#### THE UNIVERSITY OF MANITOBA

#### ATRAZINE AVAILABILITY AND PERSISTENCE IN MANITOBA SOILS

by

GORDON IAN THOMPSON

#### A THESIS

# SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF PLANT SCIENCE

WINNIPEG, MANITOBA



### "ATRAZINE AVAILABILITY AND PERSISTENCE IN MANITOBA SOILS"

by

#### GORDON IAN THOMPSON

A dissertation submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

#### MASTER OF SCIENCE

#### © 1976

Permission has been granted to the LIBRARY OF THE UNIVER-SITY OF MANITOBA to lend or sell copies of this dissertation, to the NATIONAL LIBRARY OF CANADA to microfilm this dissertation and to lend or sell copies of the film, and UNIVERSITY MICROFILMS to publish an abstract of this dissertation.

The author reserves other publication rights, and neither the dissertation nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission. ATRAZINE AVAILABILITY AND PERSISTENCE IN MANITOBA SOILS Gordon Ian Thompson, M.Sc. University of Manitoba, SUPERVISOR: Dr. E. H. Stobbe

#### ABSTRACT

The amount of atrazine breakdown over time and the efficacy of atrazine in three Manitoba soil types were investigated. Growth chamber bioassay experiments using oats (*Avena sativa* L. var. Harmon) were conducted over an eighteen month period using soil from the three locations.

Herbicidal activity of atrazine was found to be most pronounced in the sandy and low organic matter soils. Soil texture, organic matter and cation exchange are the predominant factors affecting atrazine activity.

A field bioassay was conducted in the fall of 1973 and the spring of 1974 to investigate the change in atrazine activity under field conditions over time. The field bioassay indicated atrazine activity was greater in the sandy and low organic matter soils. Spring seeded bioassays showed more atrazine activity than the fall seeded bioassay.

An analytical analysis of atrazine residues was made of all the field plots. It was found that breakdown occurred more rapidly in the sandy loam soil, but there was very little difference in the rate of breakdown between the clay loam and clay soils.

Atrazine appeared to be a persistent herbicide in Manitoba soils and under uncultivated soil conditions atrazine could cause damage to succeeding susceptible crops in most Manitoba soils.

ii

#### ACKNOWLEDGEMENTS

I wish to express my gratefulness to Dr. E. H. Stobbe, who suggested the topic and who gave so freely of his time to assist and to supply guidance and constructive criticism throughout the entire project work.

Sincere thanks are extended to Dr. Shaykewich and Prof. G. M. Young for the helpful suggestions and careful review of the manuscript during its preparation.

I wish to acknowledge with gratitude the permissions granted by CIBA-GEIGY to locate a trial on Elm River Research Farm.

Beyond this I am obviously indebted and feel grateful to B. D. Hill who generously assisted in the operation and maintenance of the analytical study and to H. R. Nelson and his staff for their efforts in making the establishment and monitoring of the field trials possible.

iii

### TABLE OF CONTENTS

|   | PAGE                                 |
|---|--------------------------------------|
| LITERATURE REVIEW   | .1                                   |
| Atrazine Activity and Dissipation<br>Soil Moisture Content<br>Uptake of Atrazine by Plants<br>Leaching and Movement of Atrazine in Soil<br>Photodecomposition<br>Organic Matter<br>Microbial Breakdown<br>Volatilization<br>Bioassay of Atrazine Residues in Soil | 1<br>3<br>4<br>6<br>6<br>7<br>9<br>9 |
| METHODS AND MATERIALS   | 10                                   |
| EXPERIMENT 1 - Effect of Soil Type on the Avail-<br>ability of Atrazine   | 11                                   |
| EXPERIMENT 2 - A Study of the Effects of Various<br>Soil Components on Availability<br>of Atrazine  | 12                                   |
| EXPERIMENT 3 - Determination of Available Atrazine<br>in Field Samples Using Oats as Bio-<br>assay Plants   | 13                                   |
| EXPERIMENT 4 - Response of Oats to Atrazine Under<br>Field Conditions   | 14                                   |
| EXPERIMENT 5 - Analytical Determination of the<br>Atrazine Level in Soil Samples  | 15                                   |
| RESULTS   | 16                                   |
| EXPERIMENT 1 - Effect of Soil Type on The Avail-<br>ability of Atrazine   | 16                                   |
| EXPERIMENT 2 - Effects of Various Soil Components<br>on the Availability of Atrazine  | 19                                   |
| EXPERIMENT 3 - Determination of Available Atrazine<br>in Field Samples Using Oats as Bio-<br>assay Plants   | 26                                   |
| EXPERIMENT 4 - Response of Oats to Atrazine Under<br>Field Conditions   | 27                                   |
| EXPERIMENT 5 - Analytical Determinations of the<br>Atrazine Level in Soil Samples   | 32                                   |

### TABLE OF CONTENTS - cont'd

| DISCUSSION   | 34 |
|--------------|----|
| CONCLUSIONS  | 35 |
| BIBLIOGRAPHY | 39 |
| APPENDIX     | 42 |

PAGE

## LIST OF TABLES

| TABLE      |   | PAGE |
|------------|---|------|
| 1          | Herbicide Treatments and Time of Application  | 10   |
| 2          | Relative Growth of Oats in Carman,<br>Glenlea and Portage Soils Treated<br>with Several Rates of Atrazine   | 16   |
| 3          | Relative Growth of Oats in the A<br>and B horizons of Carman, Glenlea<br>and Portage Soils Treated with<br>Several Rates of Atrazine                        | 20   |
| 4          | Comparison of Soil Characteristics with<br>the ED <sub>50</sub> of Oats Grown in Atrazine treated<br>soil   | 21   |
| 5          | Rates of Atrazine in Soil Samples Collected<br>from Carman, Glenlea, and Portage (as<br>Determined by Bioassay)   | 26   |
| <b>6</b> . | Percent Growth Reduction of Field Seeded<br>Oats to Atrazine Remaining in Soil Under<br>Field Conditions at Carman  | 28   |
| 7          | Percent Growth Reduction of Field Seeded<br>Oats to Atrazine Remaining in Soil Under<br>Field Conditions at Glenlea   | 29   |
| 8          | Percent Growth Reduction of Field Seeded<br>Oats to Atrazine Remaining in Soil Under<br>Field Conditions in Portage   | 30   |
| 9          | Atrazine Remaining in the Soil Collected<br>in the Fall of Applications Made Throughout<br>the Summ (Analytical Determinations,<br>Expressed as kg/hectare) | 33   |
|            |   |      |

## LIST OF FIGURES

## FIGURE

. 1

2

| Response of Oats (Dry Weight) to Increasing<br>Rates of Atrazine in Carman, Glenlea, and | · 17 |
|--|------|
| Portage Soils  | 17   |
|  |      |
| Response of Oats (Dry Weight) to Increasing  |      |
| Rates of Atrazine on the A and B Horizon of<br>Carman, Glenlea and Portage Soils         | 22   |

yii

#### INTRODUCTION

Corn acreage in Manitoba has increased substantially in the past few years. The short growing season in Manitoba requires early maturing corn varieties, combined with good management practices. Early seeding, high fertility and good weed control can hasten the maturity of the crop.

Weed control, can determine the success or failure of a corn crop. Unlike most factors, weed control can mean a crop or no crop of corn at all. The most economical means of weed control with corn is with the use of herbicides, such as atrazine. In Manitoba best weed control is obtained by using soil applied herbicides. Atrazine usually gives season long weed control but in many instances presents a problem to succeeding non resistant crops.

The purpose of this study was to determine the factors affecting availability of atrazine to plants, and the dissipation of atrazine in Manitoba soils.

viii

#### LITERATURE REVIEW

#### ATRAZINE ACTIVITY AND DISSIPATION

The activity and dissipation of triazine herbicides in the soil depends to a large extent on the herbicide-soil interaction (Bailey and White, 1970). Dubach (1970) proposed that the atrazine-soil interaction falls into 3 distinct groups:

1) distribution of the atrazine into the various phases of the open soil system.

2) chemical and biochemical transformations of the atrazine in the various phases of the soil system.

3) transformation of the various phases of the soil system due to the biological activity of the atrazine.

The effect on the soil from the absence of weeds alone presents many changes in the total soil environment (Henin, 1968). When weeds are removed crop cover is reduced, soil moisture increases, tillage practises can be reduced, microclimate will change, and organic matter deposition may be altered. These changes induced by weed removal will influence the availability and dissipation of atrazine. According to Knusli *et al.* (1969) atrazine dissipation from a soil may be due to breakdown by biological means, or its availability may be altered by adsorption, volatilization, leaching and plant uptake.

Seven factors are known to influence the fate and behavior of pesticides in soil systems (Bailey and White, 1970): 1) chemical decomposition, 2) Photodecomposition, 3) microbial decomposition, 4) volatilization, 5) movement, 6) plant and organism uptake, and 7) adsorption. The phenomenon of adsorption directly or indirectly influences the magnitude of the effect of the other six factors, therefore, the authors concluded that adsorption was one of the major factors affecting the interaction occurring between pesticides and soil colloids.

The degree of phytotoxicity is governed by the concentration of herbicide remaining in a soil solution. It has been shown that herbicides generally, and triazines particularly, are adsorbed by soils and soil components (Talbert and Fletchall, 1965). Content of organic matter, and the amount and nature of clays present, largely determine the capacity of the soil to adsorb herbicides (Upchurch and Mason, 1962).

Day, Jordan and Jolliffe (1968) used an oat bioassay, and reported that simazine adsorption by soils was an exponential function of the amount of simazine added. There was a negligible correlation with pH and clay content. Percent of silt and sand, correlated with growth reduction but had little predictive value for dosage. There was a marked interrelationship between organic matter cation exchange capacity, the equilibrium concentration of simazine in the soil solution, and the growth reduction of oats.

Factors which affect the fate of soil applied chemicals are: 1) the type of soil (content of clay, silt, sand and organic matter), 2) the type of chemicals (its stability, solubility, and physical properties), 3) the climatic conditions (rainfall, temperature, sunlight, etc.), 4) the soil biological populations, and 5) the method of application of the chemical (as a granule, wettable powder, pre-plant incorporation, pre-emergence, or post), (Lambert *et al.*, 1965).

#### SOIL MOISTURE CONTENT

Burnside, Fenster and Wicks (1971) studied atrazine dissipation from irrigated fallow plots and from irrigated corn plots and it was found that the difference in the rate of atrazine dissipation between cropped and fallowed plots depended mainly upon the amount of available moisture within the soil. They suggested that the more rapid dissipation of atrazine in fallow than in corn under dry land farming was not due to crop uptake, but resulted from the drier conditions in the corn land which led to a slower rate of breakdown within the soil.

Soil moisture limits atrazine dissipation in Manitoba soils. Elliot (1972) reported that there was less atrazine carry over in fallow plots than in plots containing corn. Similar results were reported by Nalewaja (1968) when he showed that under North Dakota conditions atrazine dissipation was greater in the warm moist soil of fallow plots than in corn plots.

Soil moisture has 3 main effects on herbicide toxicity: 1) it may provide the medium through which herbicide molecules reach the root surface, 2) it may remove herbicide molecules from the root zone through the process of leaching, 3) it may compete with the herbicide for adsorption sites on clay minerals and organic matter, resulting in increased availability of the herbicide in the soil solution (Bailey and White, 1970). In order to be phytotoxic, atrazine must be dissolved in the soil solution to the extent that it will be taken up in toxic quantities by the plant (Bailey and White, 1970). The aqueous solubilities of atrazine are 33 p.p.m. at 20°C and 160 p.p.m. at 25°C (Weed Society of America, Herbicide Handbook, 1974).

#### UPTAKE OF ATRAZINE BY PLANTS

Atrazine has been shown to be readily absorbed and translocated in sensitive and resistant plant species. Sikka and Davis (1966) reported that 20% to 25% of an initial atrazine application to soil was adsorbed by corn and sorghum (resistant) and Johnson grass *Sorghum halespense* (sensitive). Thus differences in plant uptake *per se*, do not appear to be influential in determining toxicity in soils.

Knake, Appleby and Furtick (1967) found that atrazine was toxic when placed in the shoot zone of giant foxtail (*Setaria fabrii*) and green foxtail (*Setaria viridis*) and that placement in the root zone was ineffective. Thus, to evaluate differences in toxicity in various soils it is essential to standardize herbicide placement in the soil.

#### LEACHING AND MOVEMENT OF ATRAZINE IN SOIL

Upchurch and Pierce (1958) indicated that at least 2 steps are involved in the leachability of a herbicide: (1) entrance of the compound into solution and (2) adsorption of the compound to soil particles. Entrance of the pesticide into solution can take place from the dissolution of the pesticide present in particulate form or from the desorption of pesticides present on colloidal surfaces. The factors which appear to affect overall pesticide movement most are: (1) adsorption, (2) physical properties of the soil, and (3) climatic conditions.

Harris (1966) reported phytotoxicity and movement of the herbicides in soil were inversely related to extent of adsorption. It was also reported that as the herbicides move, the concentration must decline. Diffusion will bring about some of the decrease, but adsorption will be important in reducing the concentration of those herbicides that are

. 4

low in water solubility (relatively insoluble herbicides are generally adsorbed by soil). If the soils dry out, adsorption will increase and less precipitation of the herbicide will occur than might be expected. Elliot (1972) reported atrazine did not readily leach in the soil horizon and primarily remained in the top 0 - 5 cm soil depths in Manitoba soils. Increasing the amount of herbicide applied has an effect of increasing the leaching of atrazine.

Sheets, Crafts and Drever (1962) reported phytotoxicity of the biogenesis is inversely correlated with organic matter, clay content, cation exchange capacity, exchangeable bases, and moisture equivalent. Grover (1966) has reported that many attempts have been made to correlate specific soil properties with herbicidal phytotoxicity, but in a large number of instances, properties of the soils, such as C.E.C., surface area, exchangeable cations, etc. were confounded with the types of soil constituents, such as the contents of silt, clay minerals, and organic matter. Hedling, Chesters and Corey (1964) reported that although adsorption on to organic matter seems greater in magnitude and more generally applicable to pesticides than adsorption on to clay, the role of clay is probably equally important because most soils contain much more clay than organic matter. In studies comparing the contributions of organic matter and clay to the cation exchange capacity (C.E.C.) of 60 soils, although the C.E.C. of the clay at pH 7 was only 1/3 that of organic matter, it contributed 1.7 times more to the total C.E.C.

#### PHOTODECOMPOSITION

Recently, evidence has accumulated that photodecomposition of atrazine may be considered under certain conditions. Jordan, Day and Clerex (1964) studied several s-triazines including atrazine and found marked changes in their spectral properties after irradiation with ultra violet light. His studies, however, were made under artificial conditions (high intensity ultra violet light) and it is difficult to extrapolate these results to field situations. In studies using soil treated with atrazine and exposed to natural light, Commes and Timmons (1965) show a decreased phytotoxicity with time. However, it was impossible to estimate and eliminate effects due to volatility, chemical degradation and microbial degradation to determine the separate effect of photodecomposition. The work was carried out at an elevation of 7,200 feet above sea level where radiation, especially in the ultra violet region of the spectrum, is more intense than at lower elevations.

#### ORGANIC MATTER

Grover (1966); Sheets *et al.* (1962); Tompkins, McIntosh and Dunigan (1968); and Upchurch and Mason (1962) indicate that soil organic matter consists of a complex system of substances which are generally separated into 2 groups of compounds: (a) humic substances a series of brown to black, high molecular weight polymers formed by secondary synthesis reactions, and (b) non-humic substances, consisting of compounds such as amino acids, proteins, carbohydrates and lipids. Most of the nonhumic compounds are attacked with comparative ease by soil microorganisms and have a relatively short life span. Dunigan and McIntosh (1971) indicated that from work done on the preferential removal of

parts of the organic matter made by a series of extractions with ethyl ether, ethyl alcohol, and hot water, it was found that atrazine was adsorbed in a much greater quantity on the clay and organic matter separated from a Walla Walla soil than on the clay alone with the organic matter removed. There were 40.0 mg/g adsorbed on clay without organic matter compared to 77.5 mg/g on clay with organic matter.

Weber, Weed and Ward (1969) showed that atrazine was adsorbed in the greatest amount at pH levels in the vicinity of their respective pKA values. Addition of HCl decreased adsorption as the pH was lowered and the addition of NaOH decreased adsorption as the pH was raised.

#### MICROBIAL BREAKDOWN

Environmental conditions, including soil type, temperature, moisture level, aeration, and supplemental energy source, influence capacity of microbial systems (Holly and Roberts, 1963). Generally, results have been in agreement, indicating that soil factors influencing microbial activity also influence residual life of s-triazines in the soil. Chemical and physical factors which promote or inhibit microbial activity may also affect the availability or chemical degradation of the pesticide independently of the microbial effects (Burschel, 1961). Soil microorganisms are generally more active in soils having high organic matter content than in soils having low organic matter contents. Increases in soil organic matter contents, decreased residual phytotoxicity of s-triazines. In work done by McCormick and Hiltbold (1966) it was found that addition of organic matter to soils stimulated s-triazine degradation. Results of correlation studies done by Wagner and Chakal (1966) indicated microbial degradation of s-triazines is increased in the presence

of supplemental carbon sources.

Agundis (1964) showed microbial activity increases with increased temperature. Talbert and Fletchall (1964) and Roadhouse and Birk (1961) showed adsorption of atrazine increased with decreased temperature. In addition, an indirect influence of temperature on adsorption may result from its affect on solubility (Harris, 1966).

These two factors, as Harris suggests, usually function simultaneously, therefore, both lead to decreased adsorption as temperature rises. Thus, the more rapid decomposition of s-triazine herbicides in warm soil may be a result of optimum conditions for microbial activity coupled with increased availability and solubility of the chemical. Holly and Roberts (1963) report that persistence of several s-triazines is less in moist soils than in dry soils. Harris and Warren (1964) concluded the effect of soil pH and cation-exchange capacity or residual phytotoxicity and microbial degradation of s-triazines has not been adequately investigated, however, adsorption of atrazine and simazine varies inversely with pH.

In work carried out by Burschel (1961) the following conclusions were drawn:

(1) the decomposition of simazine in soil occurs as a first order reaction. This means that under comparable conditions the same percentage of the original dose will be found in the soil at a given time, regardless of whether the dose was a high or low one.

(2) the decomposition is highly dependent on temperature. A decrease from  $25^{\circ}$ C to  $8.5^{\circ}$ C caused a 7-fold decrease in the rate of decomposition.

(3) from work done with organic matter, the conclusion was drawn

that decomposition is largely due to the activity of microorganisms.

McCormick and Hiltbold (1966) state that about 88 to 98% of the variation in herbicide inactivation in soils used in their experiments coincided with  $CO_2$  evolution and microbial activity.

#### VOLATILIZATION

Atrazine has a low vapor pressure (1.4 x  $10^{-6}$  mm Hg at  $30^{\circ}$ C) and is generally classified as a non-volatile compound.

Kearney, Sheets and Smith (1964) show that only 5% of the original atrazine in a metal planchette could be detected after 24 hours at 35<sup>o</sup>C. At 45<sup>o</sup>C more than 50% of an original application had volatilized from sandy soil and 30% from clay soils after 72 hours. Differences in the rate of evaporation were attributed to adsorption to soil colloids, and soil moisture levels. Atrazine was more volatile from a moist soil than from a dry soil, probably due to less adsorption.

#### BIOASSAY OF ATRAZINE RESIDUES IN SOIL

The bioassay is a method of determining the presence and concentration of herbicide residues in the soil. The sensitivity of a test plant to a herbicide is measured by growth reactions which may vary from growth stimulation to growth reduction and at higher rates, plant death (Dowler, 1969).

Santleman *et al.* (1971) found that uniform procedures and conditions must exist for the bioassay to be an accurate estimate of herbicide residues on different soils. Elliot (1972) working with atrazine residues, concluded that the use of a bioassay was an effective way of estimating the amount of available residual triazine herbicide in the soil.

#### METHODS AND MATERIALS

Field trials were established during the summer of 1973 at three locations in Manitoba; Glenlea Research Farm, Carman Weed Research Farm, and Elm River Research Farm at Portage la Prairie. Atrazine applications (80% wettable powder) were made at 6 different times throughout the summer. Treatments and dates of application are listed in Table 1. The experimental design was a randomized block with 4 replications. The plot size was 3.66 m x 7.62 m. Trials at each site were initiated on stubble fields which were disced and harrowed prior to applying the first treatment.

#### TABLE 1

| Herbicide   | Rate<br>kg/hectare | Time of application | Days before<br>sampling |  |
|---|--------------------|---------------------|-------------------------|--|
| <del>ارىپ بېلىرىنىيە بول كەرىپ بىلەر بىلەر يېلىرىكە بىلەر يېلىكى بىلەر يېلىكى بىلەر يېلىكى بىلەر يەرىپ بىلەر يېلىكى</del> |                    |                     |                         |  |
| Atrazine  | 2.24               | May 9               | 170                     |  |
| Atrazine  | 4.48               | May 9               | 170                     |  |
| Atrazine  | 2.24               | June 7              | 142                     |  |
| Atrazine  | 4.48               | June 7              | 142                     |  |
| Atrazine  | 2.24               | July 16             | 103                     |  |
| Atrazine  | 4.48               | July 16             | 103                     |  |
| Atrazine  | 2.24               | Aug. 5              | 83                      |  |
| Atrazine  | 4.48               | Aug. 5              | 83                      |  |
| Atrazine  | 2.24               | Aug. 21             | 68                      |  |
| Atrazine  | 4.48               | Aug. 21             | 68                      |  |
| Atrazine  | 2.24               | Sept. 11            | 46                      |  |
| Atrazine  | 4.48               | Sept. 11            | 46                      |  |

#### HERBICIDE TREATMENTS AND TIME OF APPLICATION

EXPERIMENT 1: EFFECT OF SOIL TYPE ON THE AVAILABILITY OF ATRAZINE.

Studies were conducted to determine the efficacy of atrazine in controlling oats (*Avena sativa* var. Harmon) in three Manitoba soil types. Soil was taken from the 0 - 5 cm depths at three locations in Manitoba. The location and soil types were as follows:

> Carman Almasippi very fine sandy loam Glenlea Osbourne clay Portage Assiniboine clay

To permit comparisons between experiments and soil types the procedure for all bioassay experiments was standardized as follows: All soils were dried, mixed and sieved through a 2 mm sieve before fortification. All replicates of each standard concentration were prepared individually by spraying a solution of atrazine of known concentration onto the soil (400 g air dried soil) followed by a thorough mixing. The treated soil was then placed in 16 oz ice box jars, seeded with 5 oat seeds and watered to field capacity. Water was added every 2-3 days in order to maintain the soil at or near field capacity throughout the 21 day growing period. Plants were thinned to 2 uniform seedlings per jar after the seedlings emerged. After the 21 day growing period the plants were clipped off at the ground and dry weights (oven dry temperature 90°C) were recorded. The bioassay was conducted in a growth chamber with a light intensity of 14,000 luxes. The temperatures ranged from 65 - 68°F with a light period of 16 hours per day. The dry matter weights obtained were expressed as a percentage of that produced in the control of each soil. These percentages were plotted as a function of concentration. The concentration of herbicide which reduces dry matter production to 50% of the control  $(ED_{50})$  was determined for each soil

type.

# EXPERIMENT 2: A STUDY OF THE EFFECTS OF VARIOUS SOIL COMPONENTS ON AVAILABILITY OF ATRAZINE.

A bioassay experiment was designed to study the effect of various soil constituents on the availability of atrazine in 3 soil types. Soil was sampled from the 0 - 5.0 cm depth and from the B horizon of each of the 3 profiles and prepared as outlined in Experiment 1. Each of the horizons were analyzed for physical and chemical properties and an analysis for particle size using the pipette method developed by Kilmer and Alexander (1949). Nitrogen, 10 ppm, phosphorous, 5.0 ppm, and potassium, 5.0 ppm solution fertilizer was added to all treatments and oats were grown and harvested as in Experiment 1.

# EXPERIMENT 3: DETERMINATION OF AVAILABLE ATRAZINE IN FIELD SAMPLES USING OATS AS BIOASSAY PLANTS.

On October 24, 1973 soil samples were taken from each treatment listed in Table 1 to a depth of 5 cm, frozen and stored in plastic bags at  $-10^{\circ}$ C. Each sample consisted of approximately 13 kilograms obtained from 2 sampling points from within the plot.

The samples from each treatment plot were bioassayed individually. Each treatment had 4 replications and 8 subsamples. All samples were dried and ground to a maximum diameter of 2 mm. Oat bioassays were conducted on the samples in the same manner as outlined in Experiment 1.

The levels of available atrazine remaining in the field samples were calculated from the standard curve, by measuring the percent growth reduction of oats cultured in the field samples. The rates obtained from the standard curve in ppm were converted to kg/hectare on the basis of bulk density readings obtained from each site.

#### EXPERIMENT 4: RESPONSE OF OATS TO ATRAZINE UNDER FIELD CONDITIONS.

A field bioassay was conducted by seeding oats with a minimum of soil disturbance into the plots referred to in Experiment 1 to a depth of 5 cm on September 23, 1973 and harvested October 15, when the oats were in the 3-4 leaf stage. The same procedure was repeated in the spring of 1974. Oats were seeded on May 29, 1974 and harvested on June 20.

The oats were harvested by clipping the plants off at the ground surface and drying them in an oven. Five consecutive oat plants were taken from five different locations within each treatment giving a total of 25 plants per treatment.

# EXPERIMENT 5: ANALYTICAL DETERMINATION OF THE ATRAZINE LEVEL IN SOIL SAMPLES.

Analytical determination was made to determine the absolute amount of atrazine in all field samples using the gas-liquid-chromatograph. Gas chromatograph analysis was run on subsamples from the soil samples obtained in October of 1973 and used for the bioassay work. Each plot was analyzed individually.

FORTIFICATION OF SOIL SAMPLES - Soil samples were fortified to determine the efficiency of analytical procedures. The soil was air dried, ground, and sieved through a 20 mesh screen prior to use. Soil samples (50.0 g each oven dried basis) were fortified individually in square quart bottles by pipetting 20 ml of herbicide standard solution (atrazine dissolved in methanol) onto the soil surface. Each sample was slurried with excess solvent to mix the treated soil and then air dried. A 3-day equilibrium period was allowed before extracting fortified samples.

EXTRACTION PROCEDURE - Fortified and field soil samples (50 gm air dried basis) were placed directly into the Soxhlet chamber between glass wool plugs and were saturated with 50 ml of distilled water. Samples were then extracted for 24 hours using 200 ml of methanol. The extracts were then filtered and evaporated down to 10 ml volumes prior to analysis. The atrazine standard solutions used in fortifications were employed as standards when determining levels of atrazine in field samples. Mean response from at least two injections of sample extracts was converted to namograms using pre-determined standard response curves. Any changes in detector sensitivity were monitored by observing response to standards injected alternately to field sample extracts.

#### RESULTS

#### EXPERIMENT 1: EFFECT OF SOIL TYPE ON THE AVAILABILITY OF ATRAZINE.

The response of oats to several rates of atrazine applied to soil from Carman, Glenlea and Portage is presented in Table 2. Atrazine response curves are presented in Figure 1.

#### TABLE 2

#### RELATIVE GROWTH OF OATS IN CARMAN, GLENLEA AND PORTAGE SOILS TREATED WITH SEVERAL RATES OF ATRAZINE

| SITE              | Carman | Glenlea | Portage |
|-------------------|--------|---------|---------|
| Atrazine<br>ppm/w |        |         |         |
| 0.00              | 100.0  | 100.0   | 100.0   |
| 0.25              | 103.9  | 100.6   | 107.7   |
| 0.50              | 38.3   | 95.2    | 76.8    |
| 0.75              | 19.3   | 49.8    | 33.7    |
| 1.00              | 16.4   | 37.5    | 22.0    |
| 1.25              | 14.0   | 23.9    | 21.1    |
| 1.50              | 13.2   | 18.0    | 18.2    |
| 1.75              | 13.3   | 17.3    | 12.1    |
| 2.00              | 10.5   | 14.4    | 10.0    |

(Expressed as a percent of control)





Atrazine at 0.25 ppm/w appeared to cause growth stimulation. Growth reduction was observed when atrazine at 0.5 ppm/w or greater was used. At the time the bioassay was harvested 2 weeks after seeding, complete death of oat plants was observed when atrazine was used at rates of 0.50, 1.00, and 1.00 ppm/w in Carman, Glenlea and Portage soils, respectively. These results show that atrazine can be detected in soils at levels between 0.50 and 1.00 ppm/w accurately. Both the visual and dry weight differences were marked. The results indicate that atrazine toxicity varies significantly from one soil type to another.

Carman soil showed an  $ED_{50}$  of 0.67 kg/ha (Fig. 1a), Glenlea an  $ED_{50}$  of 0.99 kg/ha (Fig. 1b), and Portage an  $ED_{50}$  of 0.83 kg/ha (Fig. 1c), indicating that atrazine is more biologically active in the Carman soil than in the fine textured soils of the Portage and Glenlea locations. Results of this experiment indicate that 1.5 times as much herbicide was required in the Glenlea soil as in the Carman soil to produce the same herbicidal effect. The greater herbicidal activity of the atrazine on the Carman soil may have been due to less adsorption of atrazine on the soil compared to the Glenlea or Portage soils.

Studies were not conducted to determine the effect of the three soil types on the growth and root development of the oat plants. Atrazine's higher level of activity in Carman soil may not result entirely from the absorption-desorption characteristics of coarser and more friable soil types. The root development of the oat plants may have been more extensive in the sandy loam soils. A more developed root system in the sandy loam soil would increase the amount of atrazine taken up into the plant.

Seed germination and seedling development was more rapid in the Carman, than Glenlea and Portage soils. This uneven germination rate

between soil types could show differences in the dry matter accumulation in the untreated plants. The weighing procedure used to evaluate the herbicidal activity would indicate slightly more atrazine activity in the Carman soil.

Plants grown in Carman soil treated with atrazine died more quickly (low dry weight) than plants grown in Glenlea or Portage soils treated with atrazine (higher dry weight).

Regardless of soil type effects that may have occurred, the study is valid for the development of an oat plant in each individual soil under bioassay conditions and would be similar to the conditions that could exist in the field.

# EXPERIMENT 2: EFFECTS OF VARIOUS SOIL COMPONENTS ON THE AVAILABILITY OF ATRAZINE.

Results of the effect of soil components on the availability of atrazine are presented in Tables 3 and 4 and Figure 2. In each soil type the difference in the level of atrazine toxicity between the A horizon and B horizon is evident. Regression analysis relating  $ED_{50}$  to soil components indicates (Table 4) that organic matter and cation exchange capacity are major factors affecting atrazine toxicity in the soil.

The  $ED_{50}$  values presented in Table 3 for the A horizons of the three soil types are considerably higher than the values obtained in Experiment 1. The reason for the higher  $ED_{50}$  values in this experiment resulted from the fertilizer solution added to the soil mixture at the time of planting. These increased  $ED_{50}$  values reflect the importance that the rate of plant growth has on the atrazine activity.

| RELATIVE | GROWTH ( | OF OATS | IN THE  | A AND | B HORIZO | ONS OF | CARMAN, | GLENLEA |
|----------|----------|---------|---------|-------|----------|--------|---------|---------|
| ANI      | D PORTAG | E SOILS | TREATED | WITH  | SEVERAL  | RATES  | OF ATRA | ZINE    |

TABLE 3

(Expressed as a percent of control) Rate of atrazine added (ppm/w)

| STTE                 | 0   | 0.25 | 0.50 | 0.75 | 1.00 |
|----------------------|-----|------|------|------|------|
| OTTE                 | v   | 0120 | 0100 |      | 2000 |
| Carman<br>0-5 cm     | 100 | 100  | 96   | 35   | 24   |
| Carman<br>B horizon  | 100 | 12   | 12   | 12   | 12   |
| Glenlea<br>O-5 cm    | 100 | 77   | 84   | 75   | 62   |
| Glenlea<br>B horizon | 100 | 92   | 63   | 24   | 17   |
| Portage<br>0-5 cm    | 100 | 102  | 77   | 72   | 41   |
| Portage<br>B horizon | 100 | 91   | 54   | 24   | 19   |

| ,   | %<br>Sand | %<br>Silt | %<br>Clay | %<br>Organic<br>matter | C.E.C.<br>meq/gm | рН   | ED <sub>50</sub> |
|---|-----------|-----------|-----------|------------------------|------------------|------|------------------|
| Carman<br>A horizon                                 | 83.0      | 6.0       | 11.0      | 2.88                   | 13.7             | 7.1  | 0.6875           |
| Carman <sup>,</sup><br>B horizon                    | 74.0      | 12.0      | 14.0      | 1.08                   | 8.6              | 8.6  | 0.1450           |
| Glenlea<br>A horizon                                | 4.0       | 38.0      | 58.0      | 5.00                   | 48.6             | 6.5  | 1.2812           |
| Glenlea<br>B horizon                                | 3.0       | 34.0      | 63.0      | 3.16                   | 44.0             | 6.5  | 0.5812           |
| Portage<br>A horizon                                | 3.0       | 56.0      | 41.0      | 4.83                   | 37.2             | 7.5  | 0.9250           |
| Portage<br>B horizon                                | 2.0       | 51.0      | 47.0      | 2.83                   | 32.8             | 7.3  | 0.5313           |
| Correlation<br>coefficient<br>with ED <sub>50</sub> | 0.54      | 0.38      | 0.46      | 0.95                   | 0.72             | 0.70 |                  |

COMPARISON OF SOIL CHARACTIERISTICS WITH THE  ${\rm ED}_{50}$  OF OATS GROWN IN ATRAZINE TREATED SOIL.

Regression Equation for Organic Matter:

 $ED_{50} = 0.252 (0.M.) - 0.139$  $R^2 = 0.909 S = 0.13$ 

Fig. 2. Response of oats (dry weight) to increasing rates of atrazine on the A and B horigons of Carman, Glenlea and Portage soils.







Fig. 2a. Carman A Horizon.

















Fig. 2e. Portage A Horizon.

The results of this experiment indicate that the soil structure effect on the biological activity of atrazine are very small. Structural differences between the Carman A horizon and the Carman B horizon were very minimal, but results show that there was considerably more activity in the B horizon than in the A horizon. There is no indication that the structural differences between the Portage and Glenlea A and B horizons caused any significant differences in the development of the oat plants, each of the soil types had similar field capacity levels in both the A and B horizons.

The pH levels in the Glenlea and Portage soil, A and B horizons, were similar. A difference in pH occurred between the Carman A and B horizons. This difference in pH may have attributed to the increased activity of atrazine in the B horizon or the high pH level may have been detrimental to the growth of the oat plant. At higher levels of atrazine the rate of kill in the A horizon was not as rapid as in the B horizon indicating that atrazine became toxic to the plants in the B horizon very early in the development of the plant. This result may be due to the pH effect on the plant growth. Yields of the control treatments in the Carman A and B horizon indicate that there was some factor affecting the growth of the plants in the B horizon and the pH change could have been enough to cause this growth reduction.

In the Glenlea and Portage, A and B horizons, control plant weights were reduced in the B horizon. However, this growth reduction was slight and could be the result of soil structure differences.

In the Glenlea and Portage soils plant growth in both horizons appears to be very similar. The rate of plant growth reduction due to atrazine was less in the A horizon compared to the B horizon, indicating

that proportionately more atrazine becomes available in the B horizon than in the A horizon as rates are increased.

An experiment was conducted using silica sand as a growth medium and this study indicated that the  $ED_{50}$  value occurred in the region of  $1/100^{th}$  ppm atrazine. This low  $ED_{50}$  value would indicate that the many factors affecting plant growth must play a major role in enabling a plant to withstand atrazine.

# EXPERIMENT 3: DETERMINATION OF AVAILABLE ATRAZINE IN FIELD SAMPLES USING OATS AS BIOASSAY PLANTS.

Available atrazine remaining in field samples collected from treated plots in the fall as determined using an oat bioassay are given in Table 5.

#### TABLE 5

| Application rate | No. of days between application and | Date    | of   | Carman | Glenlea   | Portage |
|------------------|-------------------------------------|---------|------|--------|-----------|---------|
| kg/hectare       | sampling                            | Applica | tion | k      | g/hectare |         |
| 1.121            | 170                                 | May     | 9    | .33    | .57       | .23     |
| 2.242            | 170                                 | May     | 9    | .71    | *         | . 34    |
| 1.121            | 142                                 | June    | 7    | .64    | .57       | .34     |
| 2.242            | 142                                 | June    | 7    | .76    |           | -       |
| 1.121            | 103                                 | July    | 16   | .64    | .62       | .35     |
| 2.242            | 103                                 | July    | 16   | .74    |           | ·       |
| 1.121            | 83                                  | Aug.    | 5    | .71    |           | .57     |
| 2.242            | 83                                  | Aug.    | 5    |        |           |         |
| 1.121            | 68                                  | Aug.    | 21   | .68    |           |         |
| 2.242            | 68                                  | Aug.    | 21   |        |           |         |
|                  |                                     |         |      |        |           |         |

RATES OF ATRAZINE IN SOIL SAMPLES COLLECTED FROM CARMAN, GLENLEA, AND PORTAGE (AS DETERMINED BY BIOASSAY).

Data missing because of high sensitivity of oat plants to atrazine.

#### EXPERIMENT 4: RESPONSE OF OATS TO ATRAZINE UNDER FIELD CONDITIONS.

The response of oats to atrazine under field conditions was calculated and illustrated as a percent growth reduction relative to the untreated plots and is shown in Tables 6, 7, and 8. The residual effect of atrazine was evident at each of the three locations indicating that atrazine residues are a potential problem in all areas of Manitoba. Rates as low as 1.121 kg/hectare caused growth reductions at all 3 locations one year after application.

At the Carman location, cropping during the year after application of atrazine with a susceptible crop would not be advisable according to results obtained in this study. Fall seeding at Carman did not show nearly the damage obtained in the spring seeded bioassay, this may be a result of leaching. During the winter the freezing and thawing of the soil water solutions may have had some effect on the adsorption and desorption of atrazine from the soil and organic matter particles. This increased spring activity of atrazine was most evident in the coarser soil types at Carman, but it was also more noticeable in the intermediate soil type from the Portage location than it is in the finer textured soils from the Glenlea area. The increased activity in the spring may be related to the leachability of atrazine in the differing soil types. Possibly under the water logged soil conditions common with Manitoba soils every spring and possibly every fall. The atrazine is leached down into the soil profile more in the coarse soil types than in the finer soil types. Atrazine would leach further into a sandy soil as compared to the clay soils. With increased leaching atrazine would be present in the root zone of the bioassay plants at much higher concentrations in the coarser soil types than in the fine textured soil

· 27

| Rate of    | No. of days between |             | % of C   | % of Control <sup>1</sup> |  |  |
|------------|---------------------|-------------|----------|---------------------------|--|--|
| kg/hectare | sampling            | Application | <br>Fall | Spring                    |  |  |
| 1.121      | 170 <sup>2</sup>    | May 9       | 102.4    | 41                        |  |  |
| 2.242      | 170                 | May 9       | 78.6     | 8                         |  |  |
| 1.121      | 142                 | June 7      | 95.1     | 27                        |  |  |
| 2.242      | 142                 | June 7      | 47.0     | 13                        |  |  |
| 1.121      | 103                 | July 16     | 82.6     | 8                         |  |  |
| 2.242      | 103                 | July 16     | 34.2     | 8                         |  |  |
| 1.121      | 83                  | Aug. 5      | 88.3     | 9                         |  |  |
| 2.242      | 83                  | Aug. 5      | 50.8     | 7                         |  |  |
| 1.121      | 68                  | Aug. 21     | 54.6     | 9                         |  |  |
| 2.242      | 68                  | Aug. 21     | 37.6     | . 8                       |  |  |
| 1.121      | 47                  | Sept. 11    | 40.7     | 8                         |  |  |
| 2.242      | 47                  | Sept. 11    | 32.5     | 8                         |  |  |

#### (Expressed as a percent of control)

TABLE 6

PERCENT GROWTH REDUCTION OF FIELD SEEDED OATS TO ATRAZINE REMAINING IN SOIL UNDER FIELD CONDITIONS AT CARMAN.

1. Control = 100%

2. Fall seeding only.

# TABLE 7

# PERCENT GROWTH REDUCTION OF FIELD SEEDED OATS TO ATRAZINE REMAINING IN SOIL UNDER FIELD CONDITIONS AT GLENLEA.

| Rate of    | No. of days between | Data of    |             | % of ( | % of Control <sup>1</sup> |  |  |
|------------|---------------------|------------|-------------|--------|---------------------------|--|--|
| kg/hectare | sampling            | Applicatio | Application |        | Spring                    |  |  |
| 1.121      | 170 <sup>2</sup>    | May S      | 9           | 84     | 79                        |  |  |
| 2.242      | 170                 | May 9      | 9           | 76     | 58                        |  |  |
| 1.121      | 142                 | June       | 7           | 75     | 83                        |  |  |
| 2.242      | 142                 | June       | 7           | 68     | 81                        |  |  |
| 1.121      | 103                 | July 16    | 5           | 82     | 79                        |  |  |
| 2.242      | 103                 | July 16    | 5           | 60     | 73                        |  |  |
| 1.121      | 83                  | Aug. S     | 5           | 71     | 89                        |  |  |
| 2.242      | 83                  | Aug.       | 5           | 58     | 69                        |  |  |
| 1.121      | 68                  | Aug. 21    | 1           | 81     | 91                        |  |  |
| 2.242      | 68                  | Aug. 21    | L ·         | 50     | 52                        |  |  |
| 1.121      | 47                  | Sept. 11   | 1           | 54     | 75                        |  |  |
| 2.242      | 47                  | Sept. 11   | L           | . 45   | 56                        |  |  |

(Expressed as a percent of control)

1. Control = 100%

2. Fall seeding only.

| PERCENT | GROWTH | REDUCT | FION OF | FIELD | ) SEEDED | OATS ' | TO ATRAZ | INE | REMAINING |
|---------|--------|--------|---------|-------|----------|--------|----------|-----|-----------|
|         | II     | SOIL   | UNDER   | FIELD | CONDITIC | ONS AT | PORTAGE  | •   |           |

TABLE 8

| Rate of    | No. of days between      | Date of<br>Application |    | % of ( | % of Control <sup>1</sup> |  |  |
|------------|--------------------------|------------------------|----|--------|---------------------------|--|--|
| kg/hectare | application and sampling |                        |    | Fall   | Spring                    |  |  |
| 1.121      | 170 <sup>2</sup>         | May                    | 9  | 105    | 89                        |  |  |
| 2.242      | 170                      | May                    | 9  | 72     | 52                        |  |  |
| 1.121      | 142                      | June                   | 7  | 89     | 54                        |  |  |
| 2.242      | 142                      | June                   | 7  | 60     | 26                        |  |  |
| 1.121      | 103                      | July                   | 16 | 93     | 33                        |  |  |
| 2.242      | 103                      | July                   | 16 | 51     | 21                        |  |  |
| 1.121      | 83                       | Aug.                   | 5  | 75     | 28                        |  |  |
| 2.242      | 83                       | Aug.                   | 5  | 51     | 20                        |  |  |
| 1.121      | 68                       | Aug.                   | 21 | 78     | 32                        |  |  |
| 2.242      | 68                       | Aug.                   | 21 | 48     | 19                        |  |  |
| 1.121      | 47                       | Sept.                  | 11 | 48     | 57                        |  |  |
| 2.242      | 47                       | Sept.                  | 11 | 43     | 20                        |  |  |
|            |                          |                        |    |        |                           |  |  |

(Expressed as a percent of control)

1. Control = 100%

2. Fall seeding only.

types. This differential layering of the atrazine in the soil plus the method of seeding oats (with a minimum of soil disturbance) could explain the marked increase in activity from fall seeded oats to spring seeded oats.

The answers to the question of increased spring activity probably is a combination of factors such as freezing and thawing increased leaching and also the difference in climatic conditions between the spring and fall seasons.

The temperatures under which the fall and spring bioassay grew were different (refer to Appendix B). Average temperatures for the month of June were higher than for the month of October. Crop plants seeded in the spring would transpire at a much more rapid rate than the plants grown during the month of October. The day length during June is longer than during the month of October which would again lead to increased transpiration. Higher temperatures would increase the solubility of atrazine and, therefore, increase the uptake of atrazine into the plant.

The results of the experiment indicate that atrazine residues can be very unpredictable but generally greater residual effects will be observed on the coarser textured soils than on the fine textured soil. However, if weed control is the desired objective the results clearly showed that the finer the soil texture, the greater is the amount of herbicide required to produce a given level of phytotoxicity.

Comparison of the dry weights of oats between application and sampling dates (Tables 6 - 8), would indicate that at Glenlea a 2.242 kg/hectare rate of atrazine does not adequately control weeds. Atrazine at both Portage and Glenlea showed variable control. Oats in some areas of the plots were completely killed whereas other

areas would show little or no damage at all. The inconsistent control of the oat seedlings would suggest surface movement of the atrazine instead of downward movement. Carman soil showed consistent oat suppression throughout the treated areas. The results in this experiment would suggest that atrazine was extremely persistent with 1.121 kg/hectare spring applications giving from 40 - 85% growth reduction to oats one year after application. It must be noted, however, that none of the above sites received any cultivation and this may have been the reason for the low rates of atrazine dissipation. Breakdown appeared to be consistent through most of the summer. This uniform dissipation was expected since rainfall and soil temperatures were relatively constant throughout the summer months (Refer to Appendix B through E).

# EXPERIMENT 5: ANALYTICAL DETERMINATIONS OF THE ATRAZINE LEVEL IN SOIL SAMPLES.

Table 9 contains the average amount of atrazine detected in each treatment in the soil samples collected in the fall from Carman, Glenlea, and Portage. Values have been corrected for efficiency of extraction as well as for bulk density of the soil. The extraction efficiencies were determined to be Carman 70%, Glenlea 80%, and Portage 70%.

The results indicate a similar trend as the bioassay determination. Carman soil sample readings indicate a lower level of residue than the Portage or Glenlea soil types. The half life of atrazine in the sandy soils is less than the half life of atrazine in the fine textured soils of the Glenlea and Portage locations. The results of this experiment indicate that the breakdown of atrazine occurs at uniform rates throughout the growing season.

#### TABLE 9

#### ATRAZINE REMAINING IN THE SOIL COLLECTED IN THE FALL OF APPLICATIONS MADE THROUGHOUT THE SUMMER (ANALYTICAL DETERMINATIONS, EXPRESSED AS KG/HECTARE)

| Rate of<br>Application<br>kg/hectare | No. of days<br>between application<br>and<br>sampling | Date<br>Applic | of<br>ation | Carman | Glenlea | Portage |
|--------------------------------------|---|----------------|-------------|--------|---------|---------|
| 1 101                                | 170   | Max            |             | 10     | <br>E 7 | 4.0     |
| 1.121                                | 170   | мау            | 9           | .19    | . 57    | .40     |
| 2.242                                | 170   | May            | 9           | .37    | .93     | 1.00    |
| 1.121                                | 142   | June           | 7           | .28    | .70     | .70     |
| 2.242                                | 142   | June           | 7           | .54    | .87     | .96     |
| 1.121                                | 103   | July           | 16          | .41    | .85     | .53     |
| 2.242                                | 103   | July           | 16          | .73    | 1.15    | 1.00    |
| 1.121                                | 83  | Aug.           | 5           | .48    | .93     | .73     |
| 2.242                                | 83  | Aug.           | 5           | 1.32   | 1.66    | 1.79    |
| 1.121                                | 68  | Aug.           | 21          | .73    | .96     | 1.06    |
| 2.242                                | 68  | Aug.           | 21          | 1.32   | 1.60    | 1.84    |
| 1.121                                | 47  | Sept.          | 11          | .95    | .92     | 1.15    |
| 2.242                                | 47  | Sept.          | 11          | 1.96   | 1.95    | 2.52    |
| Control                              |   |                |             | 0.0    | 0.0     | 0.0     |

#### DISCUSSION

Elliott, working with atrazine residues, concluded that the use of a bioassay was an effective way of estimating the amount of available residual herbicide in the soil. The bioassay is a fast and uncomplicated procedure to determine the level of atrazine in various soil types.

Bioassay work conducted in this particular study reveals that the bioassay method has many limitations. The  $ED_{50}$  rates are difficult to determine. Extrapolation of atrazine rates from a sigmoid curve are very inaccurate due to the nonlinearity of the curve. Conversion of the sigmoid curve to a straight line by mathematical formulas results in larger discrepancies. Atrazine causes death to oat plants over a very narrow range which makes it difficult to extrapolate atrazine levels. Soil dilution with untreated soil would not solve the problem because it would not be representative of the adsorption process taking place under field conditions. Atrazine which is a photosynthetic inhibitor cannot be adapted to  $ED_{50}$  value determination because some of the plant growth is a result of the utilization of stored food reserves in the seeds which is affected very little by atrazine.

The results from Experiments 1 and 2, when compared, would suggest that the level of fertility in the A horizons increased the rate of atrazine required to cause a 50% growth reduction. However, visual observations revealed that the toxicity of atrazine was most likely the same and the ED<sub>50</sub> rates are high because of the effect of the fertilizer on the growth of the checks within the 21 days growing period.

Variability in results within treatment was due to the inherent inaccuracy of soil sampling, combined with the biological and procedural

variability of the bioassay.

Atrazine was found to be more available in lighter soils than in the heavier textured or high clay content soil. These results are in agreement with Hedling, Chesters and Corey (1964), who found that soil with a high specific surface strongly affects the availability of herbicide to plants. The results with atrazine in silica sand illustrates that very little of the herbicide is required to cause growth reduction, which is in agreement with Anderson (1971) who concluded adsorption to be the key factor in determining the activity of atrazine in Manitoba soils.

Ambient temperature, soil temperature and rainfall data were similar for all locations which would suggest that probably the difference in the rate of breakdown between the three sites was not due to differences in climatic conditions.

Organic matter played a major role in the availability of atrazine, however, organic matter probably is not as significant as the data might suggest. These results relate closely to a study carried out by Hedling, Chesters and Corey (1964), who reported that although adsorption into organic matter seems greater in magnitude and more generally applicable to pesticides than adsorption into clay, the role of clay is probably equally important because most soils contain much more clay than organic matter. The analysis of the soils used in Experiment 2 illustrate that reducing the organic matter content of the soil by 50% did not reduce the cation exchange capacity by 50%.

The field seeded oats, both spring and fall, show evidence that crop damage can result from 1.121 and 2.242 kg rates of atrazine applied in May of the previous spring. The Carman soil type appears to have the lowest level of atrazine carryover from the early application dates,

however, the later applied rates have higher levels of residue than comparable treatments at Portage and Glenlea. The percent growth reduction in the spring was probably greater because of more stress on the plants caused by the warmer growing conditions. Fall applications and in some cases late summer application of atrazine resulted in complete oat control, suggesting that the activity of atrazine would be sufficient to give adequate weed control the following spring.

Atrazine undoubtedly breaks down at a much slower rate in Portage and Glenlea soils; this probably is a result of the reduced availability of atrazine in the heavier soils when subjected to virtually identical climatic conditions. The reduced availability of atrazine in heavier soils reduces the amount of herbicide present in the soil solution and thus reduces the rate of microbial breakdown.

The analytical determinations reveal that the rate of breakdown of atrazine is a 1<sup>st</sup> order reaction. Both the 1.21 and 2.242 kg rates dissipate at the same relative rates. Analytical determinations of atrazine levels were determined from soil samples used in the growth chamber work. The reason for the very close relationship is the fact that very little atrazine in solution is required to cause significant growth reductions. The analytical determinations show no evidence that the rate of atrazine breakdown varies over the 4-5 months summer growing season. Breakdown from the middle of September onward seems to be very limited, probably due to the low temperatures especially freezing temperatures. Rates of atrazine breakdown are definitely higher in lighter soils, but the analytical determinations do not show any conclusive differences in breakdown rates between Glenlea and Portage.

#### CONCLUSIONS

Studies were conducted to determine:

 a) differences in availability of atrazine in three Manitoba soil types,

b) the breakdown of atrazine under Manitoba conditions,

c) the soil constituents most effective in determining the availability of atrazine in Manitoba soils,

d) the relationship between available atrazine and the absolute level of atrazine in Manitoba soils.

Atrazine availability varies from one soil type to another. The available atrazine is higher in sandy soils, than in the clay and high organic matter soils. In general, the soil type appears to be the most significant factor affecting the availability of atrazine in Manitoba soils.

At all sites the rate of atrazine breakdown was constant from the beginning of May until mid September. The rate of breakdown is faster in the light than in the heavy textured soils but the amount of bound herbicide is greater in the heavy textured soils.

From this study it can be concluded that although atrazine breakdown is less in heavy than the light textured soils the possibility of residue damage to succeeding susceptible crops is much less in the heavy textured soils because of their high absorptive capacity. The soil constituent most effective in determining the availability of atrazine is organic matter. The contribution of each constituent alone could not be assessed but the four factors in combination were the major determinants of atrazine availability. Analytical determinations in general show a higher level of herbicide in the soil than bioassay determinations.

Work on the availability and dissipation of atrazine in Manitoba soils should be continued to determine:

a) the effect of fall application of atrazine on the level of residue carryover during the second succeeding crop year,

b) more precisely what soil constituents affect the availability and dissipation of atrazine,

c) the effect of freezing and thawing on the adsorption-desorption of atrazine in the soil.

#### BIBLIOGRAPHY

AGUNDIS, O. 1964. The distribution and persistence of simazine and 2,4-D in tropical soils. Weed Society America Abstract, p. 15.

ANDERSON, J. R. 1971. The Activity of Triazine Herbicides in Manitoba and Ontario Soils. Ph.D. Thesis, University of Guelph, Guelph, Ontario.

- BAILEY, G. W., and J. L. WHITE. 1970. Residue Reviews, Springer-Verlag, New York, p. 29.
- BURSCHEL, P. 1961. Studies on the behavior of simazine in soil. Weed Res. 1: 131.
- BURNSIDE, O. C., C. R. FENSTER, and G. A. WICKS. 1971. Soil persistence of repeated annual applications of atrazine. Weed Sci., Vol. 19, pp. 290-293.
- COMMES, R. D., and F. L. TIMMONS. 1965. Effect of sunlight on the phytotoxicity of some phenyl ureas and triazine herbicides on a soil surface. Weed Sci. 13: 81-84.
- DAY, B. E., L. S. JORDAN, and V. A. JOLLIFFE. 1968. The influence of soil characteristics on the adsorption and phytotoxicity of simazine. Weed Sci. 16: 209.
- DOWLER, Clyde C. 1969. A cucumber bioassay test for soil residue of certain herbicides. Weed Sci. 17: 309-311.

DUBACK, P. 1970. Residue Reviews 16: p. 19.

- DUNIGAN, E. P., and T. H. McINTOSH. 1971. Atrazine-soil organic matter interactions. Weed Sci. 17: 279-281.
- ELLIOT, J. D. 1972. The behavior of triazine herbicides in some Manitoba soils. M.Sc. Thesis, University of Manitoba, Winnipeg, Canada.
- HARRIS, C. I. 1966. Adsorption, movement and phytotoxicity of monuron and s-triazine herbicides in soil. Weed Sci. 14: 6-10.
- HARRIS, C. I., and G. F. WARREN. 1964. Adsorption and desorption of herbicides by soil. Weed Sci. 12: 120.
- HEDLING, C. S., G. CHESTERS, and R. B. COREY. 1964. Contribution of organic matter and clay to soil cation exchange capacity as affected by the pH of the saturating solution. Soil Sci. Soc. Amer. Proc. 28: 517.

HENIN, M. S. 1968. La Culture san Labour. C.R. Acad. Agr. France, 54: 126.

- HOLLY, K., and H. A. ROBERTS. 1963. Persistence of phytotoxic residues of triazine herbicides in soil. Weed Res. 3: 1.
- GROVER, R. 1966. Influence of organic matter, texture and available water on the toxicity of simazine in soil. Weed Sci. 14: 148-151.
- JORDAN, L. S., B. E. DAY, and W. A. CLEREX. 1964. Photo decomposition of triazines. Weed Sci. 12: 5-6.
- KEARNEY, P. C., T. J. SHEETS, and J. W. SMITH. 1964. Volatility of seven s-triazines. Weed Sci. 12: 83-87.
- KNUSLI, E., D. BURER, G. DUPUIS, and H. ESSER. 1969. s-Triazines. In P. C. Kearney and D. P. Kaufmann (Eds.), Degradation of Herbicides, New York: Dekker.
- LAMBERT, S. M., P. E. PORTER, and R. H. SCHIEFERSTEIN. 1965. Movement and sorption of chemicals applied to the soil. Weed Sci. 13: 185.
- McCORMICK, L. L., and A. E. HILTBOLD. 1966. Microbiological decomposition of atrazine and diuron in soil. Weed Sci. 14: 77.
- NALEWAJA, J. D. 1968. Dissipation of atrazine residue in North Dakota soils. North Dakota Farm Research 25(3): 3-5.
- ROADHOUSE, F. E. B., and L. A. BIRK. 1961. Penetration of and persistence in the soil of herbicides 2-chloto,-4,6,-bis(ethylamino)-2-triazine (simazine). Can. J. Plant Sci. 41: 252.
- SANTELMAN, P. W., J. B. WEBER, and A. F. WIESE. 1971. A study of a bioassay technique using prometryne. Weed Sci. 19: 170-174.
- SHEETS, T. J., A. S. CRAFTS, and H. R. DREVER. 1962. Influence of soil properties on the phytotoxicities of the s-triazine herbicides. J. Agr. Food Chem. 10: 458.
- SIKKA, H. C., and D. E. DAVIS. 1966. Dissipation of atrazine from soil by corn, sorghum and johnson-grass. Weeds 14: 289-293.
- TALBERT, R. E., and O. H. FLETCHALL. 1965. The adsorption of some striazines in soils. Weed Sci. 13: 46-52.
- TOMPKINS, G. A., T. H. McINTOSH, and E. D. DUNIGAN. 1968. Use of the Standford-De Ment bioassay to study atrazine soil reactions. Soil-Sci. Soc. America Proc. 32: 373-377.
- UPCHURCH, R. P., and D. D. MASON. 1962. The influence of soil organic matter on the phytotoxicity of herbicides. Weed Sci. 10: 9-14.
- UPCHURCH, R. P., and W. C. PIERCE. 1958. The leaching of monuron from Lakeland sand soil. Weed Sci. 6: 24.

WAGNER, G. H., and K. S. CHAKAL. 1966. Decomposition of carbon -14 labelled atrazine in soil samples from Sanborn field. Soil Sci. Soc. America Proc. 30: 752.

WEBER, J. B., S. B. WEED, and T. M. WARD. 1969. Adsorption of striazines by soil organic matter. Weed Sci. 17: 417-421.

# APPENDIX

#### APPENDIX A

#### PHYSICAL AND CHEMICAL PROPERTIES OF ATRAZINE

ATRAZINE - 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine MOLECULAR WEIGHT - 215.7 PHYSICAL STATE AND COLOUR - Crystalline, White PHOTODECOMPOSITION - Stable VAPOR PRESSURE - 1.4 x  $10^{-6}$  mm Hg at  $30^{\circ}$ C SOLUBILITY - Chloroform - 52000 mg/L at  $27^{\circ}$ C Methanol - 1800 mg/L at  $27^{\circ}$ C Water - 70 mg/L at  $27^{\circ}$ C

# APPENDIX B

| SOIL AND AIR TEMPERATURE READINGS AT TRIAL SITE IN CARM | iAN |
|---|-----|
|---|-----|

| N  | Air  | 2.5<br>cm   | 5.0<br>cm  | 10.0<br>cm   | 20.0<br>cm  | 50.0<br>cm  | 100.0<br>cm  | 150.0<br>cm  |
|----|--|---|--|--|---|---|--|--|
| 24 | 16.9   | 16.8  | 16.3   | 15.8   | 13.3  | 9.4   | 4.3  | 1.8  |
| 1  | 29.0   | 28.3  | 25.8   | 21.2   | 16.9  | 13.2  | 7.8  | 4.0  |
| 11 |  | 26.6  | 24.8   | 21.2   | 17.2  | 13.7  | 10.0   | 6.7  |
| 14 | 23.5   | 20.0  | 18.5   | 17.0   | 16.5  | 14.1  | 8.6  | 5.2  |
| 29 | 20.3   | 17.8  | 16.7   | 15.6   | 15.4  | 15.3  | 12.4   | 8.8  |
| 10 | 27.5   | 31.9  | 29.3   | 24.8   | 20.6  | 19.2  | 14.3   | 10.6   |
| 23 | 20.4   | 20.7  | 20.3   | 20.0   | 20.0  | 18.5  | 15.2   | 12.3   |
| 20 | 25.6   | 21.4  | 20.8   | 19.1   | 17.7  | 18.0  | 16.0   | 13.4   |
| 29 | 33.0   | 26.6  | 25.3   | 22.4   | 19.9  | 18.6  | 16.4   | 14.4   |
| 5  | 20.0   | 18.2  | 17.2   | 15.6   | 15.0  | 16.3  | 16.2   | 14.4   |
| 20 | 15.7   | 14.8  | 14.2   | 12.4   | 11.0  | 12.3  | 13.6   | 13.4   |
| 24 | 10.6   | 10.6  | 10.2   | 9.8  | 9.2   | 9.0   | 9.2  | 9.7  |
|    | 24<br>1<br>11<br>14<br>29<br>10<br>23<br>20<br>29<br>5<br>20<br>24 | AIF   24 16.9   1 29.0   11    14 23.5   29 20.3   10 27.5   23 20.4   20 25.6   29 33.0   5 20.0   20 15.7   24 10.6 | AIr 2.5 cm   24 16.9 16.8   1 29.0 28.3   11  26.6   14 23.5 20.0   29 20.3 17.8   10 27.5 31.9   23 20.4 20.7   20 25.6 21.4   29 33.0 26.6   5 20.0 18.2   20 15.7 14.8   24 10.6 10.6 | AIP 2.5 5.0   cm cm cm   24 16.9 16.8 16.3   1 29.0 28.3 25.8   11  26.6 24.8   14 23.5 20.0 18.5   29 20.3 17.8 16.7   10 27.5 31.9 29.3   23 20.4 20.7 20.3   20 25.6 21.4 20.8   29 33.0 26.6 25.3   5 20.0 18.2 17.2   20 15.7 14.8 14.2   24 10.6 10.6 10.2 | AIF   2.5   5.0   10.0     24   16.9   16.8   16.3   15.8     1   29.0   28.3   25.8   21.2     11    26.6   24.8   21.2     14   23.5   20.0   18.5   17.0     29   20.3   17.8   16.7   15.6     10   27.5   31.9   29.3   24.8     23   20.4   20.7   20.3   20.0     20   25.6   21.4   20.8   19.1     29   33.0   26.6   25.3   22.4     5   20.0   18.2   17.2   15.6     20   15.7   14.8   14.2   12.4     24   10.6   10.6   10.2   9.8 | Alf   2.5   5.0   10.0   20.0     24   16.9   16.8   16.3   15.8   13.3     1   29.0   28.3   25.8   21.2   16.9     11    26.6   24.8   21.2   17.2     14   23.5   20.0   18.5   17.0   16.5     29   20.3   17.8   16.7   15.6   15.4     10   27.5   31.9   29.3   24.8   20.6     23   20.4   20.7   20.3   20.0   20.0     20   25.6   21.4   20.8   19.1   17.7     29   33.0   26.6   25.3   22.4   19.9     5   20.0   18.2   17.2   15.6   15.0     20   15.7   14.8   14.2   12.4   11.0     24   10.6   10.6   10.2   9.8   9.2 | AIF $2.5$ $5.0$ $10.0$ $20.0$ $50.0$ $24$ $16.9$ $16.8$ $16.3$ $15.8$ $13.3$ $9.4$ $1$ $29.0$ $28.3$ $25.8$ $21.2$ $16.9$ $13.2$ $11$ $$ $26.6$ $24.8$ $21.2$ $17.2$ $13.7$ $14$ $23.5$ $20.0$ $18.5$ $17.0$ $16.5$ $14.1$ $29$ $20.3$ $17.8$ $16.7$ $15.6$ $15.4$ $15.3$ $10$ $27.5$ $31.9$ $29.3$ $24.8$ $20.6$ $19.2$ $23$ $20.4$ $20.7$ $20.3$ $20.0$ $20.0$ $18.5$ $20$ $25.6$ $21.4$ $20.8$ $19.1$ $17.7$ $18.0$ $29$ $33.0$ $26.6$ $25.3$ $22.4$ $19.9$ $18.6$ $5$ $20.0$ $18.2$ $17.2$ $15.6$ $15.0$ $16.3$ $20$ $15.7$ $14.8$ $14.2$ $12.4$ $11.0$ $12.3$ $24$ $10.6$ $10.6$ $10.2$ $9.8$ $9.2$ $9.0$ | Alf $2.5$ $3.0$ $10.0$ $20.0$ $50.0$ $100.0$ $24$ $16.9$ $16.8$ $16.3$ $15.8$ $13.3$ $9.4$ $4.3$ $1$ $29.0$ $28.3$ $25.8$ $21.2$ $16.9$ $13.2$ $7.8$ $11$ $$ $26.6$ $24.8$ $21.2$ $17.2$ $13.7$ $10.0$ $14$ $23.5$ $20.0$ $18.5$ $17.0$ $16.5$ $14.1$ $8.6$ $29$ $20.3$ $17.8$ $16.7$ $15.6$ $15.4$ $15.3$ $12.4$ $10$ $27.5$ $31.9$ $29.3$ $24.8$ $20.6$ $19.2$ $14.3$ $23$ $20.4$ $20.7$ $20.3$ $20.0$ $20.0$ $18.5$ $15.2$ $20$ $25.6$ $21.4$ $20.8$ $19.1$ $17.7$ $18.0$ $16.0$ $29$ $33.0$ $26.6$ $25.3$ $22.4$ $19.9$ $18.6$ $16.4$ $5$ $20.0$ $18.2$ $17.2$ $15.6$ $15.0$ $16.3$ $16.2$ $20$ $15.7$ $14.8$ $14.2$ $12.4$ $11.0$ $12.3$ $13.6$ $24$ $10.6$ $10.6$ $10.2$ $9.8$ $9.2$ $9.0$ $9.2$ |

(Temperature in <sup>O</sup>C)

# APPENDIX C

|        |    |     |           | · ·       |            |            |            |             |             |
|--------|----|-----|-----------|-----------|------------|------------|------------|-------------|-------------|
| GLENLI | EA | Air | 2.5<br>cm | 5.0<br>cm | 10.0<br>cm | 20.0<br>cm | 50.0<br>cm | 100.0<br>cm | 150.0<br>cm |
| May    | 24 | 7   | 15        | 13        | 11         | 13         | 9          | 5           | 3           |
| June   | 1  | 17  | 15        | 13        | 11         | 13         | 9          | 5           | 3           |
| June   | 11 | 21  | 16        | 13        | 12         | 13         | 11         | 7           | 4           |
| June   | 14 | 17  | 17        | 15        | 14         | 15         | 12         | 7           | 5           |
| June   | 29 | 17  | 17        | 14        | 14         | 15         | 14         | 10          | 7           |
| July   | 10 | 17  | 20        | 18        | 17         | 18         | 15         | 11          | 8           |
| July   | 23 | 18  | 19        | . 18      | 17         | 17         | 15         | 12          | 9           |
| Aug.   | 2  | 16  | 19        | 17        | 17         | 18         | 16         | 13          | 10          |
| Aug.   | 20 | 15  | 17        | 16        | 16         | 18         | 17         | 13          | 11          |
| Aug.   | 29 | 15  | 21        | 18        | 17         | 18         | 17         | 14          | 12          |
| Sept.  | 5  | 12  | 17        | 15        | 15         | 17         | 16         | 14          | 12          |
| Sept.  | 19 | 13  | 11        | 10        | 10         | 12         | 14         | 13          | 12          |

SOIL AND AIR TEMPERATURE READINGS AT TRIAL SITE IN GLENLEA

(Temperature in <sup>O</sup>C)

## APPENDIX D

SOIL AND AIR TEMPERATURE READINGS AT TRIAL SITE IN PORTAGE

| PORTA | GE | Air  | 2.5<br>cm | 5.0<br>cm | 10.0<br>cm | 20.0<br>cm | 50.0<br>cm | 100.0<br>cm | 150.0<br>cm |
|-------|----|------|-----------|-----------|------------|------------|------------|-------------|-------------|
| May   | 24 | 15.0 | 16.6      | 16.4      | 15.4       | 13.3       | 11.0       | 7.8         | 4.7         |
| June  | 1  | 21.9 | 20.8      | 19.1      | 17.4       | 16.5       | 14.0       | 8.8         | 5.6         |
| June  | 14 | 25.6 | 21.0      | 20.1      | 19.8       | 19.1       | 16.3       | 11.6        | 9.1         |
| June  | 29 | 23.4 | 18.8      | 17.4      | 15.8       | 14.9       | 14.7       | 12.4        | 9.7         |
| July  | 10 | 17.0 | 22.4      | 23.0      | 23.6       | 22.5       | 17.4       | 13.6        | 10.7        |
| July  | 23 | 20.7 | 20.0      | 19.9      | 19.8       | 20.1       | 18.3       | 14.8        | 12.2        |
| Aug.  | 3  | 17.7 | 20.4      | 20.8      | 20.9       | 20.1       | 17.9       | 15.6        | 13.1        |
| Aug.  | 20 | 21.6 | 15.7      | 15.2      | 15.0       | 16.2       | 18.2       | 15.8        | 13.4        |
| Aug.  | 29 | 27.6 | 21.8      | 20.2      | 19.2       | 19.4       | 19.0       | 16.2        | 14.1        |
| Sept. | 5  | 18.5 | 15.1      | 14.4      | 14.0       | 14.8       | 16.9       | 16.5        | 15.0        |
| Sept. | 19 | 10.0 | 10.2      | 11.0      | 11.4       | 11.2       | 12.2       | 13.6        | 13.4        |
| Oct.  | 27 | 8.3  | 8.2       | 7.8       | 7.4        | 7.7        | 10.0       | .10.9       | . 11.6      |
|       |    |      |           |           |            |            |            |             |             |

(Temperature in  $^{O}C$ )

|                | Carman | Glenlea | Portage |
|----------------|--------|---------|---------|
| May            | 5.35   | 4.67    | 6.60    |
| June           | 6.62   | 8.0     | 7.59    |
| July           | 9.83   | 10.67   | 9.98    |
| August         | 7.80   | 3.58    | 8.58    |
| September      | 6.35   | 6.38    | 5.69    |
| October 1 - 12 |        | *       | 2.46    |

# RAINFALL EXPRESSED IN CM OF RAINFALL PER MONTH

APPENDIX E