively. Persistence was greater at all sites for atrazine than for either of the other applied chemicals. Higher atrazine residues in the Leary sandy loam and the Ryerson sandy clay loam were found than in the Gretna clay.

Estimations of runoff losses of each of the compounds was determined using the Simulator for Water Resources in Rural Basins (SWRRB) runoff model. Although higher concentrations of pesticide loss were computed, observed trends between actual results and those through modelling were clearly visible.

## Acknowledgements

I thank G.R.B. Webster for acting as my supervisor and providing funding for this project. I thank C.F. Shaykewich for the use of his runoff plots and for his insight into soil factors used for modelling. I thank K.J. Friesen for helping with problems and giving me guidance whenever I asked. I thank D.C.G. Muir for continuous support and encouragement at every turn.

I extend great thanks to Bert Grift for giving me my first chance to work in this area, for the advice and use of equipment. I thank G.J. Racz for encouragement and support throughout my program of studies. Thank you, Len Sarna for all your helpful suggestions. I thank C. Ford and T.B. Goh for the use of imperative equipment, help and encouragement. A special thank you is extended to A. Hargrave and R. Wright for all the help in the field with sampling and set up of the plots. I thank R. Ellis, J. Hicks and K. Kort for the technical help provided.

Without the help and support from Mark Segstro, this project would have been extremely difficult. Thank you for all the help and laughter.

I would like to take this opportunity to thank my family for all the support that they have given to me through the years. I thank my husband, Jim, and my parents for listening, and for all the moral support they have given to me.

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## List of Abbreviations

ACN - Acetonitrile

DCM - Dichloromethane

ECD - Electron Capture Detector

GC - Gas Chromatograph

GC/ITD - Gas Chromatograph with an ion trap detector

GC/MS - Gas Chromatograph with a mass selective detector

ITD - Ion Trap Detector

LD<sub>50</sub> - dose required to kill 50% of the test subjects

NPD - Nitrogen Phosphorus Detector

RBF - Round Bottom Flask

## Introduction

Large amounts of herbicides are used throughout the world for weed control. It is very difficult to group herbicides into one category of compounds, with different chemicals targeted at specific types of weeds. Some herbicides used in agriculture today are considered non-persistent but exhibit high mammalian toxicity (e.g., bromoxynil octanoate LD<sub>50</sub> for rats is 130 mg/kg) (Worthing and Hance, 1991), while others are persistent under field conditions.

Persistent compounds are studied under field conditions to establish their lifetime within soil and their potential to cause contamination of non-target areas. Residues of persistent herbicides may limit crop rotation. Non-persistent herbicides are sometimes also lost from the target area through surface runoff. Potential leaching of pesticides and volatilization are among possible routes for contamination of non-target areas. Non-persistent compounds have been studied for efficacy and effects to non-target organisms (Lish and Thill, 1988; Kidder and Drummond, 1988; Peregrine and Norris, 1988). Properties of the herbicides used in the present experiment are found in Table 1.

Table 1: Physical and Chemical Properties of the Three Herbicides under Examination (Anonymous, 1989)

	Atrazine	Bromoxynil	Diclofop Methyl
Molecular Wt. (g/mol)	215.69	276.91	341.20
Vapor Pressure (Pa @ 20°C)	$4 \times 10^{-5}$	$<1 \times 10^{-3}$	$3-4 \times 10^{-5}$
Water Solubility (mg/L)	70	130	50
log Kow	2.68 <sup>1</sup>	2.60 <sup>1</sup>	6.22 <sup>1</sup>

<sup>1</sup> Dao et al., 1983

Runoff losses from agricultural fields may be a low percentage of that applied, however the concern rises with increase in use. Pesticide runoff losses equal to 0.5% of applied are found from most commercial formulations (Leonard, 1988), which does not seem very large. When a given compound is applied over a large area, runoff losses become a source of concern. In certain agricultural areas, specific crops are often grown, based on weather conditions and soil types. If there is a specific herbicide available to control weeds, without adverse effects to the crop, this chemical will be widely applied. Even though the percent loss does not increase, the total mass of herbicide lost from treated fields in the area goes up with use.

The present work focussed on two non-persistent herbicides (bromoxynil octanoate and diclofop-methyl) and one that had been studied at great length because of its persistence over a wide range of conditions (atrazine). Because of the contamination of aquifers in several areas where atrazine has been used extensively (Cohen *et al.*, 1988; Creeger, 1988), the persistence of this triazine herbicide has been studied in many soil environments. Runoff studies with atrazine have been performed in the U.S. corn belt (Klaine *et al.*, 1988; Rhode *et al.*, 1981; Triplett *et al.*, 1978). In each of these experiments, runoff events occurring soon after application produced the highest concentrations of atrazine in the runoff. Maximum losses detected in these experiments were 5.7%, however most field trials found total atrazine losses to be <1%. By using atrazine in the present field experiments a comparison to other results was made possible.

The two non-persistent compounds studied bromoxynil octanoate and diclofop-methyl, are known to undergo hydrolysis of the ester linkage in field soils (Gaynor, 1984; Smith 1977). In each case degradation occurs within a few days to a week (Smith, 1981). For this reason, the work on these chemicals generally has been focussed on efficacy and effect on non-target plants (Nalewaja and Skrzypczak, 1985). Work in Manitoba has shown presence of the hydrolysis products of these chemicals in river water

(Muir and Grift, 1987). Bromoxynil persistence in soil and water had not been studied, however, Brown *et al.* (1985) found that runoff losses of bromoxynil octanoate were not a high percentage of what has been applied to the fields. But, because bromoxynil had been shown to be toxic to rats (Worthing and Hance, 1990) and bromoxynil and diclofop has been detected in Manitoba streams (Muir and Grift, 1987), a study to determine herbicide loss in runoff water was undertaken. A maximum concentration of 71  $\mu\text{g/L}$  of bromoxynil was detected in runoff water which was considered non-hazardous to mammals and fish, Brown *et al.* (1985). However, because of the usage pattern in the prairie region this compound required study.

Bromoxynil octanoate (3,5-dibromo-4-octanoyloxy-benzonitrile) (Figure 1), a substituted nitrile, is found in the commercial formulations Bucril M and Hoegrass II (Anonymous, 1990). The butanoic ester was withdrawn from the Canadian market in 1989 because of its teratogenicity (CAPCO, 1988). Formulations such as Torch are no longer available because of the presence of bromoxynil butanoate. Tank mixes of bromoxynil octanoate are now available with other active ingredients such as MCPA and diclofop-methyl (Anonymous, 1990). Bromoxynil octanoate is also available on the market in two other formulations: Laser and Pardner. Bromoxynil is a non-selective, broadleaf herbicide which acts as a metabolic inhibitor (Ware, 1980).

Work on the persistence of diclofop-methyl has been carried out in eastern Canada and in Saskatchewan. The ester has

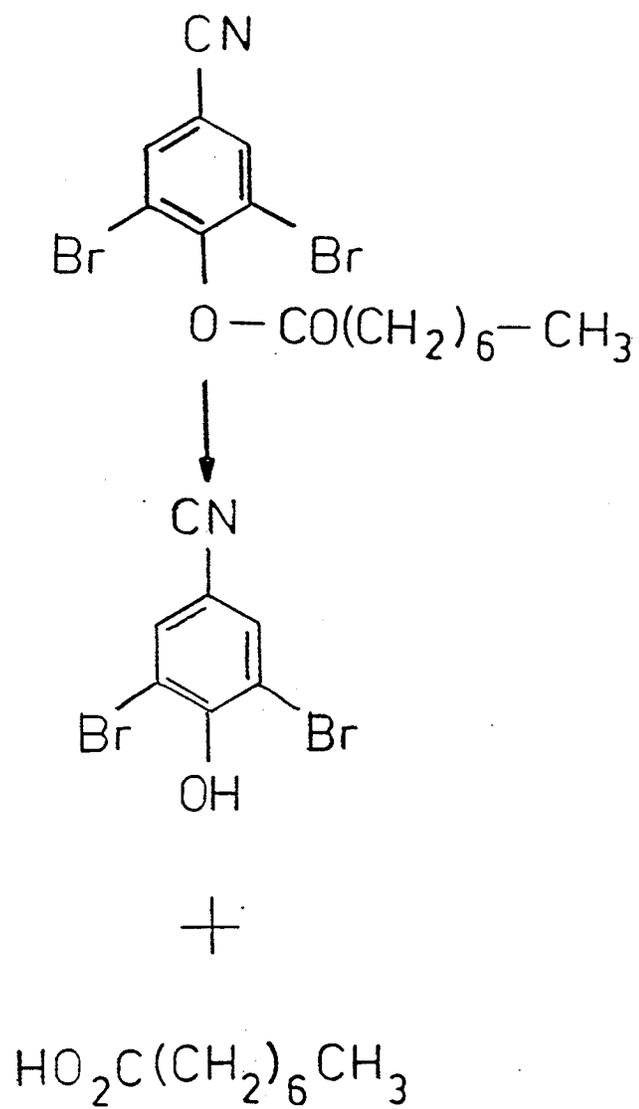


Figure 1: Bromoxynil octanoate undergoes hydrolysis to bromoxynil + octanoic acid in soil

been shown to degrade rapidly with a slower rate of degradation occurring for diclofop acid (Gaynor, 1984). Diclofop-methyl (methyl 2-[4-(2',4'-dichlorophenoxy)] phenoxypropionate) is a phenoxyalkanoic acid herbicide. It is formulated with bromoxynil octanoate in Hoegrass II or as the only active ingredient in Hoegrass 284 (Anonymous, 1990). Diclofop-methyl, like bromoxynil octanoate, is rapidly degraded to diclofop acid under field conditions, (Gaynor, 1984; Smith *et al.*, 1977), (Figure 2). Smith (1977) reported 90% of the applied diclofop-methyl was hydrolyzed to diclofop acid in 24 h. Diclofop-methyl, a broadleaf herbicide, is an auxin-like agent causing elongation and distortion of weeds until the plant collapses (Ware, 1980).

Atrazine, (2-chloro-4(ethylamino)-6-(isopropylamino)-s-triazine), has proven to be a persistent herbicide under Canadian conditions. The half-life of atrazine, based on a first order dissipation is 60 days (Helling *et al.*, 1988). This limits crop rotation possible, after use of this triazine. Because of the contamination of river systems and watersheds (Coote *et al.*, 1982; Pereira and Rostad, 1990; Wu, *et al.*, 1983) in areas with extensive atrazine use the persistence of this triazine has been studied in many soil environments. By using atrazine in the present field experiments, a comparison to other results was made possible. Atrazine is available on the commercial market

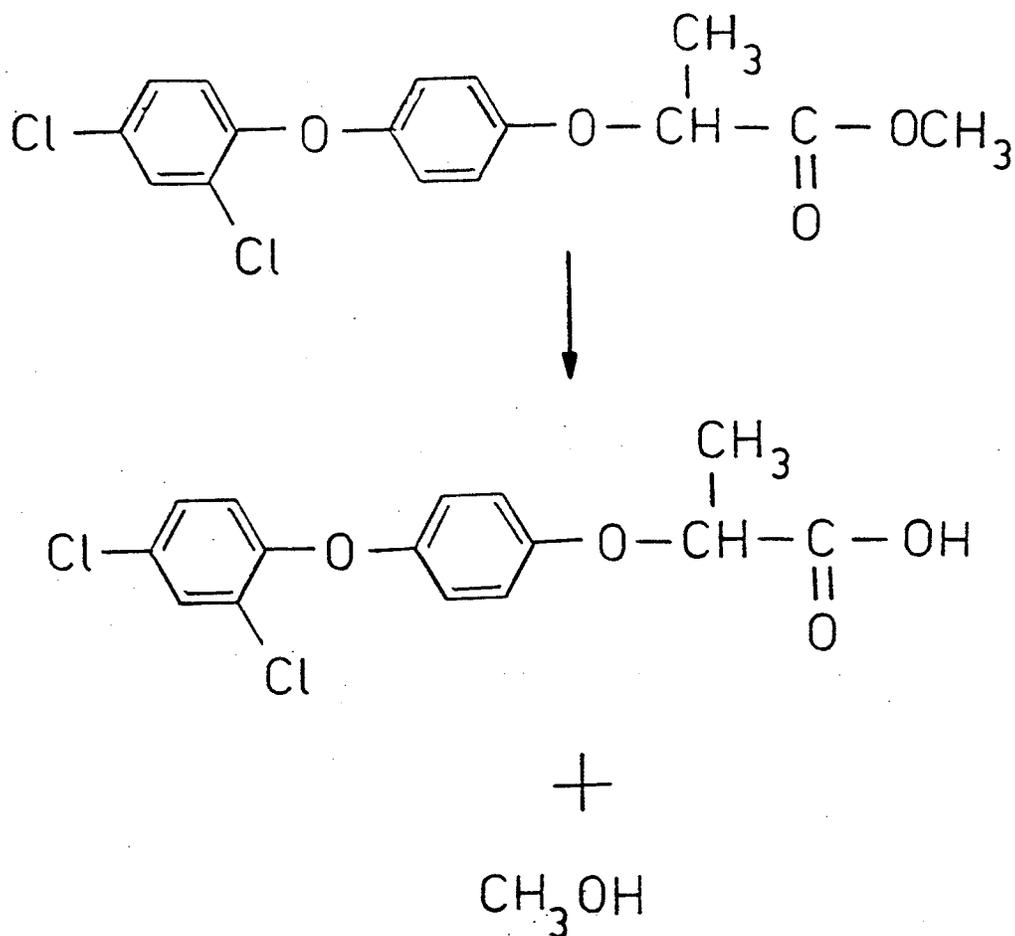


Figure 2: Diclofop methyl degrades to diclofop acid + methanol

in many formulations as the only active ingredient as well as in formulations with several other herbicides.

Agricultural land draining into river systems has led to concern over contamination of the water by pesticides.

Coote *et al.*, 1982) sampled water draining into the Great Lakes Basin. Atrazine, endosulfan and PCBs were detected in the drainage water. The highest levels of each of these compounds was found during the growing season, between May and August.

In Maryland, alachlor and atrazine are applied to corn as tank mixes. Runoff samples collected from areas draining into the Rhode River system, were found to contain both of these chemicals. Despite alachlor application levels being higher than those of atrazine, concentrations of the latter herbicide in runoff were consistently higher than the alachlor levels (Wu *et al.*, 1983).

The Mississippi river drains numerous smaller rivers through the U.S.A. Samples of drainage water from the smaller rivers were collected and analyzed for a variety of herbicides (Pereira and Rostad, 1990). Atrazine and its dealkylated degradation products were detected in the river system. The samples collected were filtered and residue levels were determined in both water and suspended sediments; only trace levels were associated with the

sediment (Pereira and Rostad, 1990). It was estimated that <2% of applied atrazine entered the Gulf of Mexico via runoff to the Mississippi River. Quantities of atrazine, de-ethyl atrazine and de-isopropyl atrazine transported into the Gulf of Mexico were estimated to be 105, 7 and 2 tonnes, respectively in 1987 and 429, 47 and 9 in 1989.

Pesticide residues have been found in river systems (Miles and Harris, 1973; Pereira and Rostad, 1990) that receive drainage from agricultural land. Such reports have led to investigations of pesticide residue loss in runoff from treated fields. Atrazine residues have been reported in runoff (Baker and Laflen, 1979; Glotfelty *et al.*, 1984). Fields with large slopes showed high concentrations of pesticides in runoff. Triplett *et al.* (1978) found up to 5.7% of total applied triazines in runoff from field plots with slopes ranging from 8-22% over one watershed year.. The first runoff events (usually the first two) post-application have been found to contain the highest loss in runoff for an entire field season (Gaynor and Volk, 1981).

There are several important degradation products of atrazine which form in soil (Tafari *et al.*, 1978), de-ethyl atrazine having been found to be the most prevalent (Bodo, 1991) (Figure 3). The dealkylation of atrazine has been found to be the most important pathway of degradation (Bodo, 1991). The major product of atrazine hydrolysis in

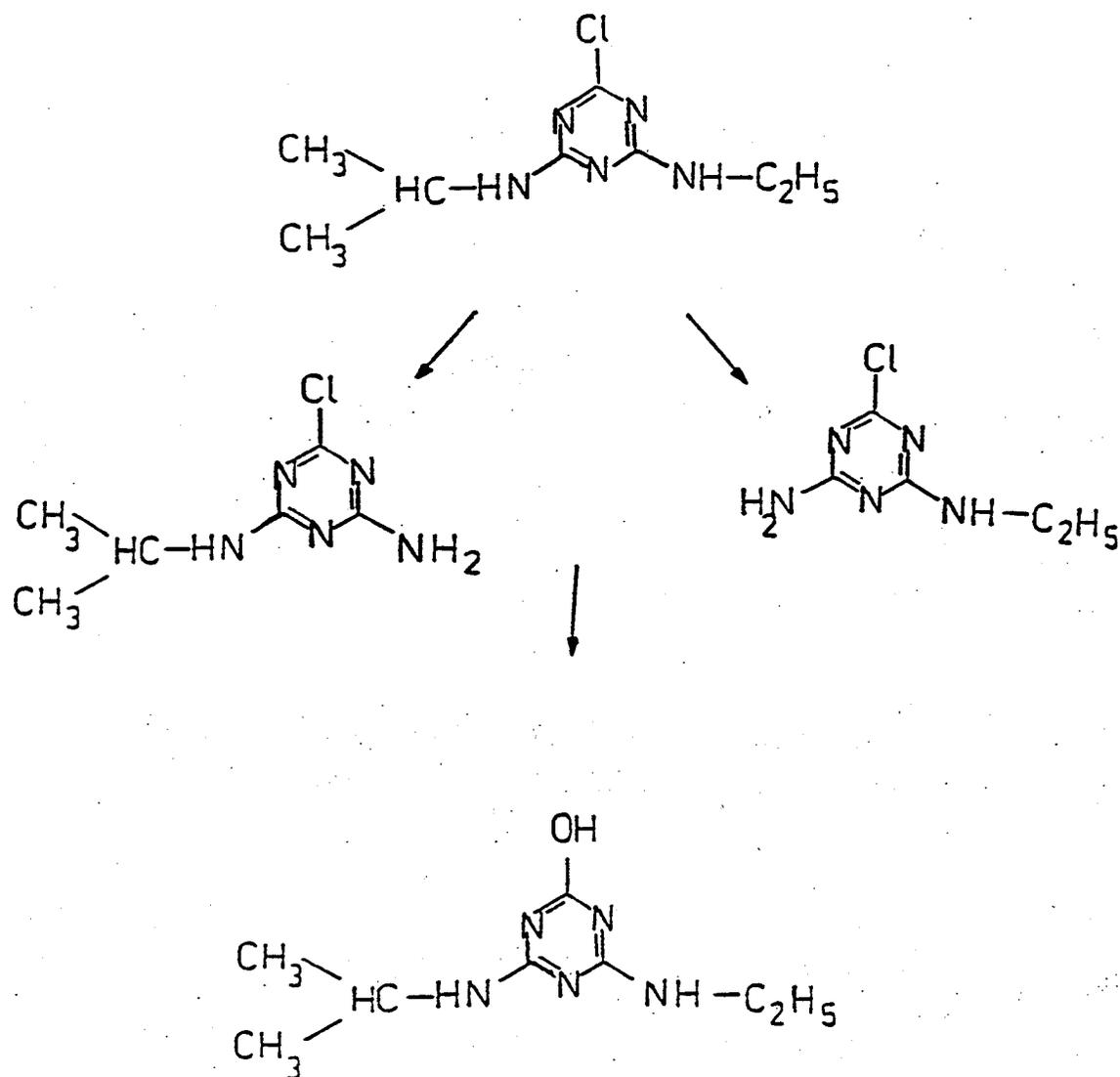


Figure 3: Atrazine and the three most common metabolites of atrazine in soil

soil is hydroxyatrazine (Bodo, 1991). The usage levels of each of these compounds has been reported by Environment Canada for the Northern and Western Region of Canada (Table 2).

Table 2: Tonnage of Herbicides used in the Three Prairie Provinces Based on Regional Sales (from Constable and Bharadia, 1990)

Chemical	Province	tonnes/yr	% of Total Regional Sales
Diclofop methyl	AB	324	6%
	SK	698	
	MB	381	
Bromoxynil	AB	258	4%
	SK	423	
	MB	253	
Atrazine	AB	21	<1%
	SK	16	
	MB	56	

The possibility of runoff from agricultural fields carrying sufficient herbicides to aquatic habitat to create a hazard for fish is worthy of investigation. The toxicity values of these compounds for rats and rainbow trout (Worthing and Hance, 1991) are listed in Table 3.

Table 3: Toxicity Data for Diclofop-Methyl, Bromoxynil, Bromoxynil Octanoate and Atrazine

Herbicide	Organism	Toxicity Data
Atrazine	Rats	LD <sub>50</sub> 1869-3080 mg/kg
	Rainbow Trout	96 hr LC <sub>50</sub> 4.5-8.8 mg/L
Bromoxynil	Rats	LD <sub>50</sub> 130-365 mg/kg
	Rainbow Trout	48 hr LC <sub>50</sub> 0.15 mg/L
Bromoxynil octanoate	Hens	LD <sub>50</sub> 175 mg/kg
	Goldfish	48 hr LC <sub>50</sub> 0.46 mg/L
Diclofop methyl	Rats	LD <sub>50</sub> 563-693 mg/kg
	Rainbow Trout	96 hr LC <sub>50</sub> 0.35 mg/L

The possibility of contamination of non-target areas has led to work on pesticide leaching and runoff losses. Persistence of herbicides in soil has been considered in conjunction with each of these other problems (Bowman, 1989; Ghadiri *et al.*, 1984; Leonard, 1988). Leaching of pesticides through the soil profile to the water table has been of concern because of the potential contamination of groundwater (McRae, 1989).

Soil persistence studies on bromoxynil octanoate and diclofop-methyl have been performed but there is a lack of leaching studies possibly because of rapid degradation of these compounds following application. In a Saskatchewan clay, diclofop-methyl was found to have been completely

hydrolyzed within a nine day period (Smith *et al.*, 1986). Earlier work with this chemical found 90% of the applied diclofop-methyl had hydrolyzed to diclofop acid in 24 h (Smith, 1977). These results were both found through analysis of the surface layer of soil (0-5 cm). Gaynor (1984) examined soil persistence of diclofop-methyl in clay soils, in southwest Ontario at the 0-10 cm depth. A rapid hydrolysis of diclofop-methyl to diclofop acid was found, followed by a slower degradation of diclofop acid.

Persistence studies with bromoxynil octanoate have been performed with Saskatchewan soils in lab experiments, (Smith, 1980). Both the applied bromoxynil octanoate and its hydrolysis product, bromoxynil were found to have degraded rapidly (95% loss was found in a seven day period). In field experiments Smith, (1980) determined that bromoxynil levels were below detection limits in both the 0-5 and 5-10 cm depths within 10 weeks. Similarly, field experiments in the United States with bromoxynil octanoate and bromoxynil have shown rapid degradation. Brown *et al.* (1985) found total bromoxynil octanoate and bromoxynil in soil (0-7 cm depth) at concentrations between 85 and 140  $\mu\text{mol/kg}$  one day following application. Levels dropped to trace amounts by the second sampling time, 135 days post-treatment. With these results Brown *et al.* were unable to determine half lives of bromoxynil octanoate under field conditions.

Review articles on triazine herbicides are available in which persistence and leaching potential of atrazine is discussed (Helling, 1970; Sheets, 1970). Atrazine was rated in terms of leachability with other compounds and found to be one of the most readily leached of the triazine herbicides, actual order of leachability was determined on different soil types (Helling, 1970). Experiments have been performed to determine atrazine leaching potential in various areas including the United States and eastern Canada. Pennsylvania soils were treated with atrazine under field conditions (Hall and Hartwig, 1978). In this experiment, atrazine was detected at the 1.2 m depth, however the highest concentrations were found in the samples taken from the top layer of soil (0-15 cm). Irrigated fields were sampled to determine atrazine leaching depths in an alluvial soil (Wehtje *et al.*, 1984). In the Nebraska soil, atrazine residues were found at higher concentrations at the top region of the soil profile. Samples taken from the 0 to 15 cm and 15 to 30 cm depth had residue concentrations ranges of 13 to 20 cm and 9 to 20 g/ha respectively, while at lower levels 1.2 to 1.5 m and 1.5 to 1.8 m depths had concentrations of 2 to 3 g/ha and 1 to 5 g/ha in the soil respectively. Field experiments performed in a Quebec sandy soil also indicated atrazine mobility (Muir and Baker, 1978).

The potential effect of tillage on the extent of runoff losses was examined by Sauer and Daniel (1987) who found there was no "consistent significant effect" of tillage on runoff losses with any of the pesticides examined. Higher concentrations of pesticides were found in runoff from conventional tillage plots (Sauer and Daniel, 1987).

Persistent chemicals such as the organochlorine insecticides have been studied at great length for persistence, leaching and runoff (Wauchope, 1978; Sleicher and Hopcraft, 1984; Willis *et al.*, 1983). Leaching studies using simulated runoff have been performed in the laboratory. By applying known amounts of "rain" to simulated fields or soil columns (Hogue *et al.*, 1981; Pestemer *et al.*, 1983), herbicide movement through the soil profile has been determined.

Half-lives of atrazine have been determined in different soil types at varying soil depths, the most common being the surface 10 cm. Results of some experiments are found in Table 4. Wehtje *et al.* (1984) found that the concentration of atrazine drops dramatically from the surface to lower soil depths (0.6 m). This shows that atrazine does leach in some soil types although the highest concentration is found in the surface layer.

Table 4: Half-lives of Atrazine in Soil (0-10 cm)

Half-life (days)	Experimental Type	Application	Reference
21.5 <sup>1</sup>	Field Plot	Flowable	Klaine <i>et al.</i> , 1988
36-68 <sup>2</sup>	Field Plot	Flowable	Pestemer <i>et al.</i> , 1983
17 <sup>2</sup>	Lysimeter	Flowable	Bowman, 1989
24* <sup>2</sup>	Lysimeter	Flowable	"
28 <sup>2</sup>	Lysimeter	Flowable	Bowman, 1990

\* Supplementary watering of experimental soil

<sup>1</sup> first order half-life

<sup>2</sup> 50% disappearance

Modelling the loss of a compound from a field with known soil properties and weather conditions is a way of estimating runoff or leaching losses. In view of the fact that it is becoming increasingly expensive to actually set up field experiments to assess potential risk (Lorber and Mulkey, 1982), mathematical models used to calculate runoff loss such as those described by Haith (1980) have been utilized. Papers comparing different models have been published recently (Crowe and Mutch, 1990; Lorber and Mulkey, 1982; Melancon and Pollard, 1986) and they find that the models often require calibrating before use. Leaching of pesticides into the root zone or to the water table have been considered in numerous models. Padilla *et al.* (1988) described a one-dimensional model showing the dependence of pesticide degradation and sorption on temperature. Heathman *et al.* (1986) have developed a non-

uniform (non-uniform mixing between the water and the soil phase) mixing model to estimate runoff losses of pesticides. Computer models have been developed so that the model may be run with minimum calculations on the part of the user. These models require physical and chemical data such as solubility, adsorption/desorption constants, photolytic rates, hydrolysis rates for the compound(s) of interest and the soil type (Leonard 1988, Leonard 1990) rather than only general groupings (availability index) for pesticides to estimate pesticide movement.

## Chapter I.

### Runoff Losses of Bromoxynil Octanoate, Diclofop-Methyl and Atrazine

#### I. Introduction

Increased awareness of pesticide residues and other possible environmental contaminants in Canada has resulted in efforts to determine areas and potential routes of contamination. The possibility of surface runoff water contaminating surface and groundwater resources has been evaluated, particularly in areas where persistent compounds are more routinely found (Di Muccio *et al.*, 1990). In the U.S.A., there have been numerous field and simulated field studies to determine if there is a problem with runoff from agricultural fields treated with herbicides (Klaine *et al.*, 1988; Gaynor and Volk, 1981).

Atrazine, a persistent triazine herbicide is used on corn in eastern Canada, as well as in the U.S. and in Europe. Losses of the herbicide atrazine in runoff, as well as its persistence in soil have been the focus of many studies (Triplett *et al.* 1978; Baker and Laflen, 1979; Smith, 1982; Utulu *et al.*, 1986), in both the U.S. corn belt and different areas in Canada. Atrazine is not used widely in western Canada, however, corn is grown in southwestern Manitoba and atrazine is used there. Other compounds

applied to crops in Manitoba are bromoxynil and diclofop (in their octanoic acid ester and methyl ester forms respectively) (Constable and Bharadia, 1990). Runoff studies for the three herbicides studied in this thesis had not previously been carried out in western Canada.

Bromoxynil, the active hydrolysis product of bromoxynil octanoate was found in river and stream water (Muir and Grift, 1987) in Manitoba; in this study diclofop was also detected. Atrazine persistence in soils and losses in runoff have been examined elsewhere (Gloufely *et al.*, 1984; Pionke *et al.*, 1988; Wauchope, 1987) but little work in prairie soils has been done, making it a good compound to be used for comparison in this runoff study. Little data on bromoxynil and bromoxynil octanoate in runoff water was found in the literature (Brown *et al.*, 1985).

In this project runoff levels of atrazine, bromoxynil octanoate and diclofop-methyl were examined. Atrazine, was applied to corn plots in the commercial formulation Aatrex, (480 g/L) while the other two herbicides were applied to wheat plots as Hoegrass II containing diclofop-methyl and bromoxynil octanoate (230 g/L : 80 g/L). The runoff losses were determined by extracting whole runoff water; losses of these compounds have been found to be associated with the water phase rather than with sediment particles (Heathman *et al.*, 1986).

## II. Experimental

### A. Chemicals

The herbicide formulation Hoegrass II, was provided by Hoechst (Winnipeg, MB). Aatrex, a Ciba Giegy product, and the petroleum oil required for Aatrex application, were provided for this experiment by the Department of Plant Science, University of Manitoba.

Concentrated  $H_2SO_4$  which was used in pH adjustments and  $HNO_3$ , used in acid cleanup of other reagents were purchased from Baxter-Canlab (Winnipeg, MB). All solvents used in the sample workup and analysis including acetone, dichloromethane (DCM), ethyl acetate, ethyl ether and hexane were Burdick and Jackson distilled-in-glass quality and were purchased from Baxter-Canlab (Winnipeg, MB).

Analytical standards, including atrazine, (2-chloro-4-(ethylamino)-6-isopropylamino)-s-triazine), metribuzin 4-amino-6-tert-butyl-3-(methylthio)-1,2,4-triazin-5-one, bromoxynil (3,5-dibromo-4-hydroxybenzotrile), bromoxynil octanoate (3,5-dibromo-4-octanoyloxybenzotrile) and diclofop-methyl (methyl 2-[4-(2',4'-dichlorophenoxy)] phenoxypropionate) were purchased from Caledon Ltd. (Georgetown, ON). *N*-methyl, *N*-nitro, *N*-nitroso, guanidine

used in the preparation of diazomethane for the derivatization of bromoxynil and diclofop was purchased from Aldrich Chemical Co. (Milwaukee, WI, USA).

Florisil used in the cleanup of samples was purchased from Fisher Scientific (Winnipeg, MB). Anhydrous  $\text{Na}_2\text{SO}_4$ , used to dry sample extracts was purchased from Mallinckrodt via Baxter-Canlab (Winnipeg, MB). Purified copper (electrolytic powder) purchased from Baxter-Canlab (Winnipeg, MB), was used in the removal of sulphur from runoff extracts.

## **B. Site Preparation**

Several years prior to the current experiment, sites at five locations in southern Manitoba were established for a soil loss-erosion study (Hargrave and Shaykewich, 1990). Three of the locations used for the erosion study were chosen for the herbicide loss-runoff experiment. Each location had a corn, wheat, alfalfa and summer fallow plot. The locations for this project (each having different soil types) were at Miami (Gretna clay), Roseisle (Leary sandy loam) and Whitewater (Ryerson sandy clay loam). A runoff collection system already in place prior to the experiment was modified by adding an additional collection container for subsampling the runoff. All of the plots used in this

study had a 9% slope. Each plot was 0.01 hectare in size (22.1 m x 4.6 m). In order to collect runoff, while allowing for the concurrent study requirements, a collection container (ceramic coated pan) was placed at the bottom of the flume as seen in Figure 4. The erosion experiment required only 1% of the total runoff from fields and thereby allowed for subsampling of the remaining 99% by this study. Table 5 shows soil properties for each location.

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Table 5: Soil Properties at Each Field Site  
(Hargrave and Shaykewich, 1990)

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Property	Miami	Roseisle	Whitewater
Soil type	Gretna clay	Leary sandy loam	Ryerson sandy clay loam
Bulk Density (g/cm <sup>3</sup> )	1.44	1.54	1.28
% Clay	50.4	11.1	22.9
% Silt	28.6	14.5	19.4
% Sand	23.0	74.5	57.2
% OM	4.3	0.9	5.8

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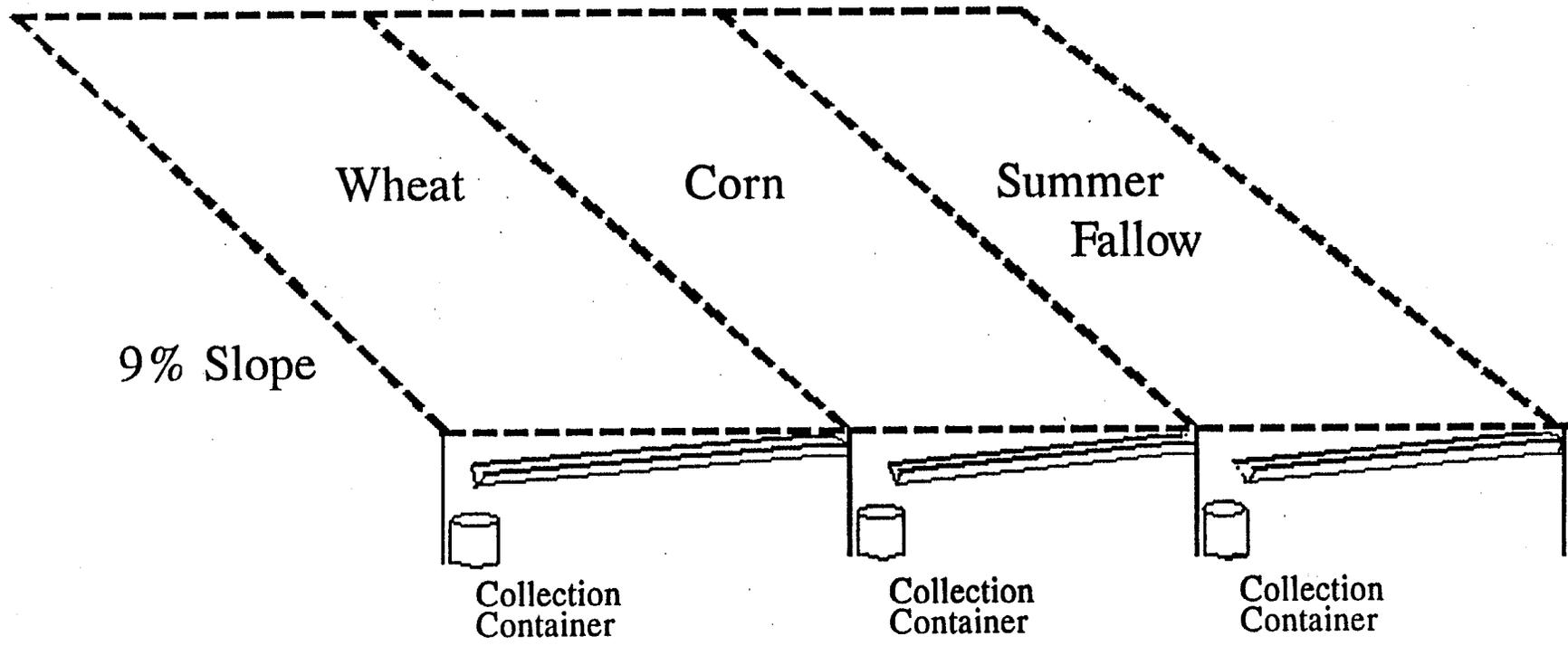


Figure 4: Runoff Collection System

### C. Herbicide Application

To measure the application rate of herbicide to each plot, glass fibre (12.5 cm) filter papers were placed on inverted petri dishes at six points along the slope to collect spray deposits. Two were placed in the top region of the plot, two in the middle portion and two were in the bottom section along the slope. Immediately after application the papers were rolled up, using tweezers and placed in 50 mL Corex screw capped tubes (Teflon lined caps) containing 50 mL DCM. The tubes were then wrapped in aluminum foil to prevent photolytic degradation during transport to the laboratory. The plots were treated with the herbicides between May 26, 1989 and June 16, 1989; application rates are shown in Table 6.

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Table 6: Application Rates (kg/ha) of Hoegrass II and Aatrex

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Site	Date	Hoegrass II		Aatrex
		Bromoxynil Octanoate	Diclofop Methyl	Atrazine
Miami	89.06.02	0.28	0.81	- <sup>1</sup>
	89.06.16	-	-	2.96
Roseisle	89.05.26	0.28	0.81	-
	89.06.02	0.28	0.81	-
	89.06.16	-	-	2.96
Whitewater	89.05.26	0.28	0.81	-
	89.06.09	0.28	0.81	-
	89.06.16	0.56	1.61	2.96

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<sup>1</sup> indicates no application

Since this project was run in conjunction with the erosion-runoff project, it was necessary to re-apply the Hoegrass II at the sites where weed problems occurred. The Roseisle site required a second application and the Whitewater site required three applications, with the final spray at twice the concentration of the others. Prior to the actual date of application, the sprayer was calibrated by applying required volumes of water over the equivalent distance to the field plots.

In preparation for application to the wheat plots, 1.11 L water was measured in a graduated cylinder and added to the sprayer tank. Hoegrass II (35 mL) was pipetted into the tank, thoroughly mixed with the water and applied to the plot. For the final spray application at the Whitewater site on the June 16, 70 mL of the formulation was added to the tank.

For the corn plots, 8.89 L of water was added to the sprayer tank, followed by 160 mL oil and 62 mL of the Aatrex formulation.

#### **D. Sampling**

Although summer fallow plots were untreated, runoff samples were taken and analyzed for each of the active ingredients applied to the experimental plots. Runoff from the first fall snowmelt was collected Nov. 2, 1988 at the Miami and Roseisle sites. The Whitewater site was not sampled at this time. Runoff from the snowmelt was collected from all three locations in early spring 1989, the dates dependent on the actual time of melt in each area (March 3 at the Whitewater site; April 7 at Roseisle and April 13 at Miami). In the case of snowmelt, 20 L ceramic containers were placed at the bottom of the flume to collect runoff samples because the soil erosion study did not require

results from this runoff event. Later in the spring when the soil erosion experiment began for the year, 1.4 L ceramic containers were used. Smaller sample collection containers were necessary to allow for the erosion project samplers. Samples were collected following rainfall events sufficient to cause runoff from the plots. Runoff samples collected were subsamples of the total runoff from the field. The percentage of total runoff collected varied with the volume of loss from the field. Samples were collected the day after runoff events occurred. The water and any sediment in the container were transferred to a 1 L amber glass bottle containing 50 mL dichloromethane (DCM), which was added to preserve the herbicide residues until extraction. The sample bottles were taken to the laboratory, stored at 4°C and extracted within 2 days.

#### **E. Extraction and Analysis**

The volumes of runoff samples collected from the plots were measured. The samples from the summer fallow plots were divided into two equal portions to act as untreated checks and processed the same as samples from the wheat and corn plots.

Runoff water samples from wheat plots were acidified to pH 2 with the addition of 3 mL conc. sulfuric acid. The water

was then transferred to a 2 L separatory funnel and 100 mL DCM was added and shaken gently, to avoid emulsion formation. The lower layer (DCM) was removed and the aqueous layer was re-extracted using a further 100 mL DCM. The combined extract was dried by passing through a column of anhydrous sodium sulfate that had been pre-washed with DCM. The extract was then quantitatively transferred to a RBF and the volume reduced to ~4 mL under reduced pressure on a rotary evaporator. The sample was then quantitatively transferred to a 10 mL graduated test tube, reduced in volume to 4 mL and divided into two, 2 mL fractions. The first fraction was reduced to ~0.5 mL under a gentle stream of dry nitrogen and hexane (1 mL) was added. This procedure was repeated to ensure complete removal of the DCM. The second subsample was reduced in volume to ~100  $\mu$ L and derivatized by addition of 1.0 mL diazomethane in diethyl ether which had been prepared using a modified method of Stanley (1966). The reaction mixture was allowed to sit for 30 min, the solvent was changed to hexane as described above and the sample prepared for Florisil cleanup by reducing it to a final volume of 1 mL.

Florisil was heated to 200°C for 6 h and allowed to cool. Distilled water (5% w/w) was added to known amounts of Florisil in a closeable container, turned until a uniform powder resulted and allowed to sit for 24 h to equilibrate. Glass columns (7.5 cm x 6 mm id) were filled with this 5%

deactivated Florisil. Florisil, after having been tapped down to 6 cm, was topped with 5 mm anhydrous  $\text{Na}_2\text{SO}_4$ . Following addition of the sorbents to the column, the column was preconditioned with 6 mL hexane. The 1 mL extract was then added to the top of the column bed and allowed to drain followed by 1 mL hexane which was also allowed to drain from the column. The column was then eluted with 2 x 5 mL 5:95 ethyl acetate in hexane volumes. The extract was further cleaned up by adding 1 g copper powder and vortexing the sample. The sample was then allowed to sit for at least 30 min and revortexed. A 1.00  $\mu\text{L}$  aliquot was then injected using a Hewlett Packard 5790 autosampler onto a 60 m DB-5 column (J&W Scientific, Folsom, CA, USA) in a Hewlett Packard 5890 gas chromatograph equipped with a  $^{63}\text{Ni}$  electron capture detector (see Table 7 for GC ECD conditions). Standards of bromoxynil, bromoxynil octanoate and diclofop-methyl were injected into the GC at varying concentrations to determine the linear range of the instrument and to construct a standard curve. Concentrations of these analytes in the samples were determined using this relationship.

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Table 7: GC ECD conditions used for the analysis of runoff sample extracts.

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Temperature Program	70°C for 2 min, 10°C/min to 250°C hold for 10 min
Injector temperature	220°C
Detector Temperature	300°C
Makeup gas	Nitrogen 40.0 mL/min
Carrier gas	Hydrogen 1.0 mL/min

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Runoff samples from corn plots were extracted using the same method as that used for the wheat plot samples, however, a pH adjustment was not required for atrazine extraction. Following actual extraction, the same procedure was followed as for runoff samples from wheat plots until after the volume reduction in the RBF. Once the sample was ~2 mL, the extract was quantitatively transferred to a graduated test tube, reduced in volume to 1 mL, switched to a 2:1 hexane : ethyl acetate solvent system and analyzed (2.00  $\mu$ L aliquot) by gas chromatography on a 30 m DB-5 column in a HP 5890 equipped with a Nitrogen-Phosphorus detector (see Table 8 for conditions). Just prior to injection of the samples, 5.00  $\mu$ L of a metribuzin solution was added to the sample in an effort to calculate actual injection volumes, however, there was a coeluting peak with the same retention time and this relationship could not be used. A standard curve over the

linear range of the instrument was determined and the gas chromatographic peak areas were related to this relationship to determine concentration values.

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Table 8: GC NPD conditions used for the analysis of runoff sample extracts for atrazine.

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Temperature Program	100°C hold for 2 min, 10°C/min to 200°C
Injector Temperature	250°C
Detector Temperature	300°C
Makeup Gas      Helium	33.6 mL/min
Carrier Gas      Helium	1.7 mL/min
Hydrogen (bead power)	3.0 mL/min
Air	> 100 mL/min

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Spray deposit samples were extracted by vortexing the tubes containing DCM and filter papers for 30 sec, allowing the sample to sit for 2 min and revortexing. The solvent was then quantitatively transferred to a 100 mL RBF. A further 25 mL DCM was added to the Corex tube containing the filter papers and vortexed. This solution was then transferred to the RBF containing the first extract.

The sample was reduced in volume to ~4 mL in the case of Hoegrass II spray deposits and followed the processing procedure of the runoff samples from wheat plots from this

point forward. The spray deposit extracts were diluted by a factor of 25 for chromatographic quantification.

Aatrex spray deposit extracts were reduced in volume to ~2 mL and treated as runoff samples from corn plots. After extraction and analysis of filter papers that had been placed at various locations along the slope for any given application of Hoegrass II, calculations to determine application rates (kg/ha) were performed using the equations presented in Appendix III. Runoff losses of the degradation products were added to runoff losses of the applied chemicals to determine total loss. The total loss values were then calculated in terms of % the applied chemical (Appendix III).

### **III. Results and Discussion**

#### **A. Spray Deposits**

The spray deposits of diclofop-methyl and bromoxynil octanoate varied widely over the treated areas. In several of the spray deposit results, free bromoxynil was detected. The degradation product formation of the diclofop-methyl were not determined, spray deposits were methylated in sample workup. This type of problem could have been avoided by ethylating sample extracts rather than

methyating them, however, the experiment had been set up to examine losses of bromoxynil octanoate and its degradation product, only. At each site the actual spray deposit, calculated by averaging the deposits, was substantially higher than the theoretical applied amount.

At the Miami site, bromoxynil octanoate spray deposits ranged from 6.5 to 0.4 kg/ha (Table 9). Both the highest and lowest levels were found at the bottom of the slope. Free bromoxynil was present in very low amounts (0.06 to 0.01 kg/ha), as expected, since the formulation was supposed to have contained bromoxynil octanoate and diclofop-methyl only. The presence of the free phenol (bromoxynil) as the methyl ether indicated that the bromoxynil may not have been completely esterified in the manufacturing process. Diclofop-Methyl spray deposits represented application rates from 27.6 kg/ha to 1.4 kg/ha.

Spray deposits at the Roseisle site showed an even greater range among samples after the first application of Hoegrass II. Diclofop levels ranged from 65 to 0.8 kg/ha; the highest concentration was found in the deposit collected at the bottom of the plot and the lowest at one of the top locations. Bromoxynil octanoate levels ranged from 11 to 0.16 kg/ha. Free bromoxynil was again detected in the spray deposits in trace levels. The second application of Hoegrass II, at the Roseisle site produced the narrowest

range of spray deposit values of any of the Hoegrass II application. Levels of bromoxynil octanoate ranged from >0.01 to 0.33 kg/ha and diclofop-methyl from 0.02 to 1.9 kg/ha. The latter application was done at 4:30 a.m., in a dead calm, evidently a possible factor in getting a more even application to the plot.

The spray deposit data at the Whitewater site on June 26, 1989 had less variation than those for the first Roseisle application. Diclofop-Methyl was found to have been applied between 38 to 0.7 kg/ha. This site was also different in that the middle portion of the plot had a spray deposit level higher than at the bottom. The low value was detected at the top of the slope. Bromoxynil octanoate was found at levels between 9.0 and 0.5 kg/ha. The second application provided the most erratic results of all applications, ranging from 94 kg/ha diclofop-methyl at one of the mid region deposits to 0.2 kg/ha at the top. With this high degree of variability, the soil sample extracts could be expected to vary considerably over a field and lead to skewed results, in this case high results. Bromoxynil octanoate levels ranged from 14 to 0.04 kg/ha. The final spray showed diclofop-methyl levels between 46 and 1 kg/ha, while bromoxynil octanoate was found between 9 and 0.2 kg/ha. Geometric means for the spray deposits at each location and spraying time are shown in examined in Table 9. Geometric means of the spray

deposits were used as a means of normalizing the highly variable results.

Table 9: Spray Deposit (Geometric Mean) Data For Compounds Present in Hoegrass II (kg/ha)

SITE	DATE	Bromoxynil Octanoate	Diclofop Methyl	Bromoxynil
Miami	June 2	1.02	3.95	0.02
Roseisle	May 26	1.85	9.70	0.02
	June 2	0.16	0.63	0.01
Whitewater	May 26	1.65	7.63	0.03
	June 9	0.53	2.84	0.01
	June 16	2.02	9.59	0.03

The spray deposits for atrazine showed a much narrower range of amounts applied than those of the Hoegrass II application. The also results showed an average value much closer to the calculated application rate. It may be that the oil used as an emulsifier in the tank mix for Aatrex application resulted in a greater uniformity in application. The Aatrex formulation is classified as a flowable and as such requires the oil to keep the active ingredient in suspension. The Hoegrass II is an emulsifiable concentrate and it is recommended that this additional ingredient not be added to the tank mix, however this formulation appears not to have been sprayed evenly over the field.

The type of sprayer used in the application initially appeared to have had an effect in that a bicycle wheel sprayer has no mechanism to assure continuous mixing. Without this, different formulations will come out of suspension more readily than others. The sprayer is equipped with air tanks to deliver the herbicide. These tanks are filled with compressed air and the pressure decreases as the application proceeds. The erratic Hoegrass II spray deposits are consistent with inadequate mixing and the gradually decreasing pressure at which the formulation was applied. The Hoegrass II spray mixture applied to the field plugged the nozzles, from time to time. The oil present in the Aatrex tank mix as an emulsifier may have resulted in a better suspension of the atrazine and thereby increased the evenness of its application.

At the Miami site, atrazine levels applied ranged from 6.10 to 2.43 kg/ha along the plot. Atrazine levels at the Roseisle site ranged from 5.28 to 3.85 kg/ha. The Whitewater location deposits ranged from 5.87 to 2.06 kg/ha atrazine. It is interesting that there were no trends along the length of the slope in terms of residue levels; there were no consistently high residues in any region of the plots. Spray deposit results from the Aatrex formulation showed much better precision than any of the

results from the Hoegrass II applications, as well as closer agreement with the calculated application rate. Geometric means for the Aatrex application are given in Table 10. No de-ethyl or de-isopropyl atrazine was detected in any of the spray deposits.

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Table 10: Spray Deposit (Geometric Mean) Data For Aatrex Formulation

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SITE	DATE	Atrazine kg/ha
Miami	June 16	3.6
Roseisle	June 16	4.5
Whitewater	June 16	3.5

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#### B. Runoff From Wheat Plots

Detection limits for bromoxynil octanoate, diclofop-methyl and bromoxynil were 10 pg, 25 pg and 1 pg respectively, based on a 3:1 signal to noise ratio. Recovery studies for each of the compounds from spiked water were performed at two levels and data from this study is provided in Appendix I.

At the Miami site diclofop residues were present in the runoff prior to application of Hoegrass II to the plot (Figure 5). (In each of the Figures, the data is shown as

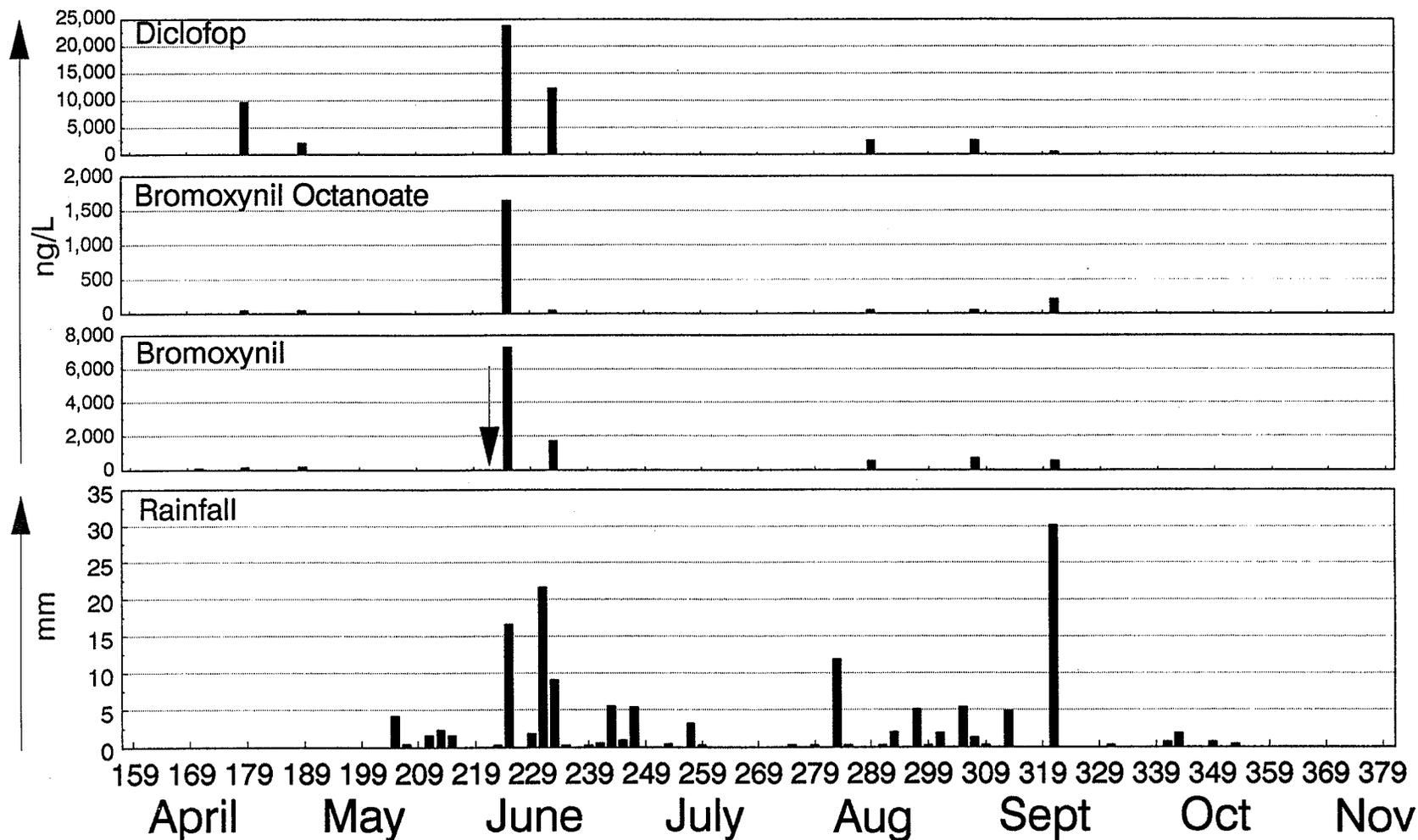


Figure 5: Rainfall and Runoff Data (2-Day Average) for Bromoxynil octanoate, Bromoxynil & Diclofop at the Miami, MB site; Arrow indicates Application 1989 (Experiment Day #s Given; Note: y-axis scaling between compounds)

a two day average). This may have been a result of drift from another field nearby, or runoff losses of residual diclofop from the application the previous year. In general diclofop-methyl is not considered to be a long lasting compound in soil, much like bromoxynil octanoate (Smith, 1971). Prior to the application, bromoxynil octanoate, as well as the free phenol (bromoxynil) was found in very minute quantities.

The highest concentrations of all compounds were found in the runoff water following the spray to the Miami wheat plot. The first rainfall following application came shortly after application, leading to the high concentration of residue in the runoff. Six days following application of Hoegrass II at the Miami wheat plot, 31.8 mm of rain washed the highest levels of diclofop (48  $\mu\text{g/L}$ ), bromoxynil octanoate (3  $\mu\text{g/L}$ ) and bromoxynil (15  $\mu\text{g/L}$ ) off the plot. On June 14, 12 days post treatment, levels of bromoxynil and diclofop present in runoff were reduced to 3  $\mu\text{g/L}$  and 24  $\mu\text{g/L}$ , respectively. Bromoxynil octanoate was below the detection limit at this time. After the first runoff event, the octanoate, when present, was found at levels  $< 0.2 \mu\text{g/L}$ . The highest level of its hydrolysis product, bromoxynil, was detected at the first runoff post application, showing bromoxynil octanoate was rapidly hydrolyzed under field conditions. This high loss shortly after application followed a pattern found in other runoff

studies, using other compounds (Edwards *et al.*, 1980). In the runoff experiment with glyphosate, Edwards *et al.* (1980) found that herbicide losses in the first runoff event following application, accounted for 99% of the total loss for the year. Diclofop levels also followed this trend with high concentrations of residues in the runoff water during runoff events soon after herbicide application. The patterns of herbicide loss over the field season can be observed in Figure 5 relating rainfall to runoff losses. Later in the field season, bromoxynil octanoate was found in runoff, perhaps as a result of applications to surrounding fields, or wash off from areas of the plot that had not lost or degraded all bromoxynil octanoate previously. The first of the two possibilities would be expected as bromoxynil octanoate is known to readily degrade in soil, with a half life of 10 days (Smith, 1971). In Manitoba, bromoxynil has been found in streams following heavy rainfall (Muir and Grift, 1987). Diclofop-Methyl is also degraded rapidly to diclofop (Gaynor, 1984). The presence of diclofop-methyl in the runoff was not initially of interest and the sample extracts were methylated. If they had been ethylated, it would have been possible to differentiate between the applied diclofop-methyl and its degradation product, diclofop. Total diclofop was considered, for the losses in runoff water. Runoff events occurred only infrequently after the initial two events following application and as a

result there were only low concentrations of diclofop detected in the runoff later in the field season.

At the Roseisle site, runoff patterns were similar to those at Miami in that the higher concentrations of the residues from the Hoegrass II formulation were found in the early runoff events following application (Figure 6). The amount of bromoxynil octanoate found in the runoff was much lower at this site than at Miami ( $<0.2 \mu\text{g/L}$ ), possibly as a result of the different soil characteristics. The Roseisle site had a sandy soil and the Miami site, a clay. Higher amounts of diclofop and bromoxynil were present in the runoff at the Roseisle site, which was expected, since the plot had been treated with Hoegrass II twice. Very low levels of diclofop, bromoxynil octanoate and bromoxynil ( $<0.5 \mu\text{g/L}$ ,  $<0.2 \mu\text{g/L}$  and  $<0.2 \mu\text{g/L}$ , respectively) were found in spring melt runoff at the Roseisle site prior to herbicide application. Early in May, a runoff event washed a high concentration of diclofop off the plot ( $12 \mu\text{g/L}$ ) but the other compounds were found at much lower levels. Between the first and second applications of Hoegrass II, there was no significant precipitation. Four days after the second treatment, 30 mm of rain fell and low levels of all three compounds were detected ( $<0.5 \mu\text{g/L}$  diclofop,  $0.3 \text{ ng/L}$  bromoxynil octanoate and  $<0.2 \mu\text{g/L}$  bromoxynil). Ten days later, another rainfall occurred and at this point

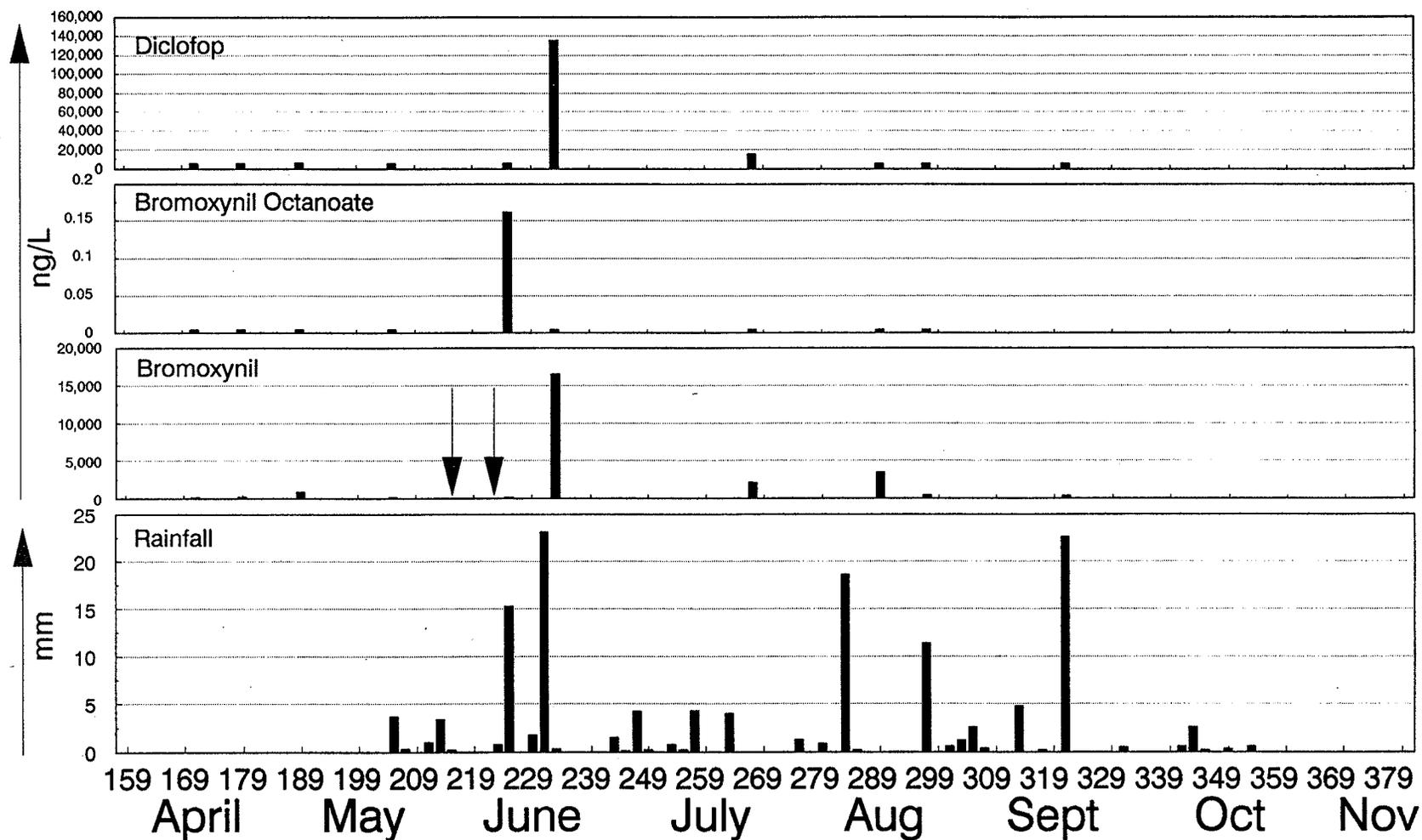


Figure 6: Rainfall and Runoff Data for Bromoxynil octanoate, Bromoxynil & Diclofop at the Roseisle, MB site; Arrows indicate Application 1989 (Experiment Day #s Given; Note: y-axis scaling between compounds)

higher levels of diclofop and bromoxynil were detected (272  $\mu\text{g/L}$  and 33 $\mu\text{g/L}$ , respectively). By this time, octanoate was detected but at levels below quantification ( $<0.2$   $\mu\text{g/L}$ ).

The Diclofop concentration in the runoff was 270  $\mu\text{g/L}$  and bromoxynil was present at 33  $\mu\text{g/L}$  from this sampling time. The next rainfall event yielding runoff occurred at thirty days post-treatment. At that time only bromoxynil and diclofop were detected (4.3 and 30  $\mu\text{g/L}$ ) respectively. Later in the season, the concentrations of these compounds dropped to below quantifiable levels.

At the Whitewater site three applications of Hoegrass II were required. The third and final application was at twice the normal application rate because of heavy weed infestation. Residue levels from the Hoegrass II did not fit the pattern of the other two sites, in that generally increasing concentrations of bromoxynil octanoate and bromoxynil were found in the runoff over the subsequent three months. Diclofop concentrations were low in the first two runoff events followed by an increase in concentration later in the field season, with two runoff events producing very similar losses, once in July and the second in August (Figure 7). Low levels of both diclofop and bromoxynil were detected in runoff samples (26  $\mu\text{g/L}$  and 36  $\mu\text{g/L}$  respectively) prior to application of Hoegrass II.

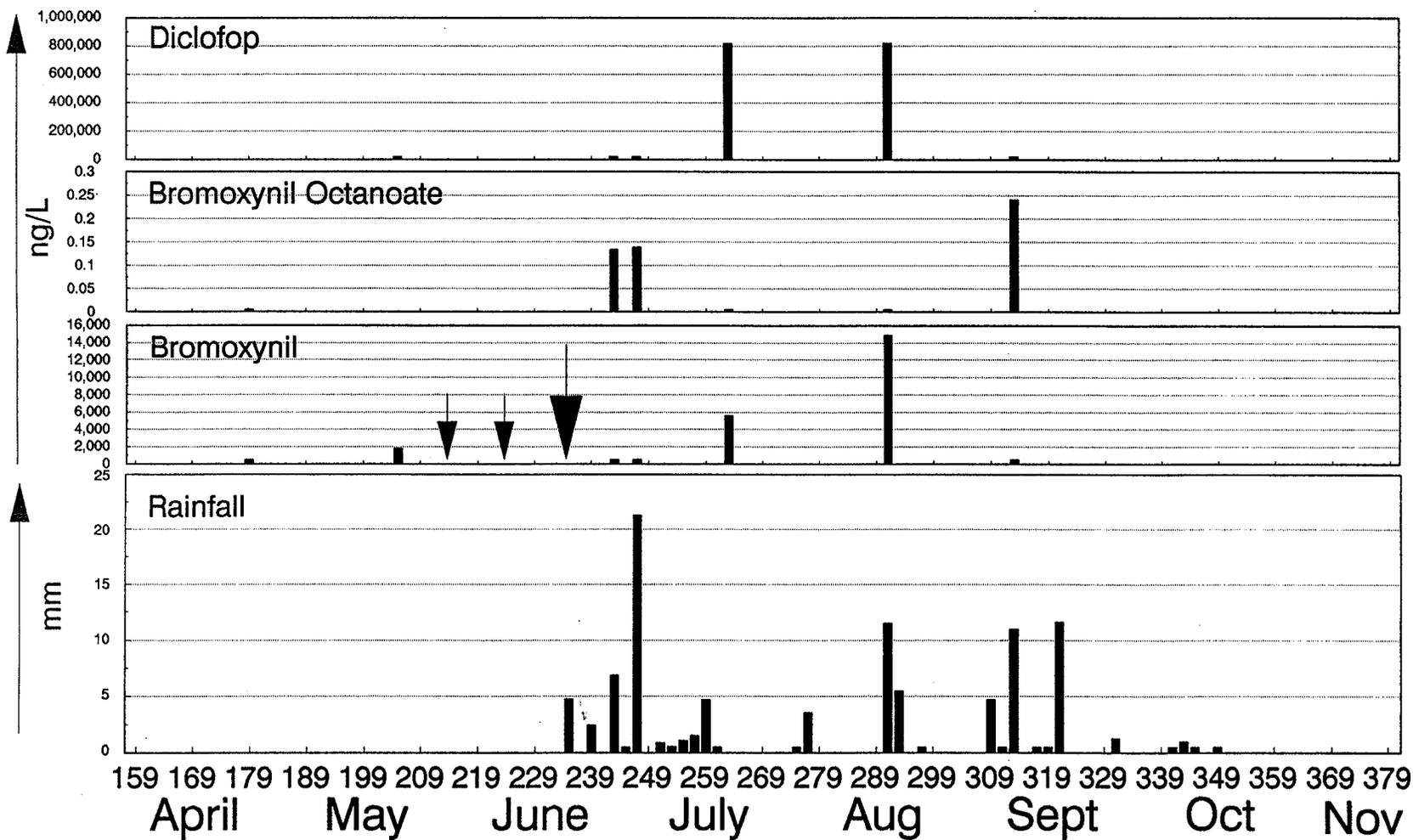


Figure 7: Rainfall and Runoff Data for Bromoxynil octanoate, Bromoxynil & Diclofop at the Whitewater, MB site; Arrows indicate Application 1989 (Experiment Day #s Given; Note: y-axis scaling between compounds)

No precipitation occurred during the time between any of the three treatments to the field plot and therefore, no runoff samples were available for collection. The first rainfall producing runoff was on June 24 and at that time low levels of each analyte were found in the runoff extract ( $<0.2 \mu\text{g/L}$  bromoxynil octanoate,  $<0.2 \mu\text{g/L}$  bromoxynil and  $<0.5 \mu\text{g/L}$  diclofop). The concentration of the degradation products increased between runoff events to a maximum of  $30 \mu\text{g/L}$  bromoxynil and  $1640 \mu\text{g/L}$  diclofop on August 11. Samples collected after this point contained decreasing concentrations of analyte (Figure 7).

### C. Runoff From Corn Plots

The detection limit for atrazine was 1 ng; a recovery study of this compound was performed at two levels (Appendix I). Spring runoff losses of both atrazine and its degradation product, de-ethyl atrazine, were found to be 13 and  $0.7 \mu\text{g/L}$ , respectively, at the Miami site (Figure 8). Residue levels decreased until after application of Aatrex. Residues of atrazine are known to carry over in soil from one season to another (Rahman *et al.*, 1978; Wauchope, 1978). Following herbicide application, runoff from the corn plot, although the corn plot was at the same location as the wheat plot, did not occur until much later in the season. At the point where runoff did occur, very high

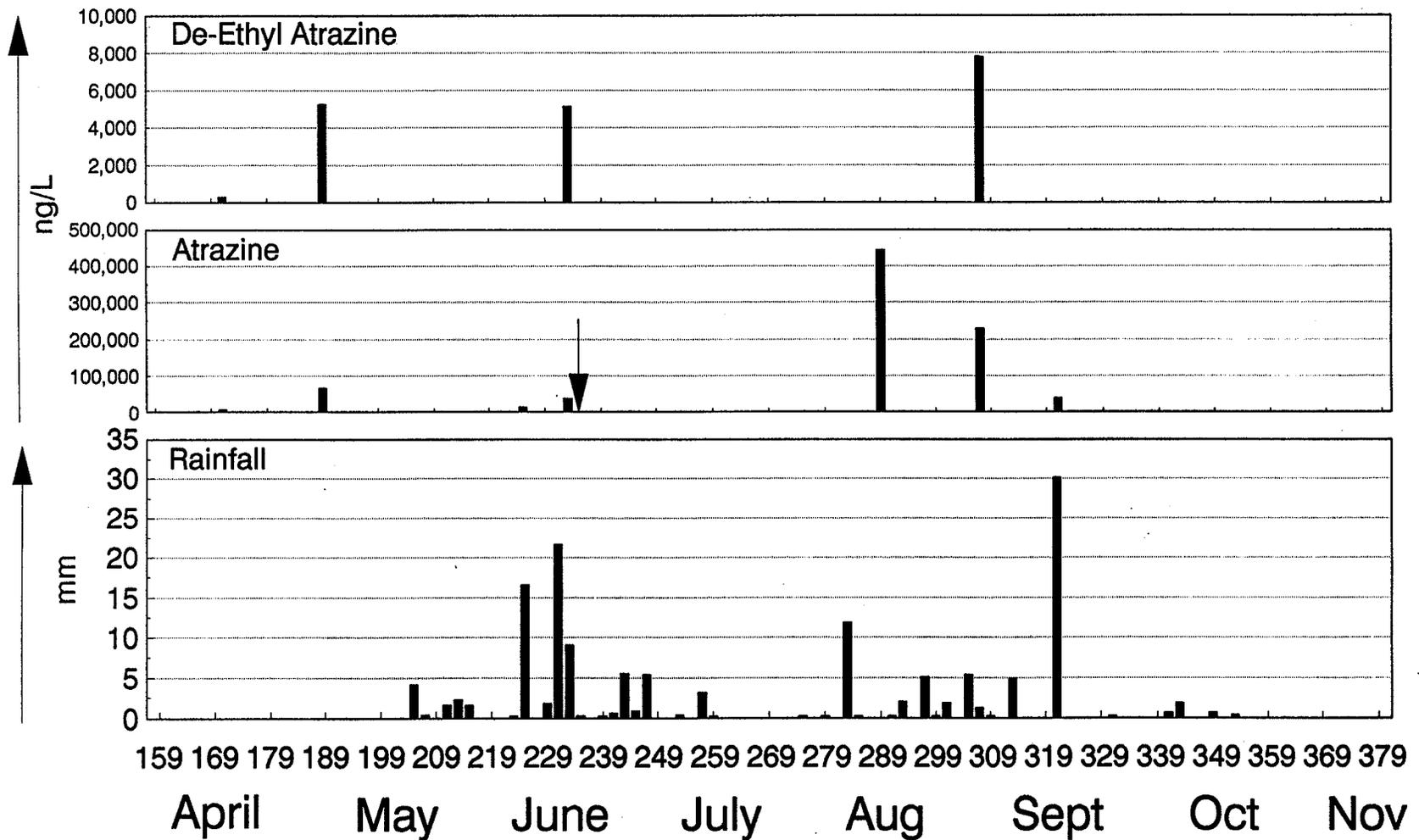


Figure 8: Rainfall and Runoff Data (2-Day Average) for Atrazine and De-ethyl atrazine at the Miami, MB site; Arrow indicates Application 1989 (Experiment Day #s Given; Note: y-axis scaling between compounds)

concentrations of atrazine were detected. Following this application, the first runoff event showed significant atrazine losses, (30  $\mu\text{g/L}$ ), but no de-ethyl atrazine was detected. At the end of August de-ethyl atrazine was found in the runoff, at 16  $\mu\text{g/L}$ , which was the highest concentration of this compound detected in runoff. The degradation product of atrazine was discovered by examining the chromatograms of the atrazine runoff (Figure 9). There were peaks prior to that of atrazine. The samples containing these peaks were then injected onto a GC/ITD in an attempt to determine the structure of the compound. It was obvious that the compound contained nitrogen or phosphorus, as the detector used in the original analysis was an NP detector. By using the library software of the GC/MS, the identity of the compounds, de-ethyl atrazine and de-isopropyl atrazine were established. Data from the GC/ITD is in Appendix IV. The compound de-ethyl atrazine was quantified by using the atrazine standard curve, assuming that both compounds had the same response factor. (Repeated efforts to obtain analytical standards of the atrazine degradation products failed).

Atrazine levels in runoff at the Roseisle site were lower than at Miami (Figure 10). De-ethyl atrazine levels throughout the field season were similar between the two

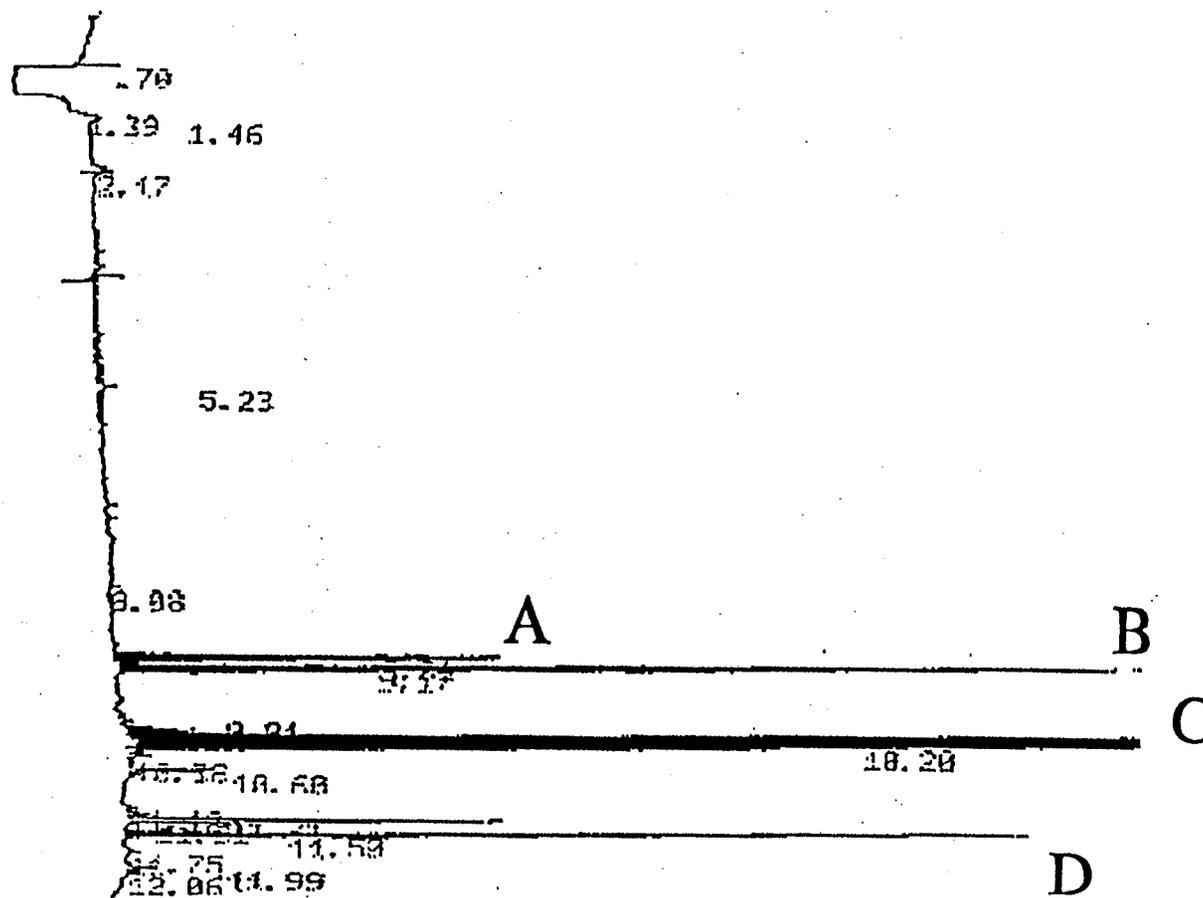


Figure 9: Chromatogram of runoff sample extract from a corn plot; unlabelled peaks were unidentifiable and areas were not related to atrazine levels.  
 A: De-isopropyl atrazine, B: De-ethyl atrazine, C: Atrazine, D: Metribuzin (internal standard)

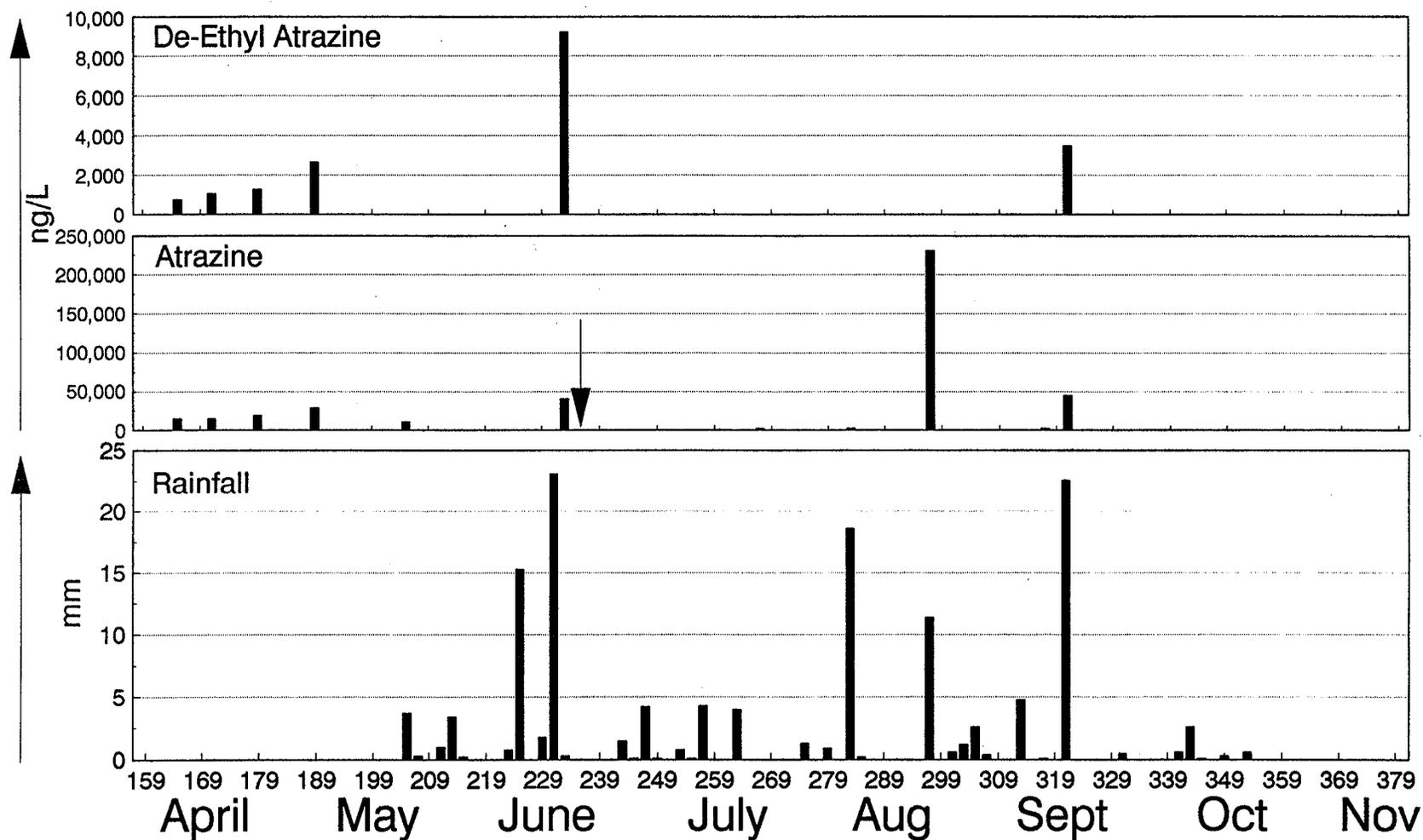


Figure 10: Rainfall and Runoff Data for Atrazine and De-ethyl atrazine at the Roseisle, MB site; Arrow indicates Application 1989 (Experiment Day #s Given; Note: y-axis scaling between compounds)

locations. The same pattern occurred at Roseisle as at Miami, in that the high concentrations of atrazine lost in runoff came later in the field season. Atrazine and de-ethyl atrazine were found in runoff from spring melt at the Roseisle site in higher concentrations than at the Miami site ( $>30 \mu\text{g/L}$  and  $>1.4 \mu\text{g/L}$ , respectively). The amount of each of these compounds increased over the spring prior to application of Aatrex to a maximum of ( $8 \mu\text{g/L}$ ) atrazine and ( $18 \mu\text{g/L}$ ) of the degradation product. Thirty-three days following atrazine application, runoff samples collected and extracted had no degradation product detectable and only a relatively low concentration of atrazine itself was found ( $4 \mu\text{g/L}$ ). Two months after Aatrex had been applied, the largest concentration of atrazine was found in the runoff extracts ( $462 \mu\text{g/L}$ ). There was no de-ethyl atrazine detected in this sample. Runoff samples after this point had decreasing concentrations of each of these compounds.

Atrazine losses at the Whitewater location differed from those at the other sites (Figure 11). Two runoff events following application resulted in low atrazine losses, but the third such event produced higher concentrations than at any point in the field season at either of the other locations. This rainfall event caused de-ethyl atrazine to be washed off the field at the highest concentration seen over the course of the experiment at any location. The Whitewater site had been treated with Aatrex only once as

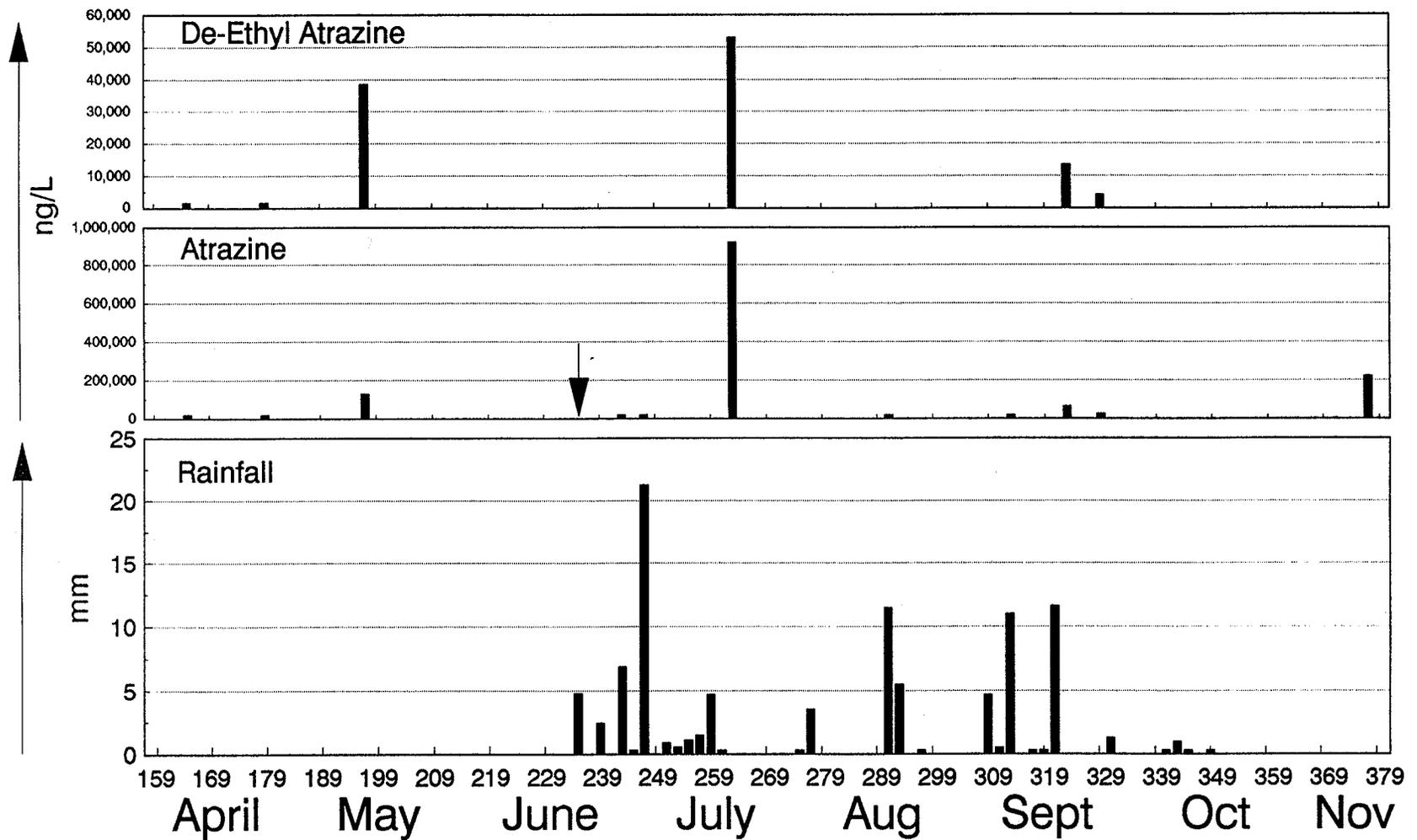


Figure 11: Rainfall and Runoff Data for Atrazine and De-ethyl atrazine at the Whitewater, MB site; Arrow indicates Application 1989 (Experiment Day #s Given; Note: y-axis scaling between compounds)

with the other locations. There was only one rainfall event at the Whitewater site over the course of the experiment producing more than 20 mm precipitation. Both atrazine and de-ethyl atrazine were detected in spring melt samples, however, a rainfall event in early May yielded runoff with higher concentrations of each of these compounds (258  $\mu\text{g/L}$  and 77  $\mu\text{g/L}$ , respectively). Rainfall samplers were not in place for this early season rainfall event and therefore the rainfall graph (Figure 11) lacks this datapoint. In the first two runoff events post treatment, low levels of atrazine were found in the sample extracts (both 3  $\mu\text{g/L}$ ). Twenty-nine days post treatment, the highest concentration of both atrazine (1842  $\mu\text{g/L}$ ) and de-ethyl atrazine (106  $\mu\text{g/L}$ ) were found. After this sampling time, the levels of atrazine were lower over the field season. The first fall snowmelt was collected from the corn plot on November 7 and in this sample, only atrazine was detected, at a high concentration (450  $\mu\text{g/L}$ ).

Total losses of each of the compounds detected and quantified in runoff samples are shown in Tables 11, 12 and 13 (calculations are in Appendix III). The total loss shown is that found after application of the herbicides to their respective plots.

Table 11: Loss of Applied Herbicides (kg/ha), over the Field Season At the Miami, MB, Site

Month	Bromoxynil	Bromoxynil Octanoate	Diclofop-Methyl	Atrazine	De-ethyl Atrazine
April	$4.7 \times 10^{-5}$	NQ <sup>1</sup>	$2.8 \times 10^{-3}$	$1.9 \times 10^{-3}$	$9.4 \times 10^{-5}$
May	$6.9 \times 10^{-7}$	NQ <sup>1</sup>	$8.5 \times 10^{-6}$	$2.5 \times 10^{-5}$	$2.0 \times 10^{-6}$
June	$8.5 \times 10^{-5}$	$1.1 \times 10^{-5}$	$4.3 \times 10^{-4}$	$3.8 \times 10^{-4}$	$3.9 \times 10^{-5}$
Aug	$5.2 \times 10^{-6}$	NQ <sup>1</sup>	$2.5 \times 10^{-5}$	$1.1 \times 10^{-2}$	$9.9 \times 10^{-5}$
Sept	$3.3 \times 10^{-6}$	$1.3 \times 10^{-6}$	$1.7 \times 10^{-6}$	$3.5 \times 10^{-3}$	ND <sup>2</sup>
Total {post application}	$9.4 \times 10^{-5}$	$1.2 \times 10^{-5}$	$4.5 \times 10^{-4}$	$1.5 \times 10^{-2}$	$1.4 \times 10^{-4}$

<sup>1</sup> NQ = not quantifiable - Samples collected had concentrations below <math>0.2 \text{ ug/L}</math> Bromoxynil Octanoate

<sup>2</sup> ND = not detectable

Table 12: Total Loss of Applied Herbicides (kg/ha), over the Field Season at the Roseisle, MB Site

Month	Bromoxynil	Bromoxynil Octanoate	Diclofop Methyl	Atrazine	De-ethyl Atrazine
April	$9.8 \times 10^{-5}$	NQ <sup>1</sup>	$5.4 \times 10^{-4}$	$4.5 \times 10^{-3}$	$2.2 \times 10^{-4}$
May	$8.0 \times 10^{-8}$	NQ <sup>1</sup>	$6.0 \times 10^{-7}$	$2.0 \times 10^{-5}$	$1.8 \times 10^{-6}$
June	$5.3 \times 10^{-5}$	NQ <sup>1</sup>	$4.4 \times 10^{-4}$	$2.3 \times 10^{-4}$	$5.1 \times 10^{-5}$
July	$4.4 \times 10^{-5}$	NQ <sup>1</sup>	$3.2 \times 10^{-4}$	$7.6 \times 10^{-6}$	ND <sup>2</sup>
Aug	$5.9 \times 10^{-4}$	NQ <sup>1</sup>	$4.6 \times 10^{-4}$	$1.7 \times 10^{-2}$	ND <sup>2</sup>
Sept	$1.1 \times 10^{-6}$	NQ <sup>1</sup>	$2.9 \times 10^{-6}$	ND <sup>2</sup>	ND <sup>2</sup>
Total {post application}	$6.9 \times 10^{-4}$	NQ <sup>1</sup>	$1.2 \times 10^{-3}$	$1.7 \times 10^{-2}$	$5.3 \times 10^{-5}$

<sup>1</sup> NQ = not quantifiable - Samples collected had concentrations below <math>0.2 \text{ ug/L}</math> Bromoxynil Octanoate

<sup>2</sup> ND = not detectable

Table 13: Total Loss of Applied Herbicides (kg/ha), over the Field Season at the Whitewater, MB Site

Month	Bromoxynil	Bromoxynil Octanoate	Diclofop Methyl	Atrazine	De-ethyl Atrazine
April	$8.3 \times 10^{-5}$	NQ <sup>1</sup>	ND <sup>2</sup>	$1.3 \times 10^{-3}$	$2.0 \times 10^{-4}$
May	$2.9 \times 10^{-7}$	NQ <sup>1</sup>	$2.1 \times 10^{-7}$	$8.8 \times 10^{-5}$	$2.6 \times 10^{-5}$
June	NS <sup>3</sup>	NS <sup>3</sup>	NS <sup>3</sup>	$5.8 \times 10^{-7}$	ND <sup>2</sup>
July	$3.8 \times 10^{-6}$	$3.4 \times 10^{-11}$	$5.6 \times 10^{-4}$	$6.3 \times 10^{-4}$	$3.6 \times 10^{-5}$
Aug	$4.7 \times 10^{-4}$	$1.6 \times 10^{-9}$	$2.6 \times 10^{-2}$	$2.1 \times 10^{-3}$	$4.4 \times 10^{-4}$
Sept	NQ <sup>1</sup>	NQ <sup>1</sup>	NQ <sup>1</sup>	$2.1 \times 10^{-3}$	$4.5 \times 10^{-4}$
Nov	NS <sup>3</sup>	NS <sup>3</sup>	NS <sup>3</sup>	$1.5 \times 10^{-4}$	ND <sup>2</sup>
Total {post application}	$5.6 \times 10^{-4}$	$1.6 \times 10^{-9}$	$2.7 \times 10^{-2}$	$6.3 \times 10^{-3}$	$1.2 \times 10^{-3}$

<sup>1</sup> NQ = not quantifiable - Samples collected had concentrations below <math>0.2 \text{ ug/L}</math> Bromoxynil Octanoate

<sup>2</sup> ND = not detectable

<sup>3</sup> NS = no sample

Table 14:           % Loss of Applied Herbicide  
                          Over One Field Season

Site	Bromoxynil Octanoate	Diclofop Methyl	Atrazine
Miami	0.05	0.06	0.51
Roseisle	0.18	0.08	0.59
Whitewater	0.06	0.83	0.23

Losses from each of the plots for the compounds applied are shown in terms of percent loss relative to amount applied in Table 14. The percent loss determined in this series of field trials ranges from 0.05% to 0.83%. The % loss of atrazine had also been studied in experiments elsewhere (Baker and Laflen, 1979; Gaynor and Volk, 1981; Triplett et al., 1978). The results found by this experiment were in agreement with other studies. Field trials examining pesticide losses through surface runoff have shown that the highest losses occur in the first runoff events after application, losses of <2% of the applied pesticides have been found over the field season. This type of work had never been attempted in Manitoba and so it was difficult to compare with other experiments because the field conditions are different than most others experiments that have been done. Bromoxynil octanoate and bromoxynil had not been studied extensively in terms of runoff losses (Brown et

al., 1985). This is a result of these compounds readily degrading in the soil. In general, they are not considered to be lost to any significant extent through runoff however, bromoxynil has been detected in stream water in Manitoba following large rainfall events (Muir and Grift, 1987). The detected residues in stream water show that although bromoxynil and diclofop are readily degraded, they are applied extensively and may present a problem in Manitoba.

In a review of pesticide losses, Wauchope (1978) stated that for the majority of commercial pesticides, total runoff losses are <0.5%. This is in close agreement with the findings of this study. Atrazine, like other compounds with greater solubility than 10  $\mu\text{g/mL}$ , is lost largely in the water phase of runoff (Wauchope, 1978) rather than bound to sediment. Unfortunately, recoveries of the residues from sediment were not determined. Only losses from whole runoff were experimentally determined.

Other studies have shown similarly low levels of pesticide loss in field experiments. Azinphos methyl and fenvalerate have been studied under field conditions for more than one field season (Smith et al., 1983). Losses of azinphos methyl and fenvalerate were 0.08% azinphos methyl and 0.02% fenvalerate of that applied, respectively. However, the following year losses were much greater. This has been

attributed to the increase in rainfall that season.

Despite the chemical differences between compounds in the Smith *et al.* (1983), runoff study and those determined experimentally in the present study, the amounts lost through runoff are similar. In this type of experiment, numerous seasons of study would be required to provide a reliable basis for comparison. Unfortunately, it was not practical to continue sampling runoff beyond one year for the current project.

The results found in this study were consistent with those from other work; Edwards *et al.* (1980) found that highest concentrations of glyphosate were lost in runoff events shortly after treatment of fields. Precipitation producing runoff shortly after herbicide application, leads to high concentrations of the herbicide in the runoff. Based on toxicity data in the Herbicide Handbook (1979) and the Pesticide Manual (1979), for each of the compounds analyzed, the levels found in the runoff are lower than those producing lethal effects in nontarget organisms (fish and small mammals). *In situ* experiments in Manitoba using two other triazine herbicides (simazine and terbutryn) found that both compounds resulted in reduction of periphyton growth at concentrations of 0.1 to 1.0 mg/L for simazine and <0.01 mg/L for terbutryn. (Goldsborough and Robinson, 1983).

#### IV. Conclusions

The runoff losses of the active ingredients in two herbicide formulations applied to field plots have been determined. Presence of the compounds of interest in runoff samples was found to be greatest shortly after treatment; concentrations decreased with time. Bromoxynil octanoate was rapidly hydrolyzed to bromoxynil, based on runoff results. This pattern is assumed to have occurred also with diclofop-methyl. Atrazine degradation was also detected; presence of de-ethyl atrazine was found in numerous runoff samples and in a few samples de-isopropyl atrazine was also detected.

Runoff losses of atrazine in this experiment ranged from 0.23% to 0.59%, consistent with the range found by other researchers in other locations (Wauchope, 1978).

Bromoxynil octanoate losses in runoff over the same field season were found to be 0.05% to 0.18% of that applied. This compound is not frequently analyzed for in runoff samples as it is so readily hydrolyzed in soil (Brown *et al.*, 1985). This is consistent with the low losses in runoff found in this experiment over the course of the field season. Diclofop-Methyl losses in runoff were also fairly low, (0.06% to 0.83%), which is also consistent with literature reports (Gaynor, 1984). In general, compounds found in runoff accounted for <1% of total applied amounts.

This experiment indicates that the losses of herbicides from fields due to runoff during rainfall events are small. The herbicides that have been considered, are known to degrade rapidly under field conditions and therefore the actual risk for organisms downstream is quite small. Atrazine residues, which were detected in runoff at the highest levels might have resulted in contamination of non-target areas if the field application have been on a greater scale, however, the toxicity of atrazine is low to mammals and fish compared with the toxicities of other the other compounds considered (Table 3). In cases where bromoxynil and diclofop have been detected in streams (Muir and Grift, 1987) it has been when rainfall events occurred early in the field season, i.e. close to herbicide application times.

## Chapter II.

### Persistence of Residues in Three Manitoba Soils

#### I. Introduction

Pesticide use for agricultural purposes has led to concern about potential environmental contamination. Groundwater and surface water contamination are resource related concerns, often involving insecticides, herbicides and fungicides (Priddle *et al.*, 1987; Creeger *et al.*, 1988; Cohen *et al.*, 1988). Translocation of residues within the soil profile and runoff from agricultural land lead to these problems and limit land and water use options. Limitations for crop rotation, possibility of water contamination effecting domestic use and viability of waterfowl habitat are directly influenced by water contamination by pesticides. As a result of these concerns, a number of researchers have studied the leaching of chemicals through the soil profile (Nicholls *et al.*, 1982; Hogue *et al.*, 1981; Poelstra *et al.*, 1973).

Atrazine, a widely used herbicide on corn, has been the focus of many persistence trials, both in laboratory and field experiments. Reviews of triazine persistence and movement in soil have been written (Helling, 1970; Sheets, 1970). The triazine herbicides in North America were the

focus of an entire volume of Residue Reviews (32). Work on triazine persistence has been done in other areas where its use is common. Rahman *et al.* (1978) found that phytotoxic atrazine residues persist in soil for up to 5-6 months, however, the levels of cyanazine, another triazine herbicide, drop to below phytotoxic levels in under 3 months. Repeated applications of atrazine to soil in Italy have shown no significant increase in residue levels when compared with soil treated only once with atrazine (Vazzana *et al.* 1981). Rhode *et al.* (1981) found that most of the atrazine present in soil remained in the surface 20 cm. Damanakis and Daris (1981) found that in a vineyard treated with atrazine annually, soil residues in the 0-10 cm layer were consistently higher than that at the lower 10-20 cm depth (see Table 15).

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Table 15: Atrazine residues in Soil at Various Depths after Repeated Application (Damanakis and Daris, 1981)

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Soil Layer (cm)	Years of Continual Herbicide Application	Application Rate (kg/ha)	Atrazine Residues (mg/kg)
0-10	6	5	1.12
10-20	6		0.47
0-10	9	5	1.05
10-20	9		0.17
0-10	14	5	1.09
10-20	14		0.39

---

From the data in Table 15, it can be seen that atrazine leaching does occur, but concentrations do not increase with repeated applications. Results of these two studies show that atrazine behaves in a similar way independent of soil type or climate conditions.

Bromoxynil octanoate, itself phytotoxic (Muir *et al.*, 1991; Constable and Bharadia, 1990), hydrolyzes readily in soil to form the active compound bromoxynil (Smith, 1971). Bromoxynil in aqueous solution has been found to be readily photolyzed in sunlight (Kochany *et al.*, 1989). Thus photochemical degradation in runoff water or at the soil surface may occur.

Diclofop-methyl is similarly hydrolyzed to diclofop in soil environments (Gaynor, 1984; Smith *et al.* 1986). The acid form is degraded further under moist soil conditions (Smith *et al.*, 1986), but not in dry soil. It has been recommended by Environment Canada (Constable and Bharadia, 1990) that diclofop-methyl in prairie streams and soil environments should be examined.

Despite the documented degradation of these two herbicides in soil and water, both bromoxynil and diclofop have been detected in river and stream water in Manitoba (Muir and Grift, 1987) where their usage is high (Constable and Bharadia, 1990). Runoff related losses of these compounds

have been repeated for more than one season (Brown *et al.*, 1985). Atrazine, while not used widely in Manitoba, is a well studied compound suitable for comparison purposes.

## **II. Experimental**

### **A. Chemicals**

The chemicals used for soil extraction, cleanup and analysis are described in the Experimental Chapter I.

### **B. Herbicide Application to Field Plots**

Application of herbicides was performed as described in the Experimental Chapter I.

### **C. Sampling**

Prior to application of herbicides to the field plots, untreated soil samples were taken. When runoff samples were collected, corresponding soil samples were also taken. At each sampling time, soil was taken from the top, middle and bottom regions of the slope. Each soil sample was taken from the 0-5 cm level using a 10 X 10 cm square coring unit, which was driven into the ground using a sledge hammer. The coring device was driven into the ground to the 15 cm level, tipped back and metal plates

were placed to separate the 0-5 cm, 5-10 cm and 10-15 cm depths. The samples were stored in polyethylene bags, kept at ambient temperature for the duration of the trip back to the laboratory and stored at -30°C until analysis.

#### **D. Workup and Analysis**

Soil samples were thawed and spread out to air dry. The soil was ground using the soil grinder provided by the Manitoba Provincial Soil Testing Laboratory (Christie Mill; 2 mm sieve). After grinding, soil samples were re-frozen and stored at -30°C until extraction.

##### **i) Extraction of soil samples from Wheat plots for Herbicides**

Ten g subsamples of soil were weighed into 50 mL Corex centrifuge tubes with Teflon lined screw caps. To each tube, 30 mL of a mixture of acetonitrile-water-glacial acetic acid (80:18:2 v/v) was added and the tubes were capped and shaken on a Burrell wrist action shaker (W.A.S.) for 1 h. Soil was allowed to sit in the extracting solvent overnight (~17 h) and shaken for a further hour. After shaking, the tubes were centrifuged for 40 min at 3000 RPM.

A 20 mL aliquot of the extracting solvent was taken and added to a separatory funnel containing 50 mL of a 5%

aqueous  $\text{Na}_2\text{CO}_3$  solution and mixed. This solution was partitioned three times with 10 mL of hexane. The aqueous layer was acidified with 7.5 mL concentrated HCl and partitioned twice with 25 mL of DCM.

The hexane extract was transferred to a 100 mL RBF and reduced in volume to ~3 mL on a rotary evaporator. The extract was transferred to a 10 mL graduated test tube (Teflon lined screw caps) and further reduced in volume to 1 mL under a gentle stream of nitrogen. The extract was cleaned up on a Florisil column, as described in Chapter I.

The DCM extract was reduced in volume to 2 mL on a rotary evaporator, transferred to a 10 mL graduated test tube and reduced in volume to 100  $\mu\text{L}$  under a gentle stream of  $\text{N}_2$ . The extract was methylated using a modification of the Stanley (1966) method and cleaned up on a Florisil column as in Chapter I; 1.00  $\mu\text{L}$  aliquots were taken for injection on the Varian Vista 6000 electron capture GC with a 60 m DB-5 column (J&W Scientific, Folsom, CA, U.S.A.). This instrument was equipped with an autoinjection system; see Table 16 for GC conditions.

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Table 16: GC ECD conditions used for the analysis of extracts of soil from Wheat Plots

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Temperature Program	70°C for 2 min 10°C/min to 150°C 3°C/min to 250°C hold for 5 min
Injector Temperature	220°C
Detector Temperature	300°C
Makeup gas	Nitrogen (40.3 mL/min)
Carrier gas	Hydrogen (1.0 mL/min)

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**ii) Extraction of soil samples from Corn plots for  
Herbicides**

A 10 g subsample of soil was weighed into a centrifuge tube (Teflon lined screw caps) and shaken with 30 mL of a mixture of acetonitrile (ACN) and distilled water (70:30) adjusted to pH 9 with concentrated  $\text{NH}_4\text{OH}$ . Samples were shaken on the W.A.S. for 1 h, allowed to sit in the extracting solvent overnight (~17 h) and shaken for a further hour. The tubes were removed from the shaker and centrifuged for 40 min at 3000 RPM. A 20 mL aliquot of solvent was removed and transferred to a 100 mL RBF and taken to dryness on a rotary evaporator. Distilled water (25 mL) was added to the flask and swirled gently, followed by addition of 25 mL DCM. The mixture was transferred to a

125 mL separatory funnel and the DCM layer drained into a 100 mL RBF. A second 25 mL volume of DCM was used to rinse the original flask and then transferred to the separatory funnel containing the aqueous ACN solution and shaken.

The DCM was drained from the separatory funnel into the second RBF. The extract was evaporated to dryness on a rotary evaporator and atrazine residues were dissolved in 5 mL trimethylpentane. A 2.00  $\mu$ L volume was injected onto a 30 m DB-5 column (J&W Scientific, Folsom, CA, U.S.A.) in a Hewlett Packard 5890 GC equipped with a Nitrogen-Phosphorus detector (see Table 17 for conditions).

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Table 17: GC NPD conditions used for the analysis of soil extracts from Corn Plots

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Temperature Program	100°C hold for 2 min 10°C/min to 200°C
Injector Temperature	250°C
Detector Temperature	300°C
Makeup gas (Helium)	33.6 mL/min
Carrier gas (Helium)	1.7 mL/min
Hydrogen (bead power)	3.0 mL/min
Air	>100 mL/min

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Recovery studies for these compounds were done on each of the soil types used for this experiment and results are shown in Appendix II.

### III. Results and Discussion

Recoveries using several extraction methods (Muir and Baker, 1978; Tafuri, 1978; Bowman, 1989) and methanol were attempted, including soxhlet, reflux and shaking techniques (different solvent mixtures and time periods). Initial work testing the recovery of atrazine from each of the three soil types, Gretna clay, Leary sandy loam and Ryerson sandy clay loam, was consistently in the range of 70-75 % for cold solvent techniques using a variety of solvents. Extraction methods using hot solvent systems yielded excessive coextractives and sample extracts could not be cleaned up. Other work with atrazine was carried out using a (1:1) benzene: diethyl ether extraction solvent (Rhode *et al.*, 1981). Smith (1981), compared a variety of extraction solvents and methods for extracting atrazine from soil. The method determined to have the best recovery using shaking extraction was followed and this method resulted in the highest recoveries from all soil types.

### A) Residues from Hoegrass II application

Residue levels of all analytes in soil samples taken from untreated summer fallow plots were below detection limits (<5 ng bromoxynil, <10 ng bromoxynil octanoate and 25 ng diclofop-methyl). The highest amounts of bromoxynil octanoate were found in the soil shortly after application at the Miami site (2 ng/g June 6, 13 ng/g June 14). Levels dropped after the first 2 sampling times (Figure 12) (all graphs show mean data of three samples which were taken from the top, middle and bottom region of the plots). Bromoxynil was detected in these same early soil samples, at higher levels than those of the octanoate (157 ng/g and 2 ng/g, respectively). Prior to the application of Hoegrass II, bromoxynil octanoate and bromoxynil were detected in the soil, at low levels. In late July, soil sample extracts showed detectable, trace quantities of bromoxynil octanoate (<15ng/g).

Diclofop was found in the Miami soil early in the field season, prior to application in relatively low quantities (Figure 13). Post treatment diclofop was present in soil samples at the Miami site in substantial amounts (598 ng/g). Diclofop-methyl however was detected, but found at

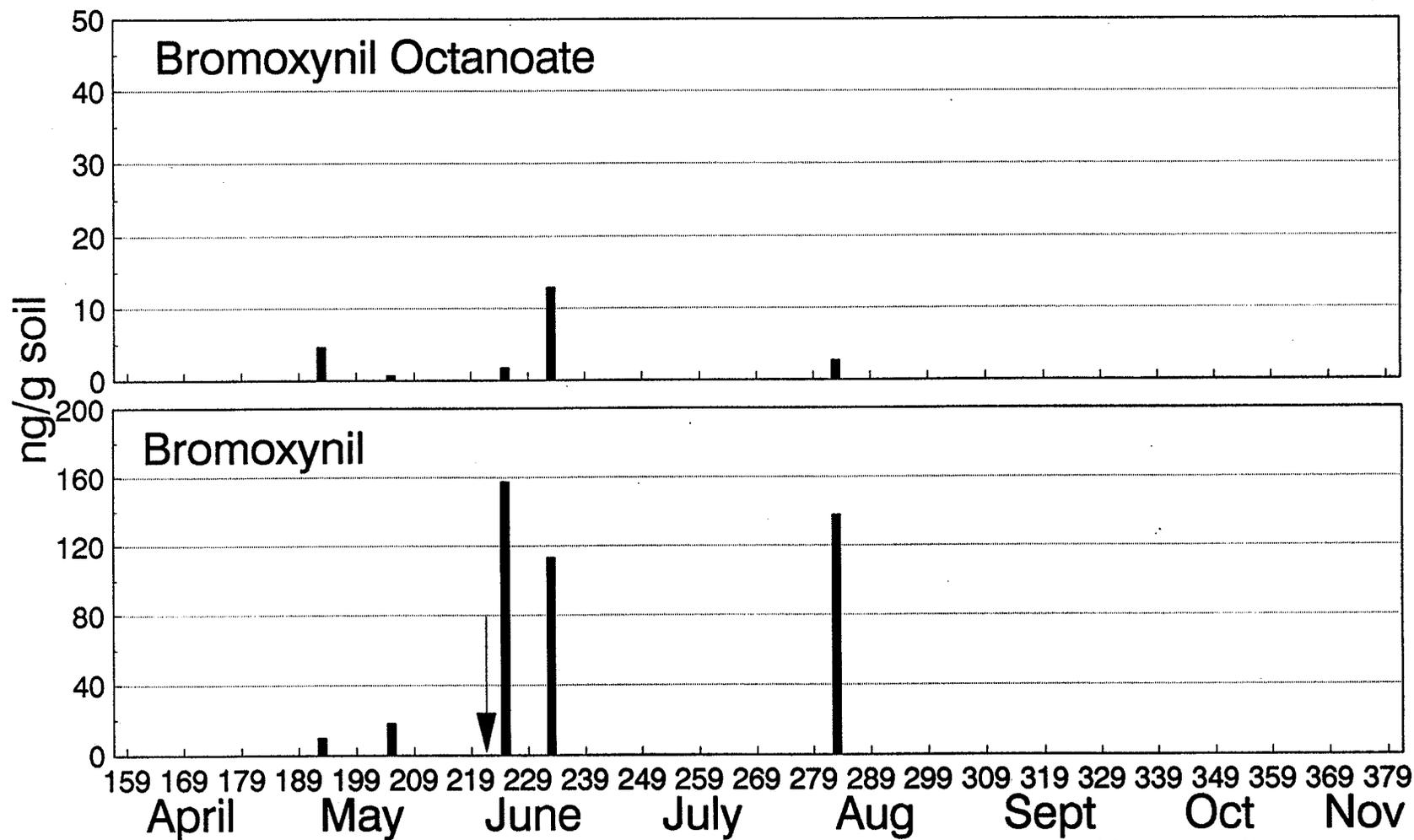


Figure 12: Soil Persistence of Bromoxynil octanoate and bromoxynil at the Miami, MB site; Arrow indicates Application 1989 (Experiment Day #s Given; Note: y-axis scaling between compounds)

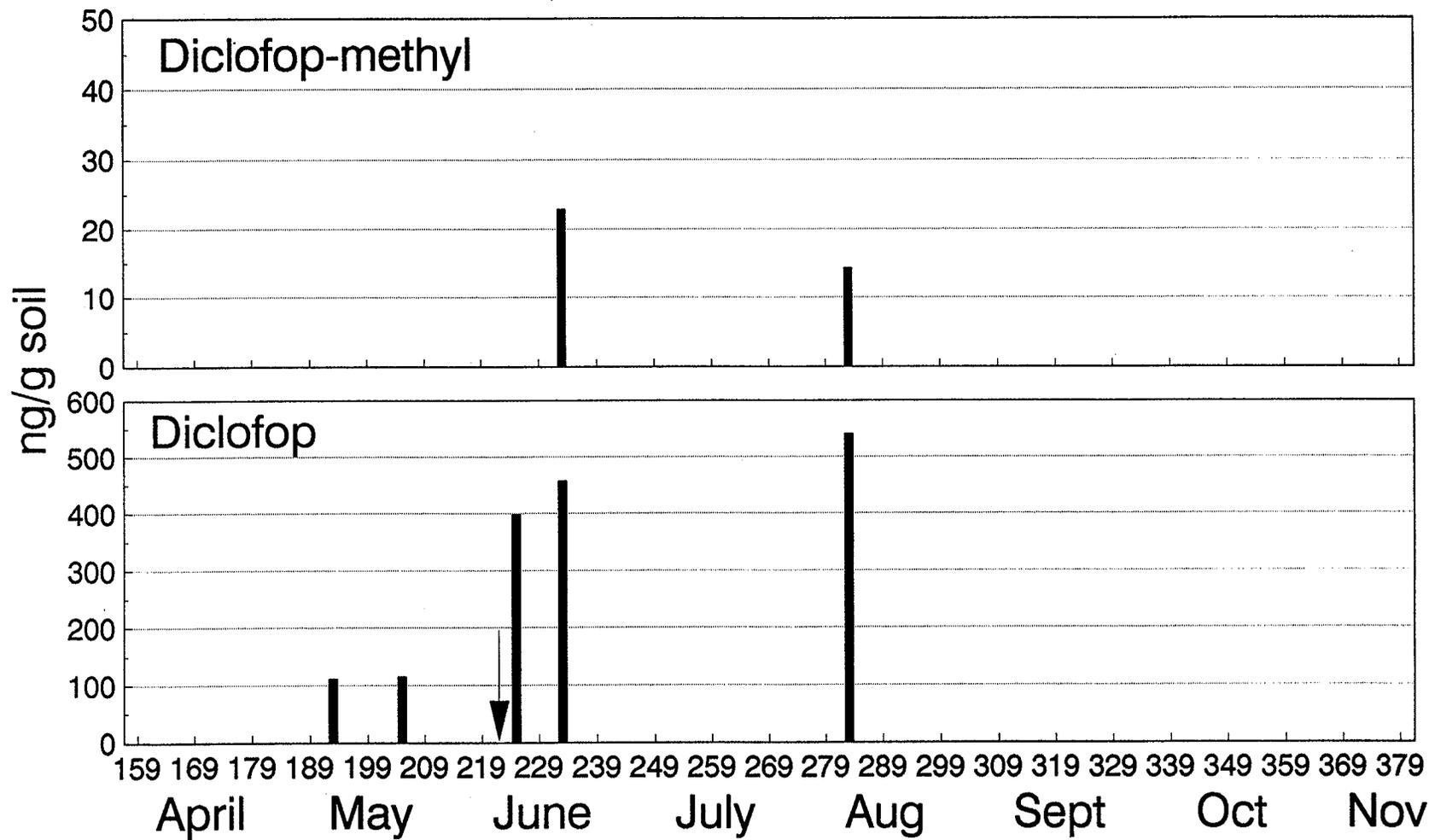


Figure 13: Soil Persistence of Diclofop-methyl and diclofop at the Miami, MB site; Arrow indicates Application 1989 (Experiment Day #s Given; Note: y-axis scaling between compounds)

very low levels prior to application (<5 ng/g). The August 3, 1989 soil sample showed diclofop-methyl residue levels at the highest concentration for the season (14 ng/g). Diclofop was present in soil at this time at the highest level for the season also (541 ng/g), probably as a result of samples having been taken from a location which received a higher diclofop-methyl application.

At the Roseisle wheat plot bromoxynil octanoate was not found in pre-treatment soil samples (Figure 14). Only low levels of bromoxynil were detected in these same samples (<5 ng/g). But as with samples from Miami, the Roseisle data showed the highest levels of both bromoxynil octanoate and bromoxynil in the first sampling period (24 ng/g and 135 ng/g, respectively), after application of the herbicide mixture.

Diclofop-methyl was not detected in the soil prior to application, however, diclofop acid was present in low concentrations (89 ng/g, May, 17) (Figure 15). After application of the formulation, 450 ng/g of diclofop was found in the soil. This dropped to 91 ng/g by the next sampling time in July. Diclofop-methyl residues were found in soil samples only shortly after application. Following the initial high level of diclofop, the residues in soil dropped rapidly.

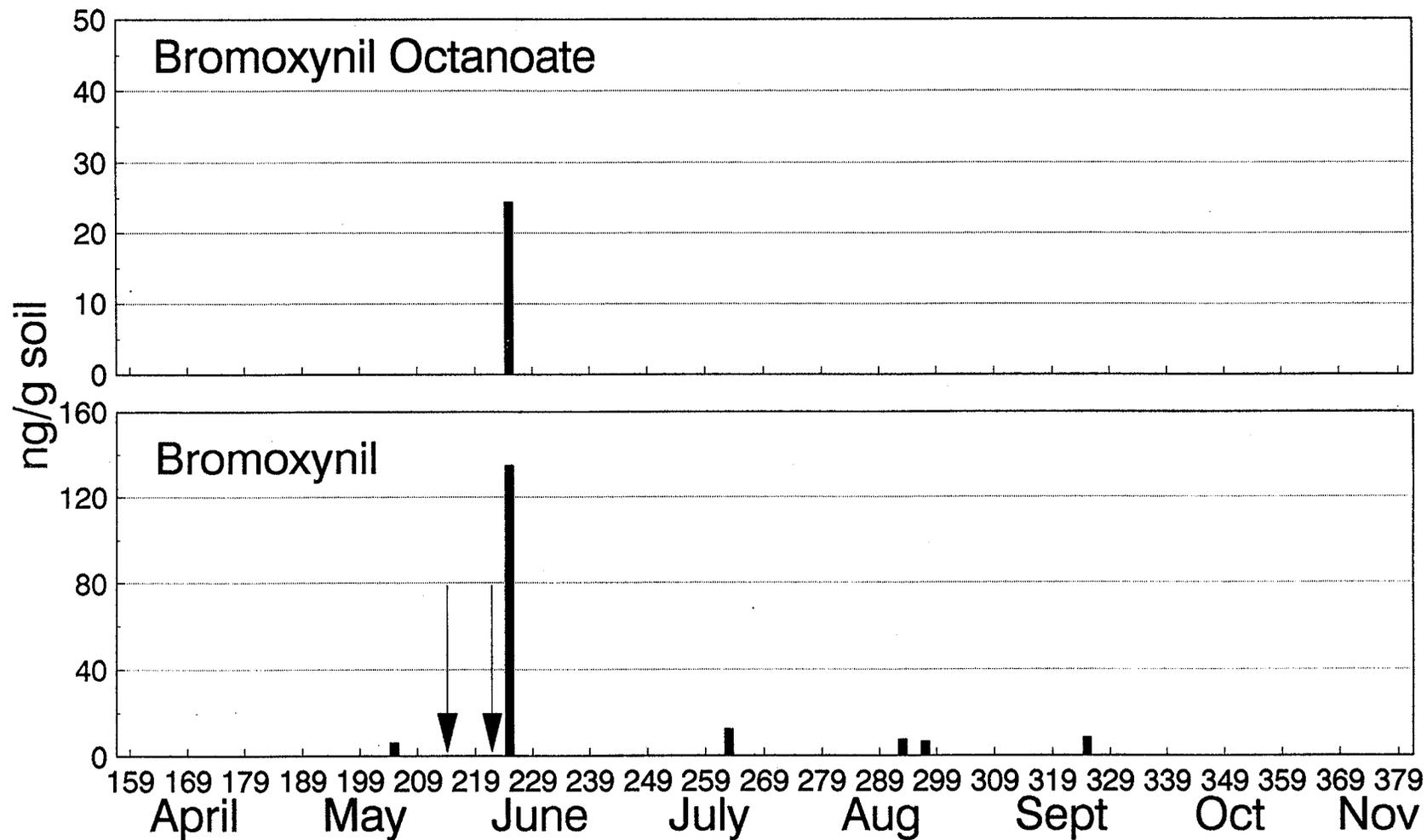


Figure 14: Soil Persistence of Bromoxynil octanoate and bromoxynil at the Roseisle, MB site; Arrow indicates Application 1989 (Experimental Day #s Given; Note: y-axis scaling between compounds)

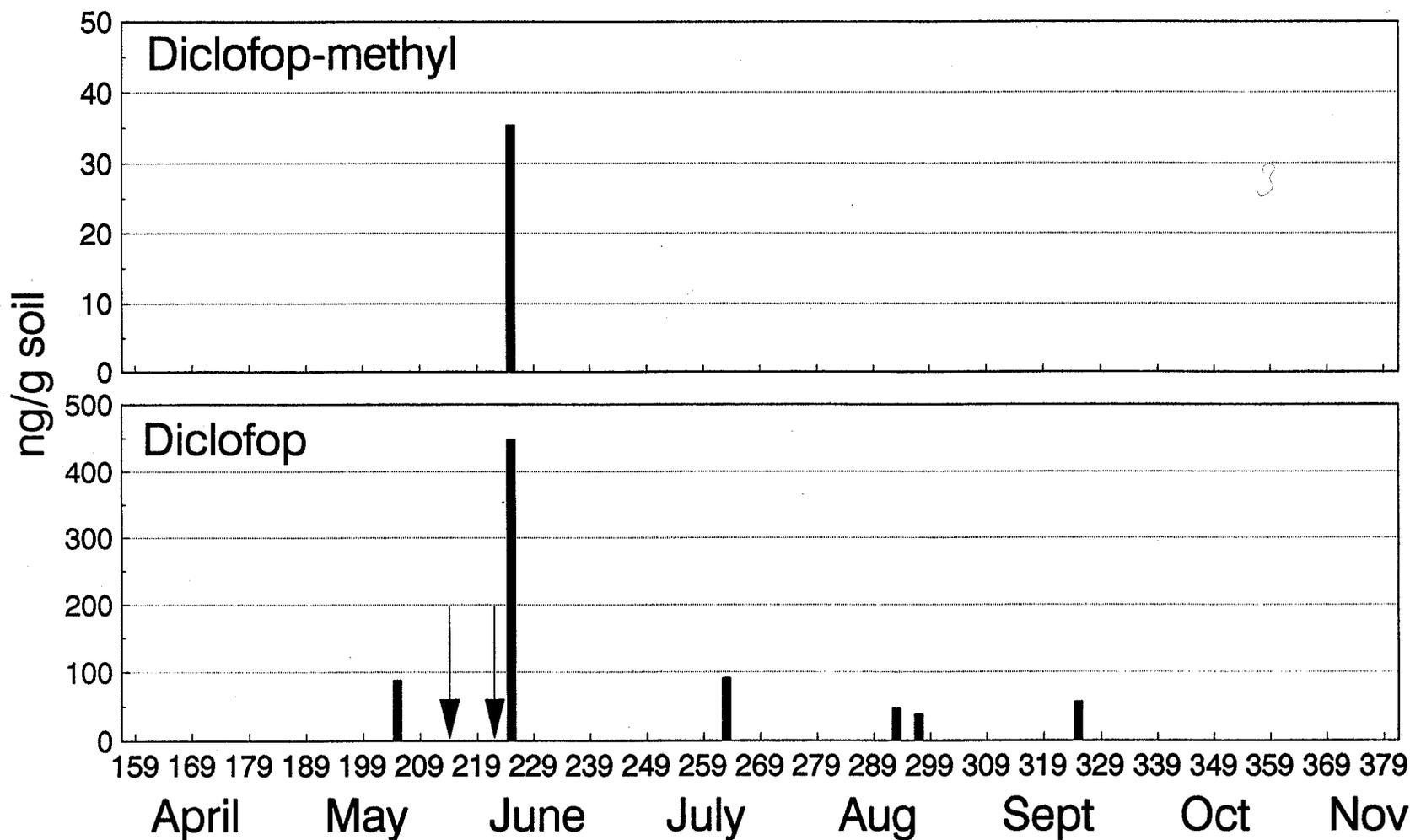


Figure 15: Soil Persistence of Diclofop-methyl and diclofop at the Roseisle, MB site; Arrow indicates Application 1989 (Experimental Day #s Given; Note: y-axis scaling between compounds)

At the Whitewater site, bromoxynil octanoate was detectable at all sampling times (Figure 16). Bromoxynil was detected in the highest amount, 94 ng/g, at 28 days after application. Subsequently, the bromoxynil residues were found to decrease more gradually than at either of the other sites under study possibly due to the multiple applications. Diclofop-Methyl, when detected in soil, was at very low concentrations (<5 ng/g). The diclofop, however, was detected in the highest amount (243 ng/g) the first sampling time after application and dropped to 29 ng/g by the last sampling of the season (144 d post-application) (Figure 17).

There have been relatively few persistence studies of bromoxynil octanoate and bromoxynil in soil (Brown *et al.*, 1984). Methanol has been used as the extracting solvent using a soxhlet method (Crouch and Pullin, 1975). This method had been found to reduce extraction efficiency with lower levels of analyte in the soil based on recovery study data. Smith (1980) performed a series of experiments to determine persistence of bromoxynil octanoate in various soils. The results of this study (Smith, 1980) show the rapid degradation of bromoxynil octanoate to bromoxynil. The bromoxynil was reduced to <5% of that applied in both a heavy clay and a sandy soil within 7 days. Under field

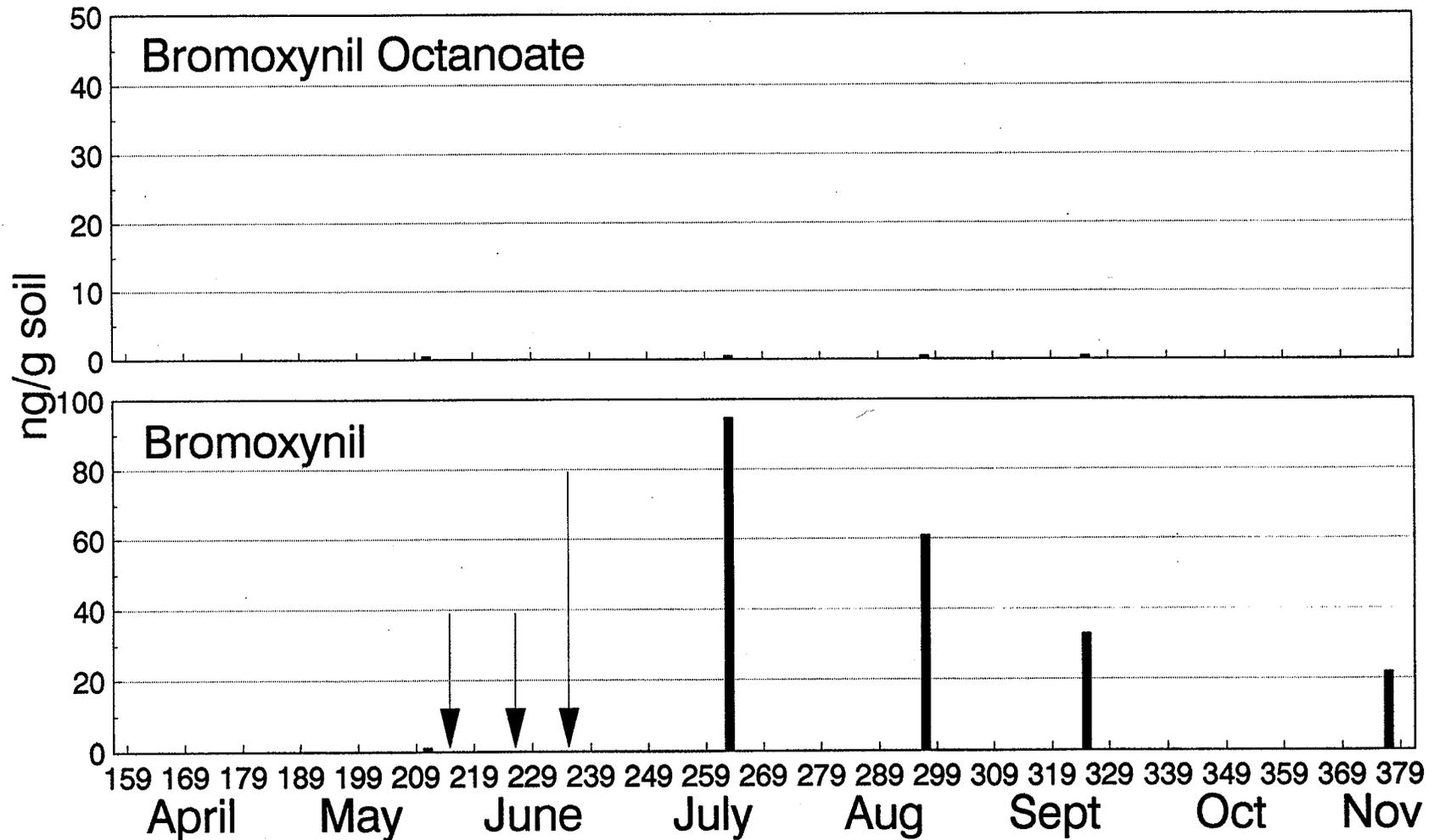


Figure 16: Soil Persistence of Bromoxynil octanoate and bromoxynil at the Whitewater, MB site; Arrow indicates Application 1989 (Experiment Day #s Given; Note: y-axis scaling between compounds)

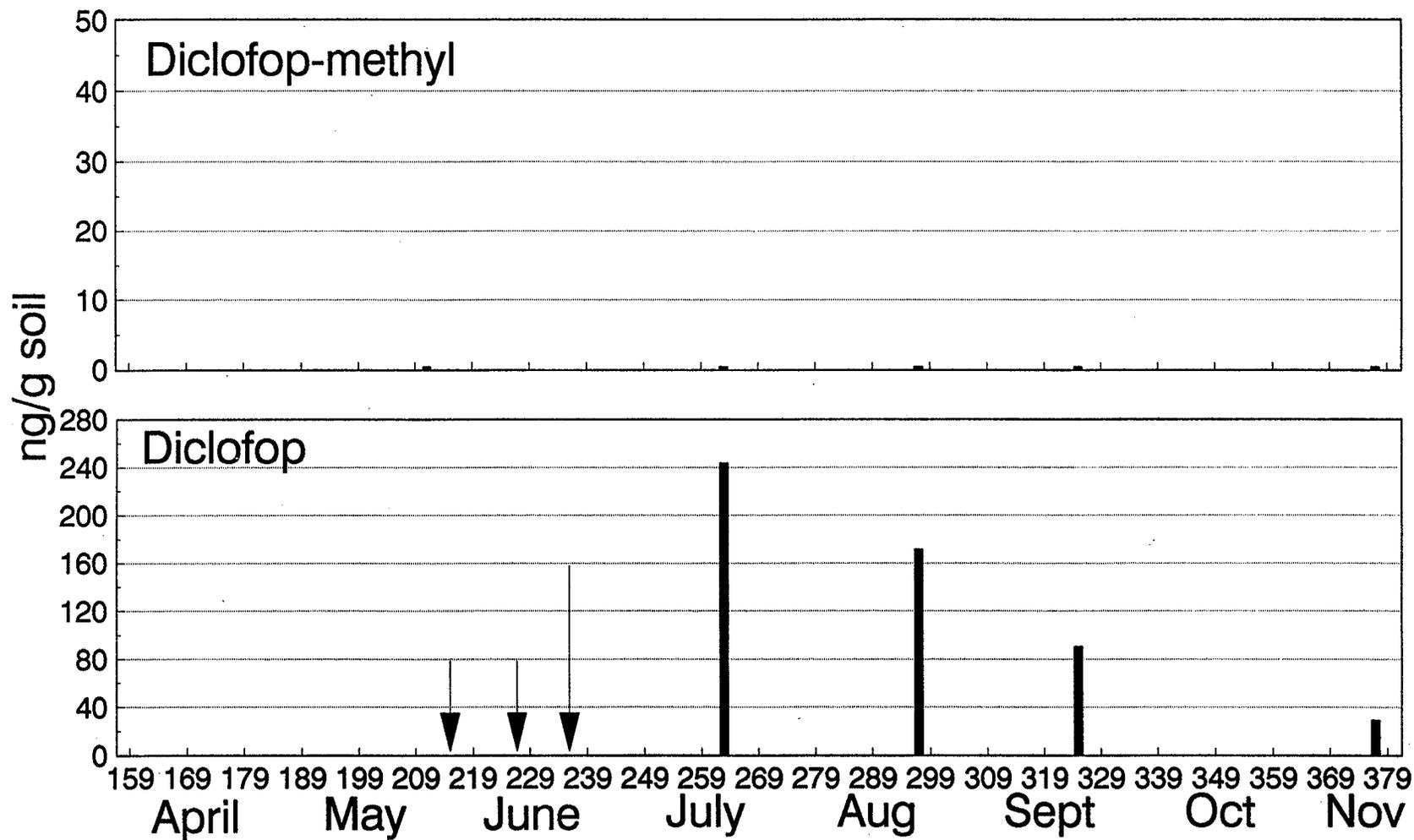


Figure 17: Soil Persistence of Diclofop-methyl and diclofop at the Whitewater, MB site; Arrow indicates Application 1989 (Experiment Day #s Given; Note: y-axis scaling between compounds)

conditions, the half life of bromoxynil was found to be of the order of 10 days (Smith, 1971). This loss of bromoxynil octanoate and bromoxynil in the present study agrees with data of Smith (1980).

Diclofop losses in this study do not compare well with those of Smith (1977). The data collected in the present experiment found diclofop-methyl to be rapidly degraded under Manitoba field conditions. Diclofop residues were found to decrease rapidly at the Roseisle site, in contrast to the results of Smith (1977). The diclofop residues detected in the Whitewater soil samples agreed more closely with data found in other studies. The last soil sample at the Miami site (August 3) was taken too early in the season to allow for the rate of loss of diclofop to be described. Martens (1978) found that diclofop-methyl was rapidly degraded to diclofop under moist conditions. Laboratory trials have shown that diclofop-methyl is more rapidly degraded in soil of a high pH (>pH 7) (Gaynor, 1984). In field trials, Gaynor (1984) has shown that a very rapid initial degradation of diclofop-methyl occurs in soil (first month post-application) followed by a slower rate later in the field season. Diclofop-methyl hydrolysis has been shown to occur rapidly in several Saskatchewan soils, with nearly complete hydrolysis in 9 days (90% of applied diclofop-methyl was hydrolyzed within 24 h) (Smith *et al.*,

1986). The degradation of diclofop acid was found to be much slower.

#### **B) Atrazine**

No degradation products of atrazine were found in the soil extracts from any of the locations under study.

Dealkylated metabolites of atrazine were present, however, in runoff samples. The dealkylation of atrazine has been described as the most important pathway in atrazine metabolism (Tafuri *et al.*, 1978), with de-ethyl atrazine the major metabolite. The results of the present runoff experiment confirmed this observation.

Atrazine was present in the soil prior to Aatrex application at all sites. At the Miami site the levels of atrazine detected in the soil over the entire season were lower than those found at the other locations (Figure 18). The first post-treatment samples have the highest atrazine residues 2.0  $\mu\text{g/g}$ ; levels drop by the 2nd and final post treatment sample of the season to 1.0  $\mu\text{g/g}$ .

Post-treatment samples at the Roseisle site show the highest level of atrazine (7.9  $\mu\text{g/g}$ ) in the soil over the entire field season (Figure 19). For the rest of the field season, much lower levels were found in the soil; by the second sampling residue levels had dropped to 1.3  $\mu\text{g/g}$ .

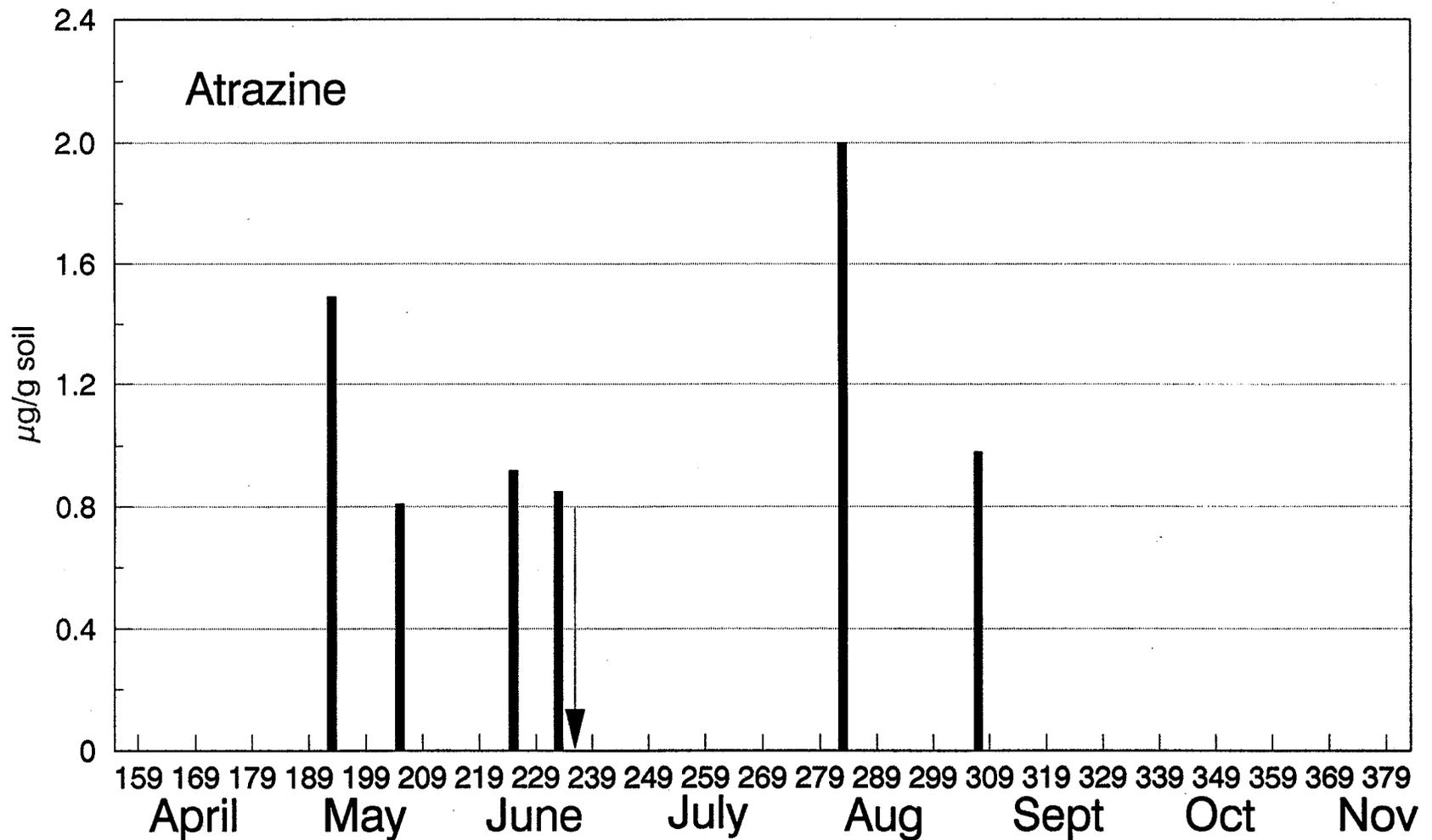


Figure 18: Atrazine Persistence in Soil at the Miami, MB site;  
 Arrow indicates Application  
 1989 (Experiment Day #s Given)

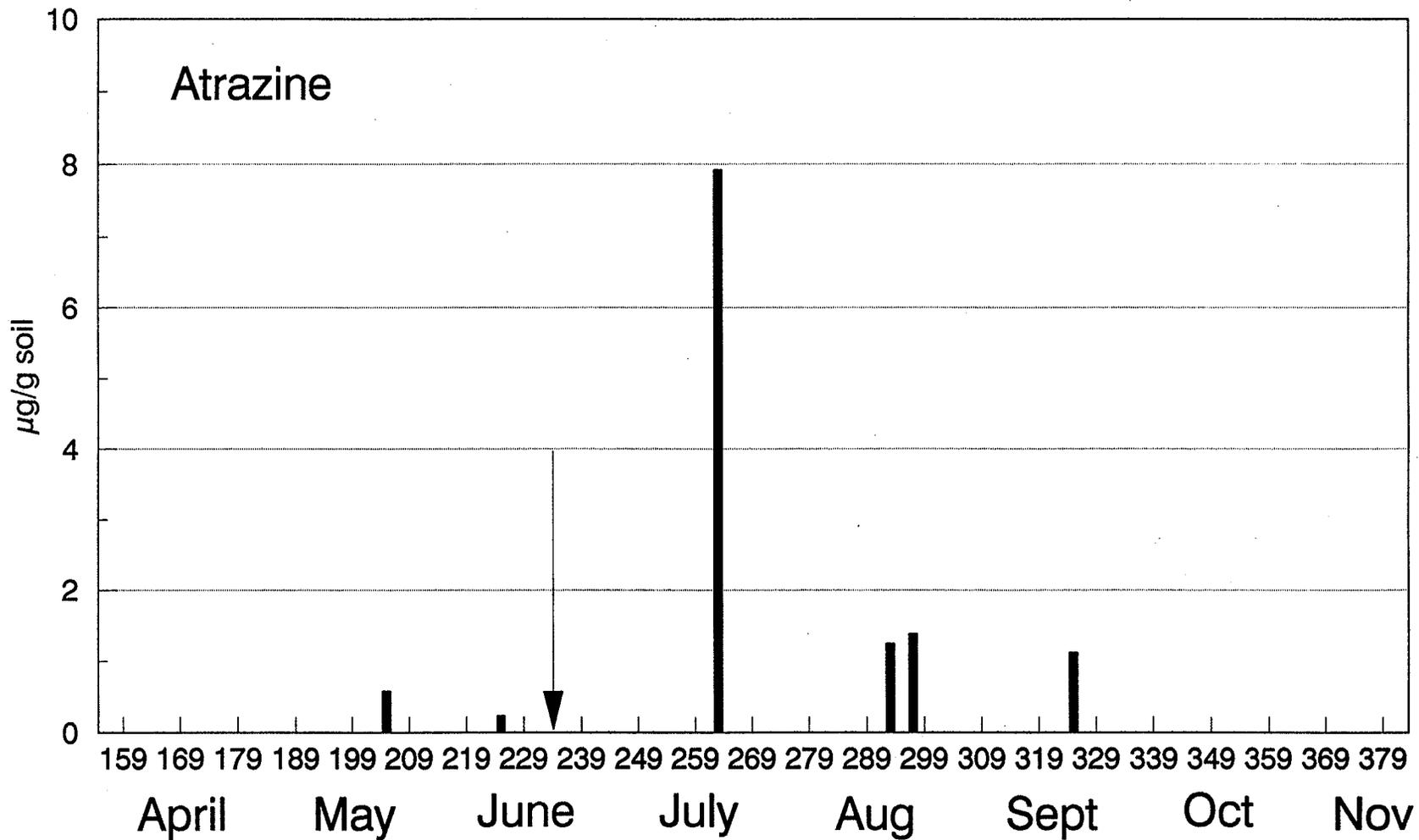


Figure 19: Atrazine Persistence in Soil at the Roseisle, MB site;  
 Arrow indicates Application  
 1989 (Experiment Day #s Given)

At the Whitewater site, the first two post application samples have the highest atrazine concentrations in soil (7.8  $\mu\text{g/g}$  and 8.0  $\mu\text{g/g}$ ) (Figure 20) than the samples collected during the rest of the field season. Levels decreased to 3.3  $\mu\text{g/g}$  in November. At this site, a more gradual loss of atrazine was found over the course of the field season than at either of the other locations used in this study.

Jamet and Thoisy-Dur, (1988) studied the mobility of several pesticides including atrazine in a variety of soil types and found atrazine to be only slightly mobile in a classification system ranging from immobile to very mobile. Atrazine has been found to sorb to soils (sediments) with high organic carbon content (>11%) and therefore shows little movement down the soil profile (Isensee, 1987). By determining the concentration of atrazine at numerous depths over 83 days, Nicholls *et al.* (1982) have shown that in a sandy loam soil atrazine is not prone to leaching. On the basis of this data, it was decided that only the 0-5 cm layer of soil needed to be analyzed. Nearpass *et al.* (1978) found the greatest loss of atrazine within the first 60 days post-application. Following an initial rapid decrease in atrazine levels, a more gradual loss in atrazine residues in the soil samples was detected. Because of less consistent soil sampling schedule in the

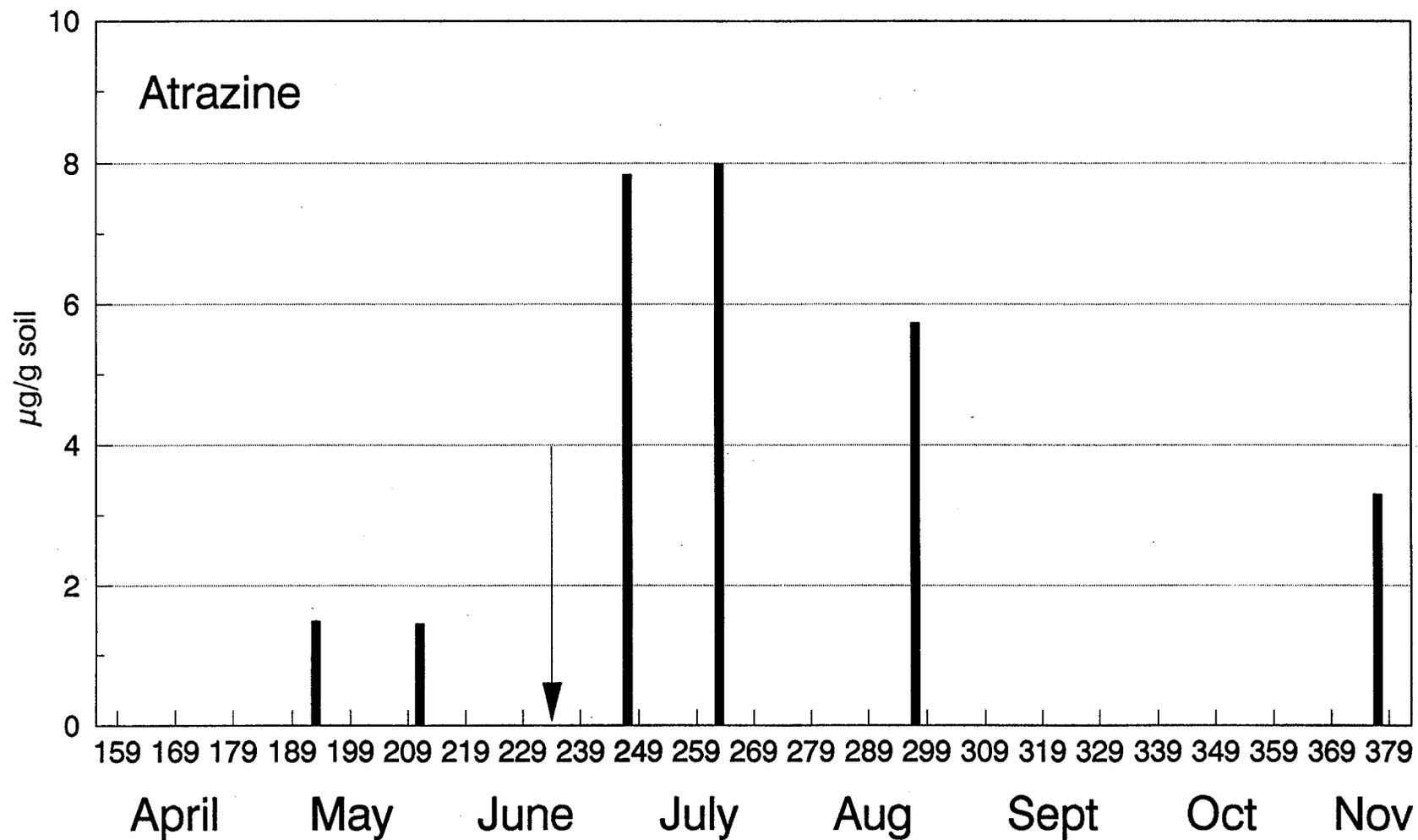


Figure 20: Atrazine Persistence in Soil at the Whitewater, MB site;  
 Arrow indicates Application  
 1989 (Experimental Day #s Given)

present study, (soil only having been sampled following a runoff event), this pattern was not seen in the data of the present experiment.

In the past, several experiments have been done to examine one particular aspect of a field trial and related atrazine persistence to that one factor (Rhode *et al.*, 1981), (Hiltbold and Buchanan, 1977). In the current experiment, the soil persistence of atrazine as well as the other residues under investigation were a secondary consideration. Because of the lower priority of soil persistence when the field experiment was developed, details were neglected that could have resulted in a better persistence determination. Better soil persistence data could have been determined if the soil had been sampled on a regular basis, throughout the entire field season.

#### **IV. Conclusions**

Field applications of Hoegrass II were performed on 3 different soil types. At each site, the persistence of the 2 active ingredients in the formulation were followed. In both cases, rapid losses of the applied compounds were detected on all soil types. Both bromoxynil octanoate and diclofop-methyl were readily hydrolyzed to their phenol and acid form, respectively. The bromoxynil was also found to be lost from the surface layer of the soil over one field season, in part perhaps due to photolytic degradation of

this chemical. Bromoxynil has been found to degrade through photolytically in aqueous solutions (Kochany et al., 1989).

Atrazine was applied to corn plots on a Gretna clay, a Leary sandy loam and a Ryerson sandy clay loam in the commercial formulation Aatrex. Despite the fact that degradation products were found in the runoff from each of these fields, they were not detected in soil extracts from any of the field sites under consideration. The Miami clay soil was found to have the lowest extractable atrazine levels. This may have been due to the high clay content and high organic matter content of this soil rather than differing application rates, as all sites were treated with the same Aatrex application. However, the rainfall was different at each site.

The most gradual loss of each of the applied compounds was found at the Whitewater site. This location had the least amount of precipitation over the course of the experiment. Low precipitation has been found to lead to slower degradation of compounds in field soil by Smith (1977).

### Chapter III.

## Runoff Modelling of Bromoxynil Octanoate, Diclofop-Methyl and Atrazine

### I. Introduction

Models have been developed to determine the mobility of pesticides in soils as well as the runoff losses of herbicides from fields. Some models available use empirical formulae to determine runoff losses (Wauchope and Leonard, 1980), e.g.,

$$C_t = AR (1 + 0.44t)^{-1}$$

where:  $C_t$  = Runoff Concentration at time  $t$

A = Availability Index

R = Spray Application Rate (kg/ha)

$t$  = Time

In the empirical model considered, both the application time and the chemical applied were considered. The chemicals were grouped into four classes and given an availability index (A). This method was developed as a way of obtaining a first estimate of runoff losses (Leonard, 1988). In other models used, the soil factors such as bulk density, universal soil loss equation, layers to root zone and active surface zone depth (cm) are the significant components. In the model described by Haith (1980), the soil factors coupled with the time between application and rainfall were

the most important variables. Another model was developed by McCall and Lane (1982) using partition coefficients, soil erodibility factors and an assumption that pesticides in soil decay exponentially. The model output was then compared with results found using the model described by Haith (1980). The data comparison performed by McCall and Lane showed a much better agreement between the observed results and those obtained using their model than predictions using Haith's model in their findings. The model developed by McCall and Lane split the pesticide content into sorbed and dissolved phases using physical characteristics of a given pesticide such as the adsorption/desorption partition coefficient (McCall and Lane 1982).

Other models have been used for the estimation of runoff losses of a pesticide from agricultural fields. Three models used to estimate runoff losses of pesticides, CREAMS (Chemical, Runoff and Erosion from Agricultural Management Systems), ARM (Agricultural Runoff Management) and CPS (Continuous Pesticide Simulation), were compared to determine the best model by Lorber and Mulkey (1982). It was noted that all of these models required adjustments prior to producing results that compared with the actual loss of pesticide found. The CREAMS model is also used for estimating leaching of chemicals in the root zone (Leonard, 1990).

Other computer programmed models, such as the SWRRB (Simulator for Water Resources in Rural Basins) model, can be run for different chemicals: This model is briefly considered in the review articles written by Leonard (1988 & 1990). The SWRRB model was developed from hydrology and erosion/sediment submodels of the Pesticide Runoff Simulator (Leonard, 1990). This model is used to estimate runoff losses based on pesticide characteristics, soil characteristics and crop cover. This type of model is useable for comparison of predicted and experimental runoff losses in a given year providing an annual precipitation record is available. It is important to realize, as is pointed out by McCall and Lane, (1982) that these models are only as good as the input data.

## **II. Model Input**

SWRRB is a computer run model that factors in more influences than the pesticide and its application date. Because of these extra parameters, it was chosen over the non-computerized and simpler models.

The model has three main sections into which input values are required. The rainfall and sunlight data, at a given site is one of the three input files. The crop/soil data is

the second input file and is the most difficult to set. The data in this file includes bulk density and other soil parameters combined with crop cover data. The third file is that of the pesticide data. Specific input factors used in this model are in Appendix V.

### **III. Results and Discussion**

The data at the beginning of the meteorology file (Appendix V) was taken from Grand Forks, ND to run the model. This data consists of monthly rainfall intensity factors, temperature and solar radiation. Grand Forks data was used for modelling at each site because all of the required information was not available for each site and a file with Grand Forks data was provided with the model. Use of Grand Forks data is justified because the sites are in south western Manitoba, only ~250 km north of Grand Forks this estimation was possible in similar climatic conditions. The rainfall intensity factors, however, may not reflect actual occurrences. The rainfall data for the Miami and Roseisle, sites were actually taken from the closest site with year round rainfall data, Morden, Manitoba. These are limitations of the model used, but it was necessary to have a complete precipitation dataset for reasonable results. The Whitewater site rainfall was estimated as that of the Peace Gardens as that was the closest site with year round data to Whitewater.

The crop files were the most difficult to set up, because there was not a spreadsheet into which values could be entered. The crop file has a limitation on the field size of estimation of 0.0001 mi<sup>2</sup>. This field size is larger than the fields used for the actual experiment which were 0.00004 mi<sup>2</sup> (0.01 ha). The file was set up to have soil properties input for each of the soil layers to the water table, however, the properties that were available were for the top layer only. Having only the topsoil layer information, a limitation to the estimation of the losses from the fields was created. Some initial estimation of several input factors based on other model descriptions, such as leaf area indices and erosion control practices, was required.

The pesticide file was the easiest to use. There were differences among pesticide files at the three sites, since herbicides were not applied on the same date and application rates were varied (see Table 4; Chapter I). The pesticide dataset was not extensive and limitations were found when constants were required but have not been determined on the soil types used. If there had been more input factors used in the model, such as hydrolysis and photolysis rates, the output might have closely approximated experimental results.

The estimation of runoff (and other factors) using a detailed model could reasonably be expected to be more reliable than models with only one or two factors. Results

of the model simulators showed that there would be loss of the bromoxynil octanoate and diclofop-methyl shortly after application as a result of the rainfall producing runoff from the fields at that time. The SWRRB model estimated very little actual runoff from any of the field sites examined. The model also was only able to estimate losses of the parent compounds but not loss of the degradation products that are formed. This type of problem is a particularly significant deficiency in the case of the two easily hydrolyzed compounds, bromoxynil octanoate and diclofop-methyl. The atrazine runoff data does not fit the experimental results as well as the others. At the Roseisle site only one runoff event producing atrazine loss was estimated and it was very late in the field season.

The SWRRB model estimated the amount of pesticide leached into the top 1 cm of the soil. This parameter was somewhat difficult to assess in a real life experiment as the soil surface was not uniform and varied by more than 1 cm from one spot to the next along a given field. The predicted loss of atrazine was found to be mostly through this leaching. It was not possible to compare this prediction to the experimental results since the soil samples collected were taken of the top 5 cm rather than extraction of 1 cm layers.

The runoff concentrations predicted for bromoxynil octanoate from the fields were much higher (an order of magnitude or more) than observed and the output concentration values were closer to the bromoxynil values that were detected (Figures 21-23). Diclofop-methyl runoff losses in the model output were also higher than actually determined, however, the diclofop-methyl residues were not determined in the runoff water and therefore a comparison could not be made as discussed earlier in Chapter I (Figures 24-26). Despite the fact that the model values were not in agreement with those determined experimentally, the trends fit closely to the experimentally determined pattern.

The model output did not show a similar pattern of runoff loss to the experimental results for atrazine. The model data showed runoff losses at different times than those found experimentally (Figures 27-29). The concentration values produced by modelling were not consistently higher than detected analytically as was found with the other analytes. The output results in Appendix VI show the actual loss in terms of g/ha.

This model shows runoff loss patterns that compare with those found in field experiments. Many other models do not have the scope to compare individual events, only the average of seasonal events can be compared (Haith, 1980).

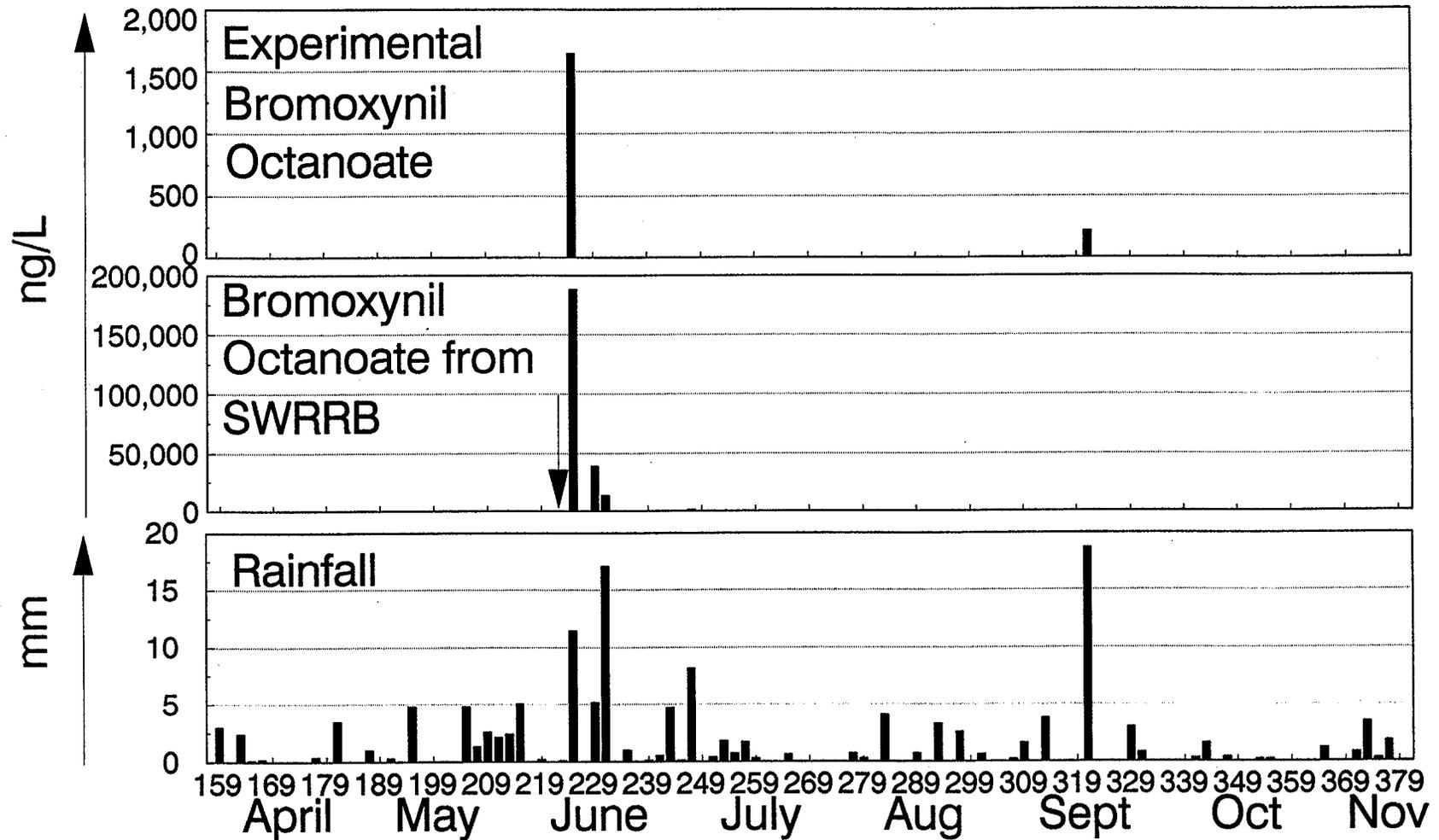


Figure 21: Bromoxynil Octanoate Concentrations (2-Day Average) in Runoff found Experimentally and Predicted by the SWRRB Model at the Miami, MB site; Arrow indicates Application

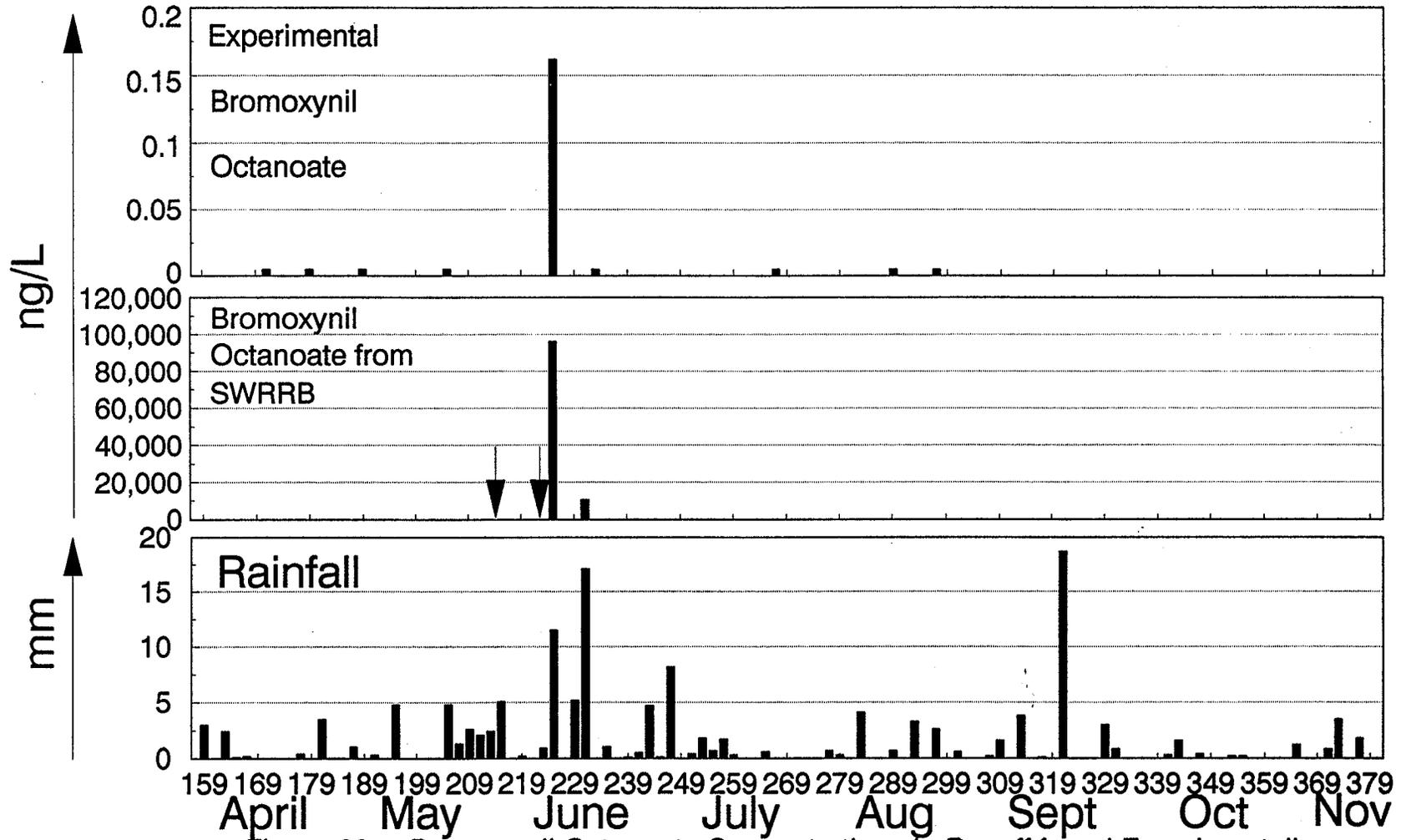


Figure 22: Bromoxynil Octanoate Concentrations in Runoff found Experimentally and Predicted by the SWRRB Model at the Roseisle, MB site; Arrows indicate Application

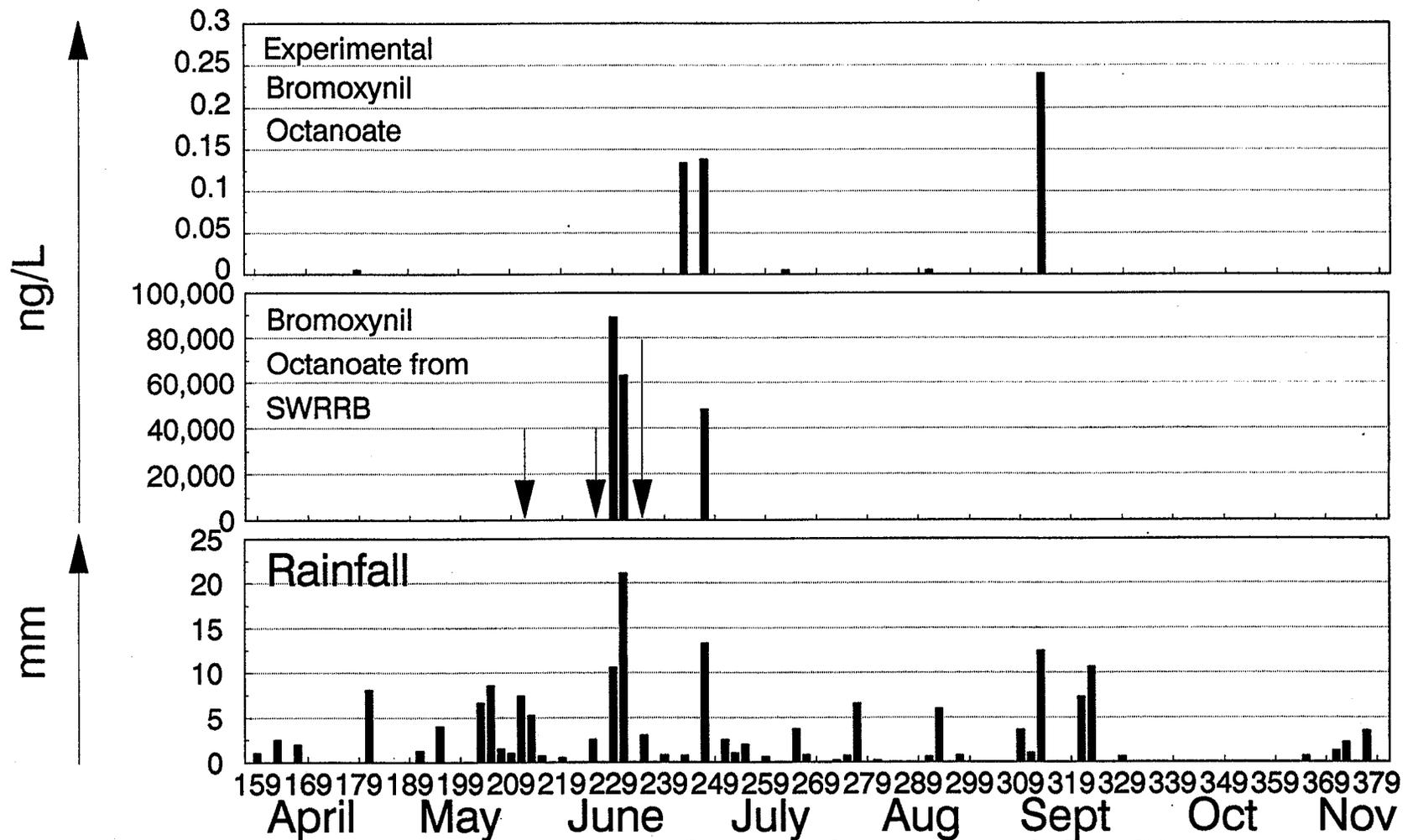


Figure 23: Bromoxynil Octanoate Concentrations in Runoff found Experimentally and Predicted by the SWRRB Model at the Whitewater, MB site; Arrows indicate Application

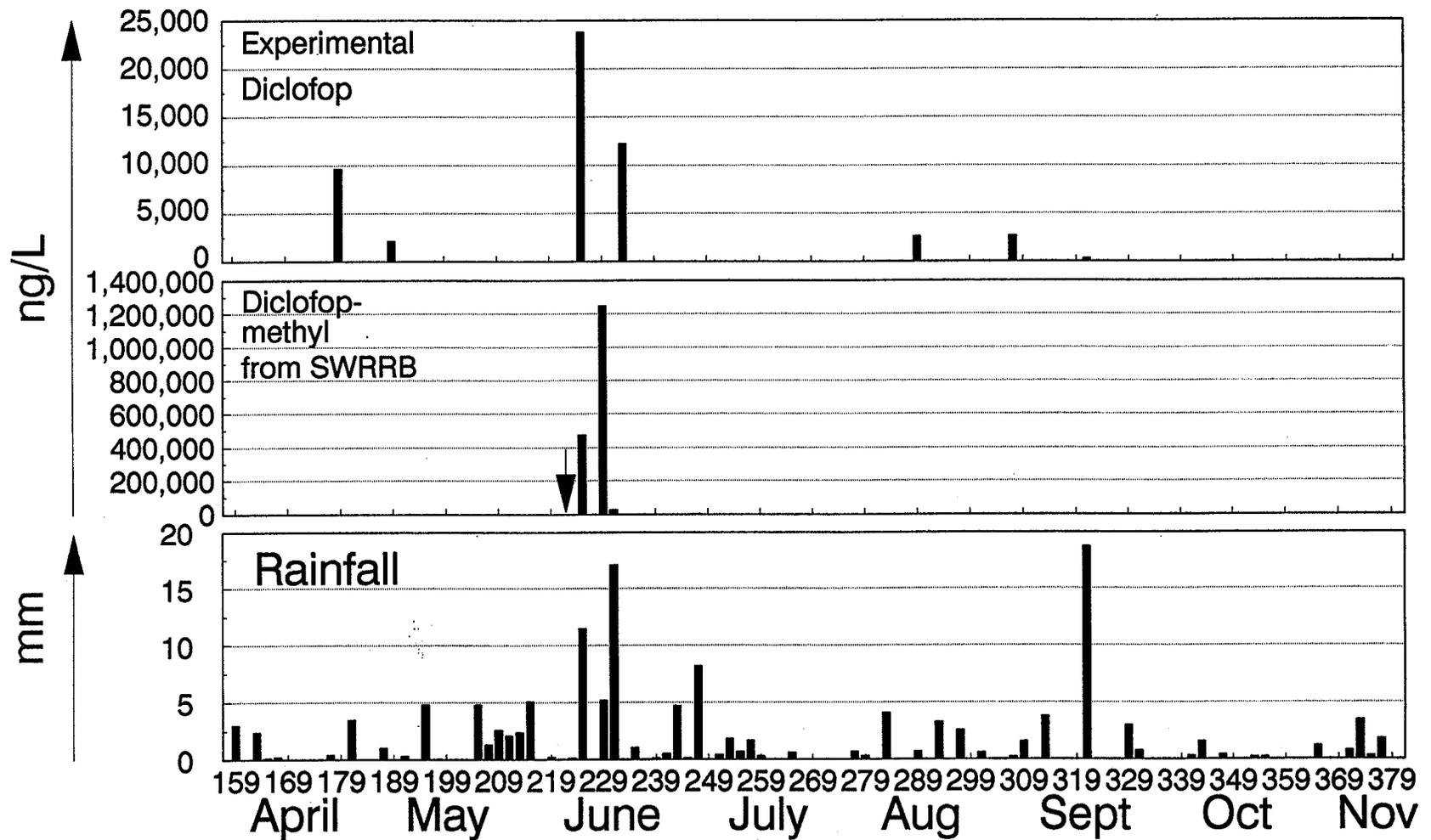


Figure 24: Diclofop-methyl Concentrations in Runoff found Experimentally and Predicted by the SWRRB Model at the Miami, MB site; Arrow indicates Application

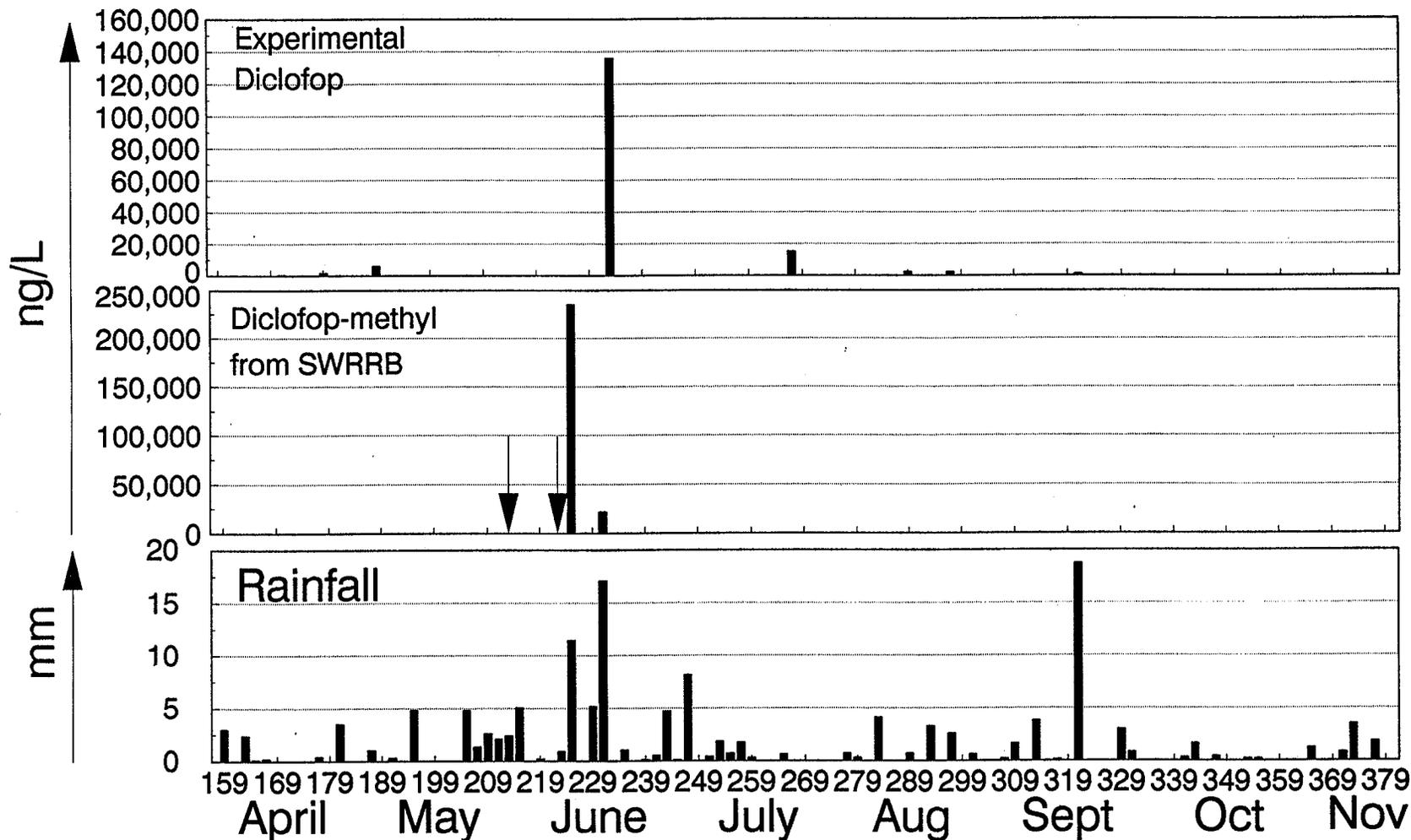


Figure 25: Diclofop-methyl Concentrations in Runoff found Experimentally and Predicted by the SWRRB Model at the Roseisle, MB site; Arrows indicate Application

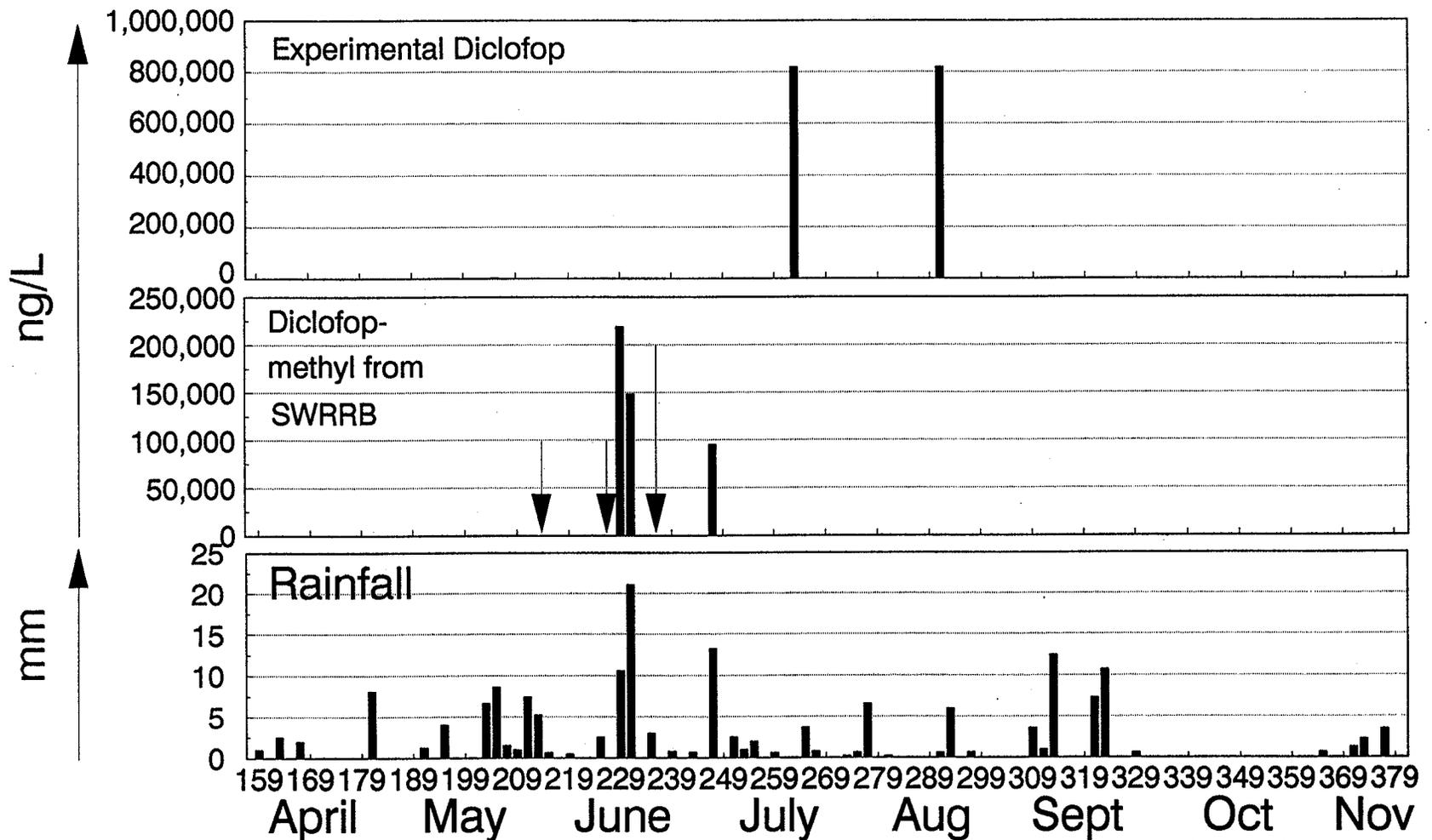


Figure 26: Diclofop-methyl Concentrations in Runoff found Experimentally and Predicted by the SWRRB Model at the Whitewater, MB site; Arrows indicate Application

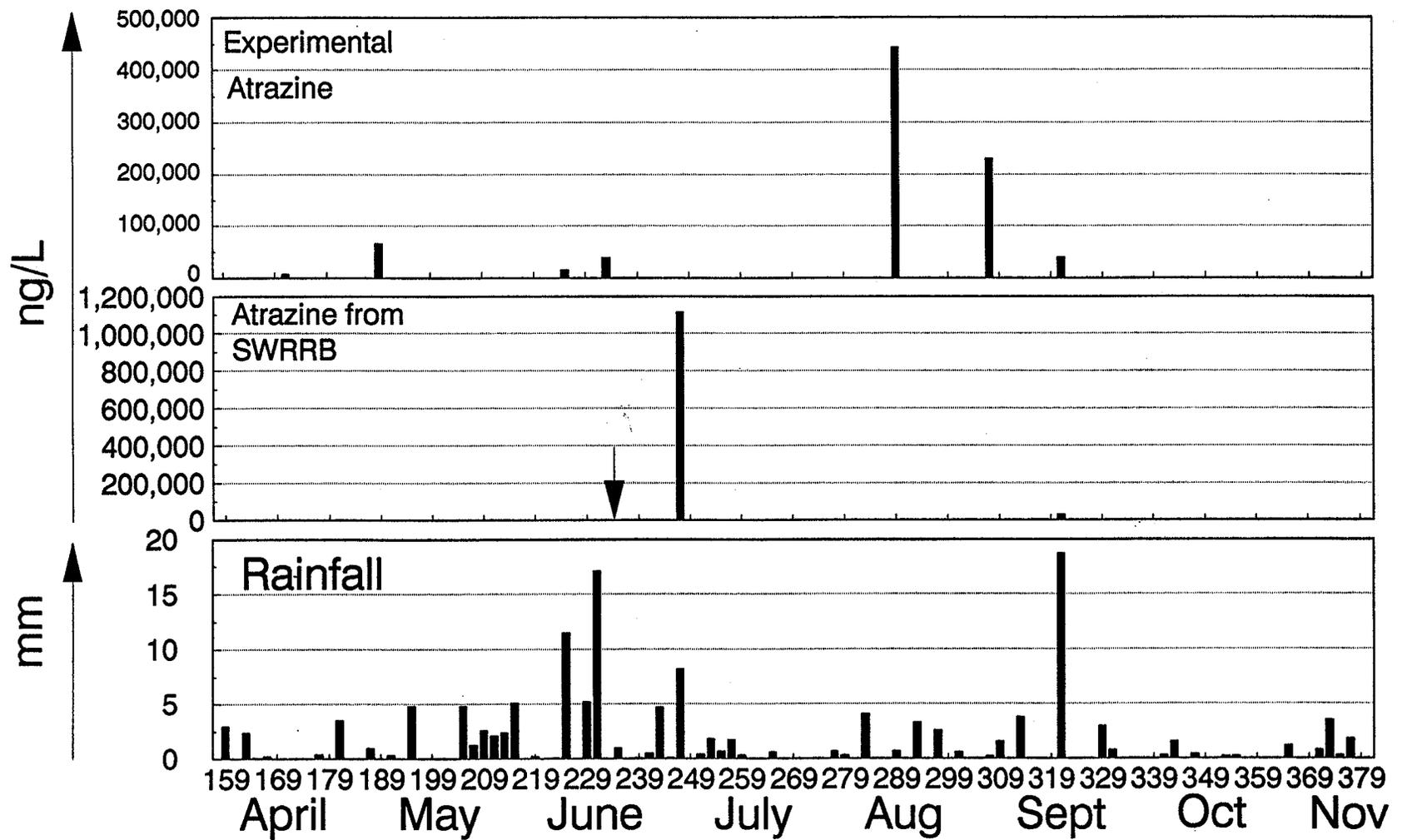


Figure 27: Atrazine Concentrations in Runoff found Experimentally and Predicted by the SWRRB Model at the Miami, MB site; Arrow indicates Application

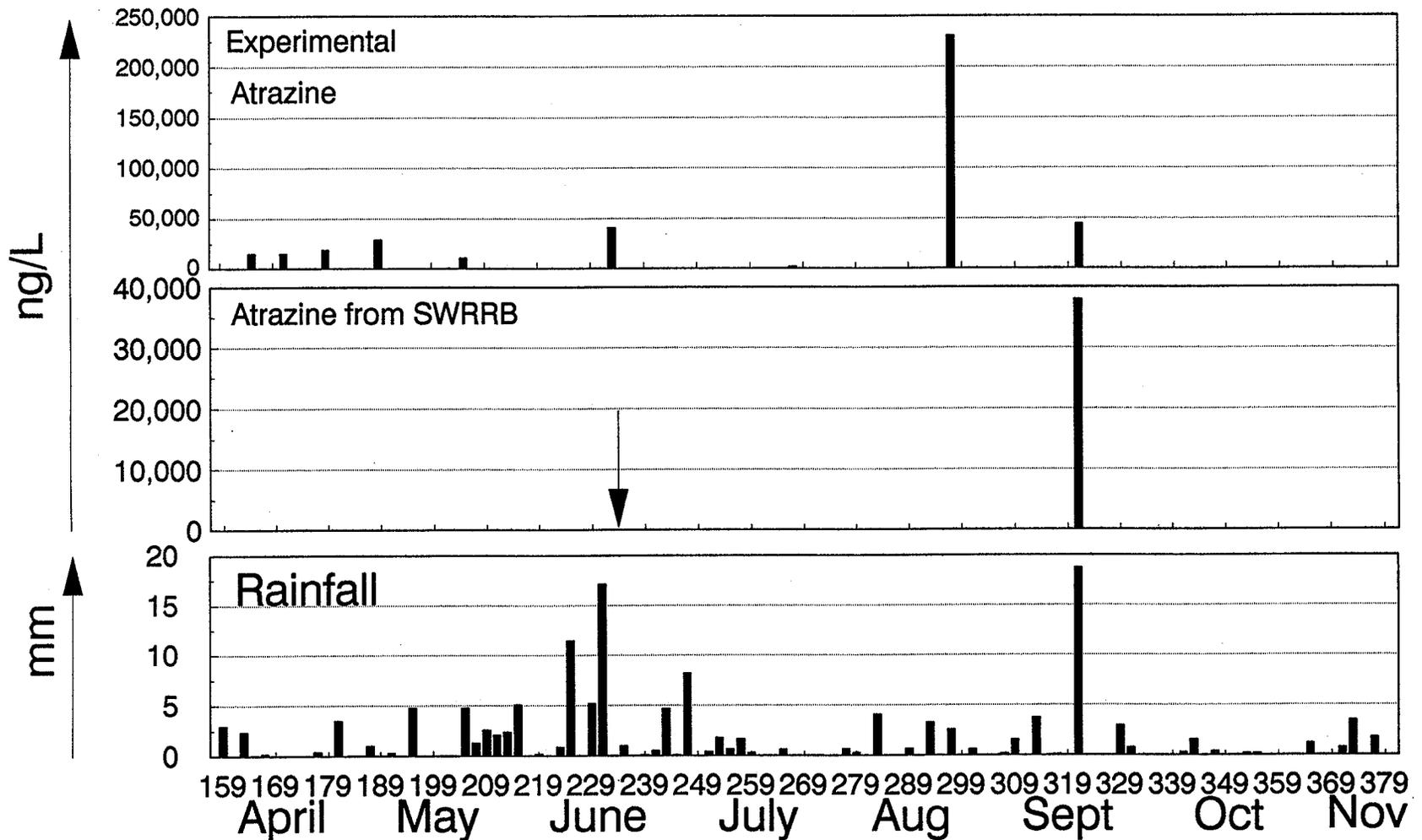


Figure 28: Atrazine Concentrations in Runoff found Experimentally and Predicted by the SWRRB Model at the Roseisle, MB site; Arrow indicates Application

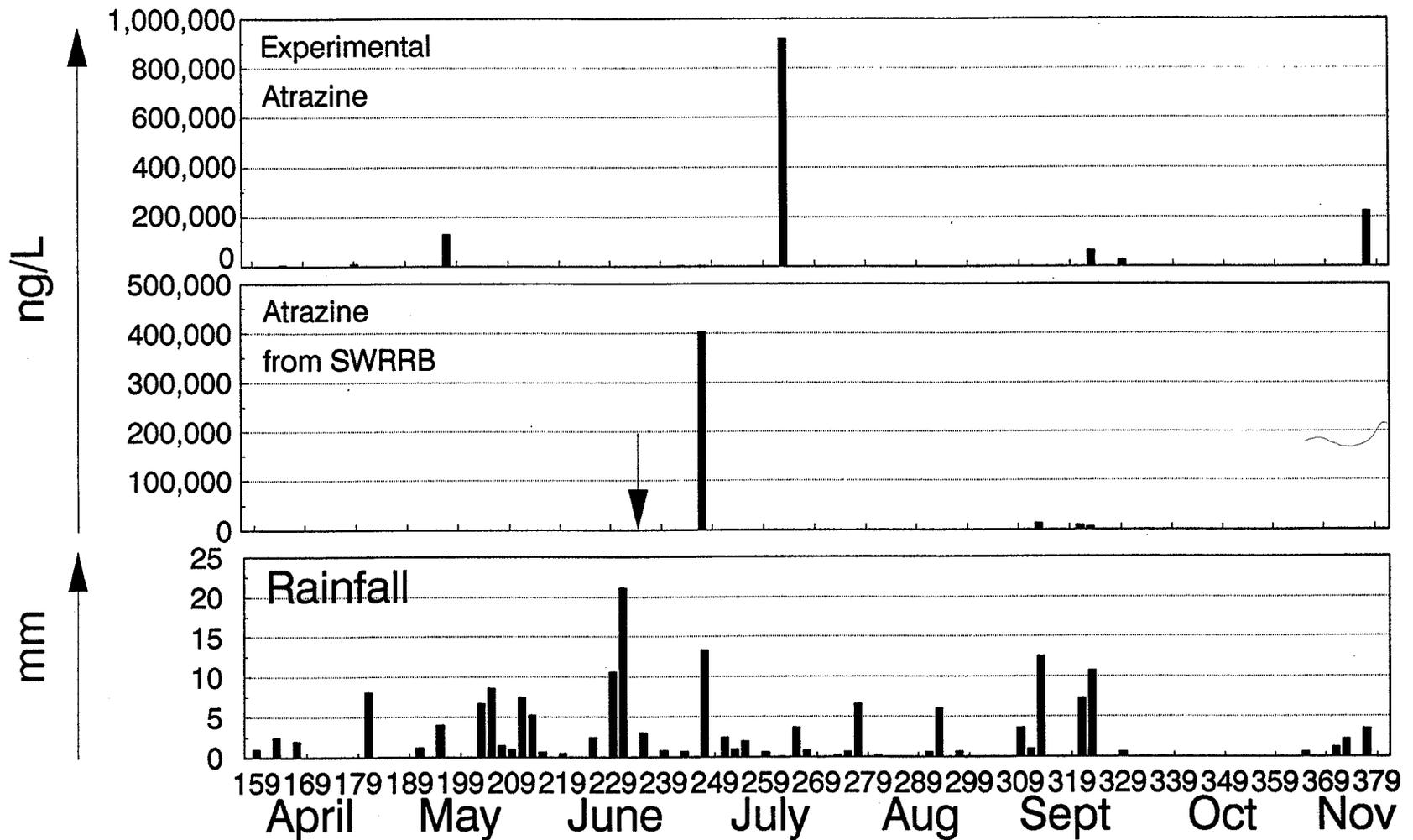


Figure 29: Atrazine Concentrations in Runoff found Experimentally and Predicted by the SWRRB Model at the Whitewater, MB site; Arrow indicates Application

#### IV. Conclusions

The runoff model SWRRB was chosen to estimate pesticide losses from theoretical field sites, as close to those actually worked on as possible, using information available and within limitations of the model. Although the actual values determined in the runoff concentrations did not fit those found experimentally, the trends shown are similar. This model was chosen in part because it could be run on a computer, rather than having to calculate each data point manually and it was already available in computer program format. It was also chosen because of the many parameters that were included in the consideration of the losses. Other models, including the one proposed by Haith (1980) state that a correlation between the actual events and the model results for each distinct data point is not very good.

It is important to realize that the model results are not only a reflection of the model itself but also of the input variables that may not have been as accurate as if the initial project had been planned to consider each parameter in the model more closely. The model does however have very definite limitations which adds to the margin of error. If the SWRRB model used more pesticide variables in conjunction with the detailed hydrology and meteorology data, a closer

comparison between experimental and model results might be able to be found.

This type of field trial would be useful over a long period of time so that runoff loss and persistence patterns of specific compounds could be determined over a wide range of conditions. The current project could have been, with more hands available to work, a more useful and valuable piece of work. The capacity for the examination of corresponding leaching patterns of these herbicides would also have added to the value of this research. A comprehensive field study conducted over a number of years and including the above enhancements would make it possible to determine the optimum conditions under which the model would work.

The SWRRB model might never accurately predict runoff losses in field trials, even if all these other aspects of sampling were considered. A discrepancy might always be present between this model and experimental results since SWRRB was developed for a warmer and more humid environment (southern United States) and assumptions built into the model might be incorrect for Manitoba; further work would need to be done to evaluate these questions.

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## APPENDICES

## Appendix I.

## Recovery Study on Water\* of All Analytes

Level	% RECOVERY			
	Bromoxynil	Bromoxynil Octanoate	Diclofop-Methyl	Atrazine
Blank	0	0	0	0
Low	122 ± 16	81 ± 11	101 ± 11	110 ± 3
High	96 ± 14	99 ± 11	95 ± 8	95 ± 6

## Where Spiking Levels:

Low - Bromoxynil = 50 µg/L  
 - Bromoxynil Octanoate = 50 µg/L  
 - Diclofop-Methyl = 50 µg/L  
 - Atrazine = 500 µg/L

High - Bromoxynil = 500 µg/L  
 - Bromoxynil Octanoate = 500 µg/L  
 - Diclofop-Methyl = 500 µg/L  
 - Atrazine = 5000 µg/L

\* Tap water was used for the recovery study

## Appendix II.

Recovery Study Data For all Analytes on :Gretna Clay  
 Leary Sandy Loam  
 Ryerson Sandy Clay

Soil: Gretna Clay

Recovery %

Level	Bromoxynil	Bromoxynil Octanoate	Diclofop Methyl	Atrazine
Blank	0	0	0	0
Low	107 ± 9	111 ± 4	80 ± 5	122 ± 14
High	112 ± 12	113 ± 2	120 ± 11	123 ± 12

Soil: Leary Sandy Loam

Blank	0	0	0	0
Low	144 ± 39	85 ± 14	144 ± 12	122 ± 12
High	109 ± 3	116 ± 4	131 ± 10	102 ± 5

Soil: Ryerson Sandy Clay Loam

Blank	0	0	0	0
Low	160 ± 16	111 ± 2	173 ± 5	109 ± 3
High	108 ± 10	116 ± 4	121 ± 12	104 ± 9

Where Spiking Levels:

Low - Bromoxynil = 0.02 µg/g  
 - Bromoxynil Octanoate = 0.025 µg/g  
 - Diclofop-Methyl = 0.1 µg/g  
 - Atrazine = 0.1 µg/g

High - Bromoxynil = 0.25 µg/g  
 - Bromoxynil Octanoate = 0.25 µg/g  
 - Diclofop-Methyl = 0.5 µg/g  
 - Atrazine = 0.5 µg/g

**Appendix III.**

Equations used to calculate amount of each compound in:

- i) Spray Deposits
- ii) Runoff
- iii) Soil

i. a) Spray Deposits on wheat plots

(Bromoxynil, Bromoxynil octanoate, Diclofop-Methyl)

$$\frac{(\text{peak area} - b)}{m} \mu\text{g/mL} * \left( \frac{\text{mL} * 1 \times 10^8 \text{ cm}^2 / \text{ha}}{(122.7 \text{ cm}^2 * 1 \times 10^9 \mu\text{g/kg})} \right) = \text{kg/ha}$$

Where:

m = slope of line from standard curve \*

b = y-intercept from standard curve \*

$1 \times 10^8$  = area factor

122.7 = area of filter paper (12.5 cm diameter)

$1 \times 10^9$  =  $\mu\text{g}$  to kg conversion

\* a standard curve was run for each compound to determine the slope and intercept. One standard from the standard curve was run every six samples, varying in concentration throughout. The same standard curve was used throughout the study.

b) Spray Deposits on corn plots

(Atrazine, de-ethyl atrazine)

$$\frac{(\text{peak area} - b)}{m} \mu\text{g/mL} * \left( \frac{\text{mL} * 1 \times 10^8 \text{ cm}^2 / \text{ha}}{(122.7 \text{ cm}^2 * 1 \times 10^9 \mu\text{g/kg})} \right) = \text{kg/ha}$$

Where:

m = slope of line from standard curve \*

b = y-intercept from standard curve \*

122.7 = area of filter paper (12.5 cm diameter)

\* a standard curve was run for each compound to determine the slope and intercept. One standard from the standard curve was run every six samples, varying in concentration throughout. The same standard curve was used throughout the study.

## ii. a) Runoff from wheat plots

$$\frac{(\text{peak area} - b)}{m} \mu\text{g/mL} * \frac{20\text{mL}}{(\text{vol. sample mL})} * 1 \times 10^6 (\text{ng}/\mu\text{g}) (\text{mL}/\text{L}) = \mu\text{g}/\text{L}$$

Where:

m = slope of line from standard curve  
 b = y-intercept from standard curve  
 20 = dilution factor

## b) Runoff from corn plots

$$\frac{(\text{peak area} - b)}{m} \mu\text{g/mL} * \frac{0.5 \text{ mL}}{(\text{vol. sample mL})} * 1 \times 10^6 (\text{ng}/\mu\text{g}) (\text{mL}/\text{L}) = \mu\text{g}/\text{L}$$

Where:

m = slope of line from standard curve  
 b = y-intercept from standard curve  
 0.5 = injection factor (2  $\mu\text{L}$  injection)

## iii. a) Residues in soil of wheat plot

$$\frac{(\text{peak area} - b)}{m} \mu\text{g/mL} * \frac{(30/20 \text{ mL/mL}) (10 \text{ mL})}{\text{Wt Sample g}} * 1 \times 10^3 \text{ ng}/\mu\text{g} = \text{ng}/\text{g}$$

Where:

m = slope of line from standard curve  
 b = y-intercept from standard curve  
 30 & 20 = extraction, aliquot factors  
 10 = dilution factor

## b) Residues in Soil of corn plot

$$\frac{(\text{peak area} - b)}{m} \mu\text{g/mL} * \frac{(30/20 \text{ mL/mL})}{\text{Wt Sample g}} * 5 \text{ mL} * 0.5 * 1 \times 10^3 = \mu\text{g}/\text{g}$$

Where:

m = slope of line from standard curve  
 b = y-intercept from standard curve  
 30 & 20 = extraction, aliquot factors  
 5 = dilution factor  
 0.5 = injection factor

Equations used to calculate % Loss of Analytes

- i. Bromoxynil octanoate and Atrazine
- ii. Diclofop-Methyl

i.a)

$$\frac{\text{M.W. of applied compound}}{\text{M.W. of degradation product}} \times \text{Total Wt of Metabolite} = \text{Total loss of Metabolite in runoff (field season)}$$

b) Total Loss = Loss of applied compound + Loss of degradation product

c)  $\frac{\text{Total Loss of Analyte}}{\text{Total Analyte Applied}} \times 100 = \% \text{ Loss}$

ii.  $\frac{\text{Total Loss of Diclofop-Methyl}}{\text{Total Diclofop-Methyl applied}} \times 100 = \% \text{ Loss}$

Equations used to Calculate total loss of applied herbicides

$$\frac{\text{Concentration of Residue Lost in Runoff Sample (ng/L)}}{\text{Volume of Runoff from Field Plot (L)}} \times 100 = \text{ng/ha (Plots 0.01 ha)}$$

**Appendix IV.**

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**GC/ITD Conditions**

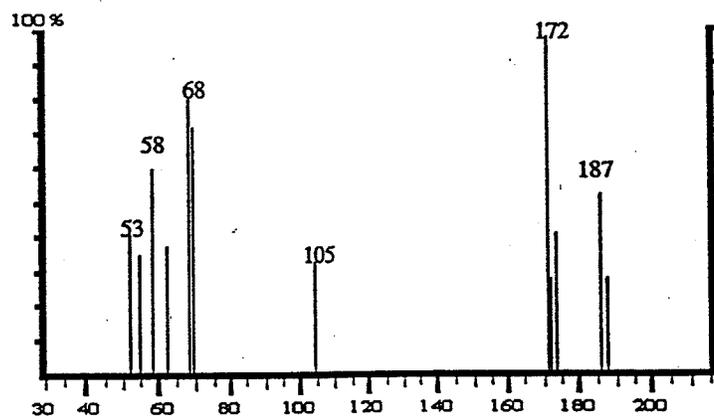
---

Temperature Program	70°C hold for 2 min 10°C/min to 200°C hold for 10 min
Injector Temperature	250°C
Detector Temperature	300°C
Ion Energy	70 eV
Carrier gas (Helium)	1.5 mL/min

---

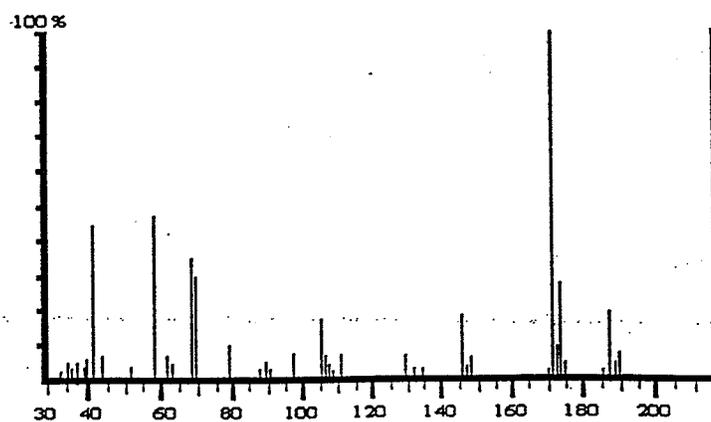
Mass spectra comparisons are shown with mass spectra of standards of:

De-ethyl atrazine  
De-isopropyl atrazine.

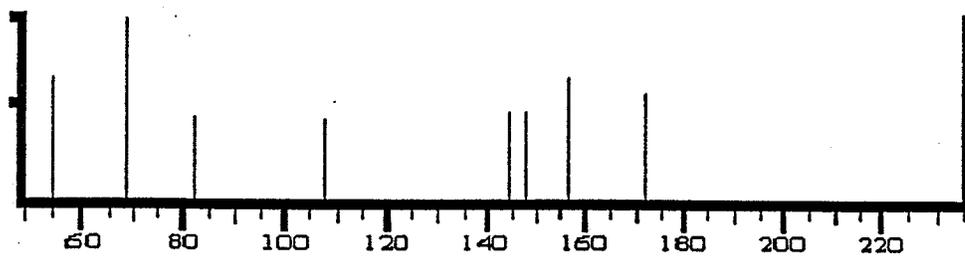


### DE - ETHYL ATRAZINE

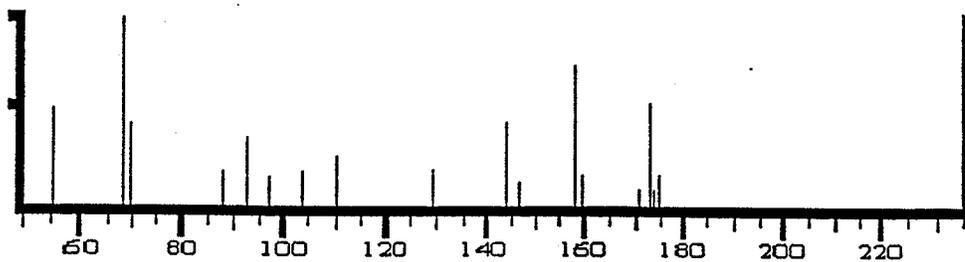
GBRI/MS No.40, Quadrupole GS/MS, Research Std.



De-isopropyl atrazine



100% 1,3,5,-TRIAZINE-2,4-DIAMINE, 6-CHLORO-N-ETHYL



Formula: C<sub>5</sub>H<sub>8</sub>N<sub>5</sub>Cl.

Rank 1 Index 11979

**Appendix V.**

Input Factor used for the SWRRB Model

Meteorology File:

First Year of Modelling           # Years Run  
Watershed Concentration Coefficient  
Rainfall Coefficient  
Temperature Fourier Coefficients  
Solar Radiation Coefficients  
Rainfall Intensity Factors (monthly)  
Year of Rainfall (amounts cm or inches)

Crop/ Hydrology Dataset:

# subareas, # crops  
basin area (mi<sup>2</sup>), LA/S for curve number equation (0.2)  
Portion of land in each subarea  
Root zone depth in each subarea  
SCS CNII condition curve number for each subarea  
Return flow travel time (Days)  
Soil erodibility factor each subarea  
Erosion Control Practice factor each subarea  
Slope length and steepness factor each subarea  
Bulk Density of surface layer each subarea  
Total soil porosity each of eight layers  
Water Content - wilting point - 8 layers  
Water Content - field capacity - 8 layers  
Saturated conductivity - 8 layers  
Crop management factor - monthly  
Winter coverage factor (0.5 or 1) each crop  
yearday, leaf area index, comment

## Pesticide File:

	Atrazine
Soil Adsorption	5.16 <sup>1</sup>
Foliar Washoff Fraction	0.30 <sup>2</sup>
Foliar half life	4.00 <sup>3</sup>
Soil Decay Constant ( $d^{-1}$ )	0.02 <sup>3</sup>
Application Efficiency	0.85 <sup>4</sup>
Initial Pesticide on Foliage	0.00
Enrichment Ratio for pesticide (by subarea)	1.50 <sup>5</sup>
Pesticide Application Schedule	Day 167 2.64 lb/ac <sup>6</sup>

Bromoxynil Octanoate	Diclofop- Methyl
1.04	1.00
0.60	0.80
2.40	2.50
0.03	0.07
0.85	0.85
0.00	0.00
1.50	1.50

<sup>1</sup>Clay *et al.* 1988<sup>2</sup>Worthing and Hance, 1990<sup>3</sup>Helling, 1970<sup>4</sup>Anonymous, 1990<sup>5</sup>Default value<sup>6</sup>Equivalent to 2.96 kg/ha

**Appendix VI.**

The output data from the SWRRB Model can be found on the enclosed 720 K disk. The output files can be read using Wordperfect, using the Text in/ out commands; Microsoft WORD , using the Load command; or DOS, using the type or print commands.